Selected Bibliography of Chemistry

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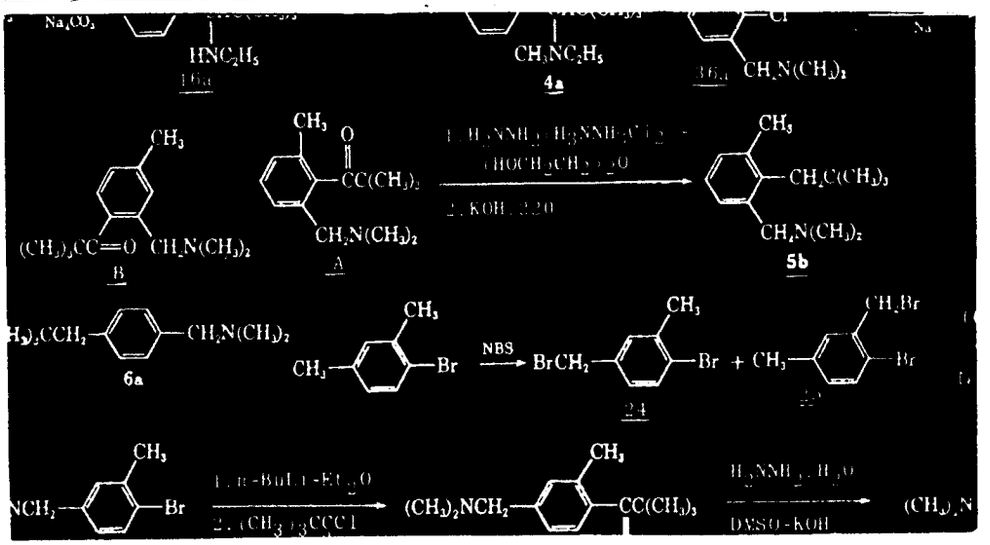

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Volume 1 Number 1 September 1971

فهرست گزیده مقالات در شیمی

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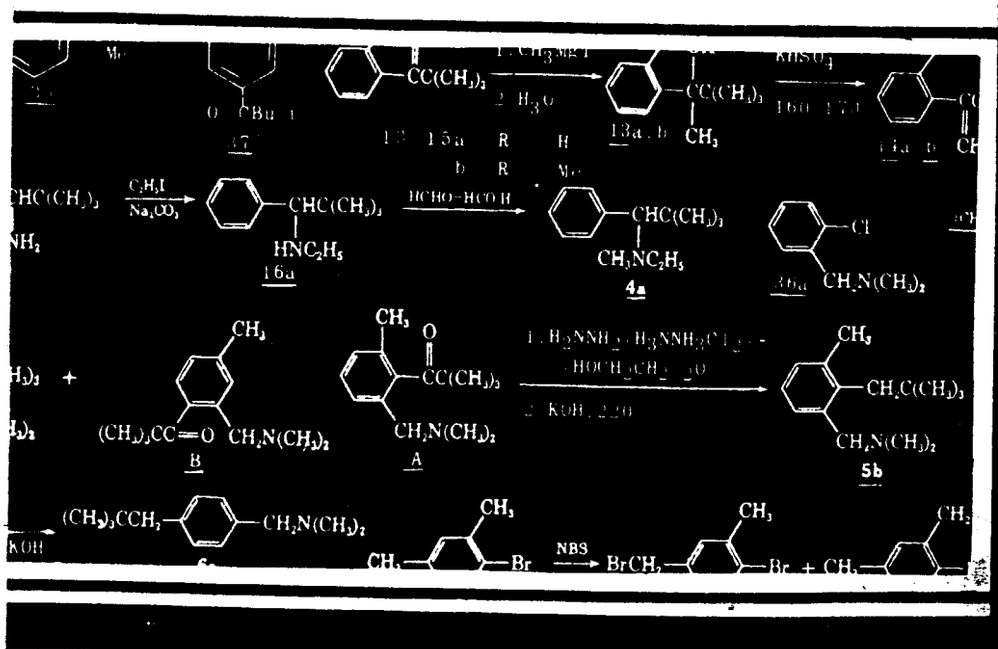

مرکز مدارک علمی

مؤسسه تحقیقات و برنامه ریزی علمی و آموزشی

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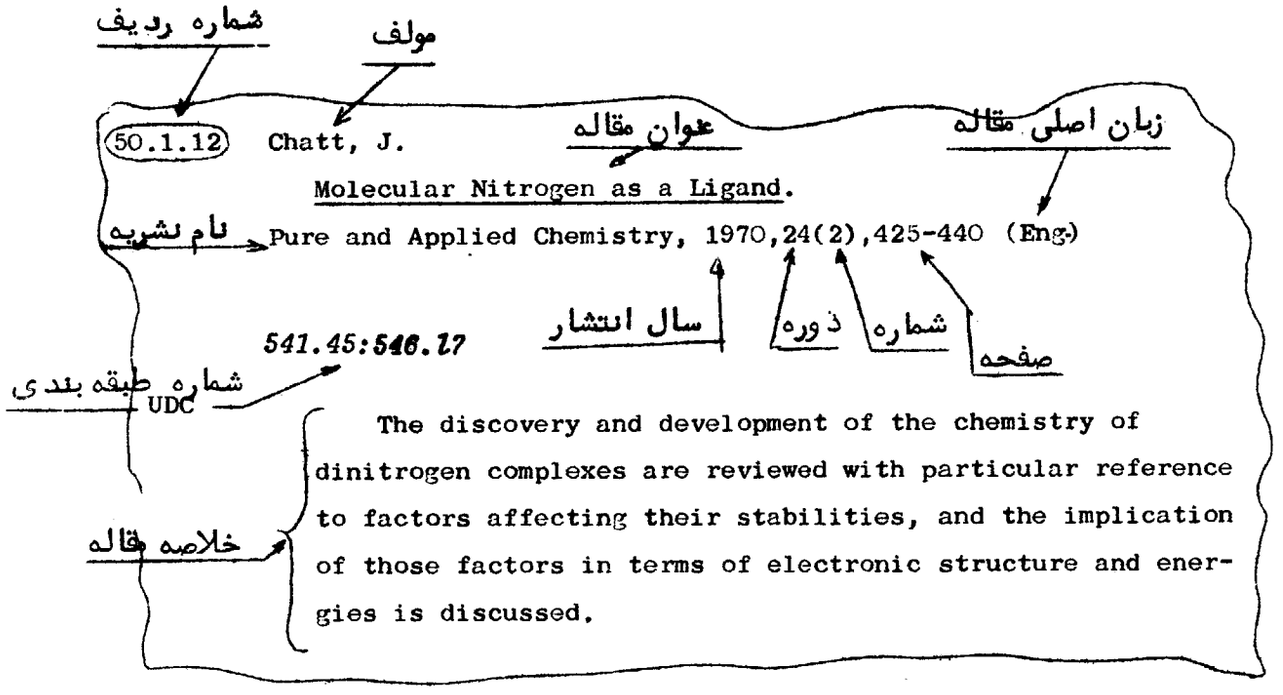

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541. *Theorethical Chemistry*

50.1.1 Franck,E.U.

Water and Aqueous Solutions at High Pressures and Temperatures.

Pure and Applied Chimistry,1970,24(1),13-31

541.11.034.2 *541.11.036*

A survey is given of recent results on properties of water and aqueous solutions at high pressures and high temperatures with emphasis on supercritical conditions. New PVT-data for water from static measurements are available to 1000 °C and kb. Dielectric constants and viscosity have been measured to 550 °C and 5 kb. Infra-red and Raman spectra of OD-vibrations of HDO in H_2O to 400 °C and 5 kb give information about the extent of hydrogen bonded structure. Critical curves of binary aqueous systems with one inert component, for example argon, extending to 3 kb and 400 °C are discussed. Absorption spectra of bivalent cobalt and nickel chlorides are measured to 500 °C and 6 kb and conclusions about the stability of octahedral and tetrahedral complexes are drawn. Shock wave and static conductance measurements to 1000 °C and more than 100 kb demonstrate the increase of the ion product of water by twelve orders of magnitude or more at these conditions.

50.1.2 Vol'pin,M.; Dvolaitzky, M. and Levitin,I.
Reduction Through an SN_2 Mechanism of Organic Halides by Sodium Borohydride in Dimethylformamide.(Fr)
Bulletin de la Société Chimique de France,1970,(4), 1526-1528

541.124:542.942:547

The reaction of sodium borohydride in dimethyformamide on a series of organic halides is studied. Primary and secondary alkyl iodides, primary bromides, benzyl and allyl chlorides are shown to be reduced smoothly to the corresponding hydrocarbons at room temperature. Kinetic evidence is presented for an SN_2 mechanism for these reactions.

50.1.3 Bahsoun,A. and Lefebvre,J.
Kinetic Study of the Reduction of Pentavalent Antimony by Iodides in an Acidic Medium.I. Reduction of Hexahydroxoantimoniate. (Fr)
Bulletin de la Société Chimique de France, 1970,(3),881-86

541.127:546.865

A potentiometric device facilitates recording of the kinetic curves for the reduction of potassium hexahydroxoantimoniate by iodides in a perchloric medium.

The rate law observed is

$$v = -\frac{d(Sb^{V})}{dt} = \left[k_1(I^-)^2(H^+)^2 + k_2(I^-)^2(H^+)^4\right](Sb^{V})$$

At 25°C and for an ionic strengh μ =2,92 M in a sodium perchlorate medium the values k_1 =1.0.10^4 M^{-4} mn^{-1} and k_2 =2.3 x 10^3 M^{-6} mn^{-1} are obtained. The reaction rate is relatively sensitive to the ionic strength. For $\mu < 1$ M and $[H^+] < 1$ M, conditions in which the first term of the rate law is predominant, the rate constant k_1 has the value $[1.65 \pm 0.25]10^3$ M^{-4} mn^{-1}. A reaction mechanism is suggested, then discussed: the order two with respect to iodide can be lowered by the intervention of a competing nucleophilic reagent such as $S_2O_3^{2-}$.

50.1.4 Soumillion,J.Ph.

La Substitution Radicalaire des Composés Aliphatiques par le Chlore.

Industrie Chimique Belge, 1970,35(10),851-878

541.127:542.944.2:547.1/.4

- Mécanisme de la Photochloration.
- Les Réarrangements.
- L'effet Vicinal.
- Cinétique de Chlorations.
- Ordres de Réactions-Constantes de Vitesse Chloration d'une Chaîne Aliphatique: Réactions Jumelles.

- Réactivities Relatives et Effets de Substituants.
  La Chloration des Alcanes.
  Les Hydrocarbures Alicycliques.
- Conclusions.
  ref: 334

50.1.5 Lagrange, J.

Determination of the Apparent Acidity Constants of Acetic Acid and Aniline,and the Apparent Second Acidity Constant of Sulphuric Acid, in Mixtures of Electrolytes Na_2SO_4-$NaClO_4$. (Fr)

Bulletin de la Société Chimique de France,1970,(3), 887-91

541.127.2:54.08

The apparent acidity constants of acetic acid, aniline and the apparent second acidity constant of sulfuric acid are determined in binary mixtures of supporting electrolytes: Na_2SO_4-$NaClO_4$. It is shown that, for constant molar concentrations, the apparent pK values vary linearly with the composition of the mixture of supporting electrolytes.

50.1.6 Fiaud, Ch., Aucouturier, Ch. and et all.

Application of Various Electrochemical Methods to a Study of the Inhibition of Copper Corrosion by Mercaptobenzothiazole. (Fr)

Bulletin de la Société Chimique de France,1970,(2)465-72

541.138.2:541.183

The inhibiting effect of mercaptobenzothiazole on copper corrosion is studied by various electrochemical methods, especially by measuring the differential double layer capacity.

The reaction process, the influence of concentration, and the nature of the metal-inhibitor bonding are defined. A bonding hypothesis is proposed.

50.1.7 Fuerstenau,D.W.

Interfacial Processes in Mineral/Water Systems.

Pure and Applied Chimistry, 1970,24(1),135-165

541.183

Factors that control the selective adsorption of both inorganic and organic ions at mineral/water interfaces are reviewed and summarized.In particular, the role of the electrical double layer in the adsorption of surface-active materials on oxides in aqueous media is stressed. The importance of interfacial processes to mineral chemistry is illustrated through the application of specific adsorption phenomena to the understanding of the physical chemistry of flotation systems.

50.1.8 Fontaine,J. and Vandorpe,B.

Dielectric Isotherms. (Fr)

Bulletin de la Société Chimique de France,1970,(3), 872-876

541.183:536.712

Slope variations and inflexion points observed on dielectric isotherms are generally attributed to modifications in the behaviour of adsorbed molecules. These conclusions may be erroneous. Dielectric study of an "adsorbed-adsorbing" system at constant temperature and variable frequency reveals that a low frequency relaxation range can modify the form of the isotherm.This relaxation range occurs every time the adsorbed molecules can be bonded by a hydrogen bridge to the surface of the porous material. These inflexion points, and slope changes depend on the frequency used for the measurement. To eliminate errors the dielectric constant value must not be influenced by an abnormal dielectric polarization at all concentrations. A method for the selection of the best measurement frequency is given.

50.1.9 Laviron,E.

Influence of the Adsorption of the Depolariser or of a Product of the Electrochemical Reaction on Polarographic Current.XII.Experimental Investigation of the Influence of the Adsorption and the Orientation of the

Depolariser Molecules in Linear Potential Sweep Voltammetry. (Fr)

Bulletin de la Société Chimique de France,1970,(4), 1637-1643

541.183:543.253

An experimental investigation has been made of the peaks obtained in linear potential sweep voltammetry in the case of reversible or irreversible reactions, with strong adsorption of the depolariser. At low concentrations only the adsorption peak is observed; at higher concentrations a diffusion peak appears, which may overlap with the adsorption peak.In the case of an irreversible reaction,the adsorption peak frequently becomes abnormally narrow and sharp. This anomaly has been shown to be caused by the compactness of the film.

50.1.10 Squires, Arthur M. and Graff,Robert A.

Panel Bed Filters for Simultaneous Removal of Fly Ash and Sulfur Dioxide. III. Reaction of Sulfur Dioxide With Half-Calcined Dolomite.

Journal of the Air Pollution Control Association, May 1971,21(5),272-276

541.183.26SO_2:628.512

Half-calcined dolomite, $[CaCO_3+MgO]$ is a candidate solid for use in panel bed filters which can

simultaneously remove fly ash and SO_2 from flue gas. Unpublished work by Coke, summarized here, showed that good reactivity is obtained at about 600 °C, making the device usable in a boiler ahead of the economizer. We have confirmed Coke's results. Further, we have demonstrated that the solid can be regenerated by reduction of calcium sulfate to calcium sulfide, followed by release of H_2S from the sulfide by its reaction with steam and carbon dioxide. Three absorptions with intermediate regeneration showed no significant loss of reactivity or capacity. A flowsheet example is presented for the cyclic use of half-calcined dolomite in a process producing elemental sulfur for the market.

50.1.11 Hagenmuller, Paul.

Recherches Recentes Sur Les Composés à Large Domaine D'existence Contenant un Même Elément à Deux Degrès D'oxydation Différents. (Fr)

Pure and Applied Chimistry,1970,24(1),67-95

541.22

In the scope of a general study of non-stoichiometric compounds with a large homogeneity range, the interest of insertion compounds having an oxide or fluoride network is emphasized. The main features of these classes of compounds are described, several structural or physical problems are resolved.

50.1.12 Chatt, J.

Molecular Nitrogen as a Ligand.

Pure and Applied Chimistry, 1970,24(2),425-440

541.45:546.17

The discovery and development of the chemistry of dinitrogen complexes are reviewed with particular reference to factors affecting their stabilities, and the implication of those factors in terms of electronic structure and energies is discussed.

50.1.13 Coulson,C.A.

Recent Developments in Valence Theory.

Pure and Applied Chimistry,1970,24(1),257-287

541.5

In the early 1930s valence theory was confused by a conflict between molecular-orbital and valence-bond approximations. But during the 1940s a reconciliation between the two methods was found; and from that time until now much the greater effort has been put into MO calculations. These calculations have been tremendously enriched in the 1960s by the widespread use of electronic computers, and package programmes.

A study of the charge distribution calculated for covalent bonds shows that the early picture of

a bond as being associated with a build-up of charge between the nuclei is still valid. However, if bonding electrons are drawn into this region, other electrons tend to get forced out of it; recent studies show the importance of these two effects. The early representation of these charge-clouds in terms of hybridization was particularly fruitful in the 1940s, but is now recognized as too restrictive.

The development of the experimental techniques of photoelectron spectroscopy and x-ray spectroscopy now enables a direct verification to be made of the early ideas of individual molecular orbitals. In this way Mulliken's original theoretical descritions have been triumphantly justified.

Another aspect of valence theory that has developed in recent years is that of the relation between σ and π electrons. No longer may the electrons be treated as if they were independent of the σ electrons, but a close relationship exists between them.

The account concludes with a descrition of those situations where the number of valence electrons is either too few (electron-deficient molecules) or too large (electron-rich molecules) to provide the normal complement of two electrons per bond. In each case the simple concept of a bond needs to be modified. Attention is drawn to the remarkable way in which theoretical concepts have recently received

experimental verification.

50.1.14 Van Vleck, J.H.

Spin,The Great Indicator of Valence Behaviour.

Pure and Applied Chimistry, 1970,24(1),235-255

541.5

This paper opens with a comparison of the electron shell model of Langmuir with the assignment of quantum numbers made by Bohr and slightly modified by Stoner in the years immediately preceding quantum mechanics. A discussion is given of the role of spin in the development of quantum mechanics, culminating in the relativistic Dirac Equations. Because of the exclusion principle spin is the great indicator of valence behaviour. This is shown particularly clearly by a vector-model formula first derived by Dirac. The Heitler-London-Slater-Pauling and Hund-Mulliken approaches are compared. The two methods each have their difficulties but there is often comforting agreement in their conclusions. The results are displayed of some early calculations of binding energies of the hydrogen molecule and of resonance energies.

The final portion of the paper discusses the development of the crystal field theory of the paramagnetic susceptibilities of salts of the iron group during the first decade of quantum mechanics, and how this theory

furnishes the key to the theoretical inorganic chemistry underlying the diverse behaviour of the various ions in this group.

50.1.15 Taube, Henry.

Recent Progress in the Study of Inner-Sphere Electron Transfer Reactions.

Pure and Applied Chemistry,1970,24(2),289-305

541.6

Progress made during the past ten years or so by the author's associates in studying inner-sphere electron transfer reactions is reviewed, emphasizing organic molecules as bridging groups. Evidence is outlined for reduction by remote attack in the reaction of chromous ion with isonicotinamidepentaamminecobalt(III) and with the analogous nicotinamide complex. That there be a conjugated bond system in a bridging group, even when there is a suitable remote polar group, is not a sufficient condition for effective mediation by the bridging group in electron transfer by remote attack. Moreover, conjugated bond systems are shown to exert effects even when they are not in the direct line of electron transfer, that is, when they are in pendent positions. The reducibility of the bridging group appears to be important in determining its capacity to mediate in electron transfer between Cr(II) and Co(III).

In the systems referred to, with reducible bridging ligands, electron transfer is understood as taking place in a stepwise manner. As was anticipated by Halpern and Orgel, the symmetry properties of the donor, carrier and acceptor orbitals are important in determining rates and mechanisms. Thus the mechanism of electron transfer seems to be different when Ru(III), a π electron acceptor, rather than Cr(III) or Co(III), which are σ acceptors, is oxidant.

The electronic sturctures of the metal ions are important also in determining the lability of binuclear precursor and product complexes. A number of product binuclear complexes are mentioned containing both Ru(II) and Cr(III) bound to a bridging group, and evidence for an electromeric equilibrium in such systems is cited. The study of the binuclear complexes is an interesting subject in its own right, and the ion (XXI) (see text) is introduced as illustrating some of the issues relating to the interaction between metal ions which arise in considering binuclear species. Finally, some of the opportunities and problems facing those interested in the field are outlined.

50.1.16 Daudel, Raymond.

Relation Between Electronic Structure and Chemical Reactivity of Organic Molecules.

Pure and Applied Chemistry,1970,24(1),217-234

541.6

This paper gives a brief history of the establishment of relations between electronic structure and chemical reactivity of molecules obtained by using quantum mechanical techniques. After a short introduction devoted to the qualitative period a more important part of the paper is concerned with the discussion of the methods which permit some estimations of the constant rates. Both static and dynamic indices are described. The effect of the solvent is taken into account. Various applications are given showing how it has become possible to predict theoretically new kinds of reactivity or even of reactions which have been really discovered later. The role of electronic computers is stressed. It is stated that quantum chemistry will become more and more important in the near future in the field of biochemistry, chemical industries and in particular pharmacology.

50.1.19 Kornprobst, J.M. et all.

Electrolysis of Acids in Acetonitrile Solutions.II Rearrangement and Reaction Mechanism. (Fr)

Bulletin de la Société Chimique de France,1970,(4), 1490-1497

541.6:661.73:542.8

The electrolysis of various aliphatic carboxylic

acids in which the functional group is primary, secondary or tertiary has been investigated in acetonitrile solution. Rearrangements which result from the formation of intermediate carbonium ions are postulated. The stereo-chemistry of the N-acylamide obtained in the electrolysis of the cis and trans 2-methylcyclohexane carboxylic acids is discussed.

The reaction mechanism is discussed and the following results are obtained: when the N-alkyl group is tertiary and the acyl group is primary or secondary, there is formation and decomposition of the N acyl amide; on the other hand when the acyl group is tertiary, the formation of an iso-imide which reacts with a carboxylate anion to give an acid anhydride is observed.

50.1.18 Tocanne, J.F.

Relation Between Molecular Rotation and Conformation in the Metadioxane Series.Application to the Determination of One Absoloute Configuration in the β-Diol Series. (Fr)

Bulletin de la Société Chimique de France, 1970,(2)750-758

541.63:547.851

Brewster rules are used to calculate molecular rotation values for preferential conformations (Selected by conformational analysis and spectroscopic data)

of some(cis or trans) 4,5- dialkyl-1-1,3-dioxanes of known configuration. Correlations observed between the calculated and experimental molecular rotation values define the absolute configuration of 4,6-dialkyl-1,3-dioxanes and consequently those of the corresponding bisecondary B-diols. Application of this method leads ot the R,R-configuration for the B-diol system of phtiocerol-A and phtiodiolon-A. These conformational and polarimetric orrelations suggest a skew-boat from in 2,2-dimethyl-trans-4,6-dialkyl-1,3-dioxanes.

50.1.19 Cheradame,H. and Sigwalt,P.
Cationic Polymerization of Ethylenic Monomers Initiated by Lewis Acids.II.A Study of Titanium Tetrachloride in Various Solvents. (Fr)
Bulletin de la Société Chimique de France, 1970,(3), 849-852

541.64:547.313

A new type of isobutene polymerisation initiation by titanium tetrachloride is described. Polymerization occurs when the reagents are condensed after being brought into the gaseous state, whereas it does not occur with the same reagents in the liquid phase. These results cannot be explained on the basis of the action of a cocatalyst, according to the classical theory of cocatalysis, and several hypotheses are discussed in order to explain this phenomenon.

50.1.20 Cheradame, H. and Sigwalt,P.

Cationic Polymerisation of Ethylenic Monomers Initiated by Lewis Acids.I. Poymerisation by Condensation under Vacuum of the Isobutene-Titanium Tetrachloride-Methylene Chloride System. (Fr)

Bulletin de la Societe Chimique de France, 1970,(3) 843-848

541.64:547.313

A possible explanation for the initiation step of isobutene polymerisation is given as the auto-association of titanium tetrachloride. Dielectric polarization measurements at room temperature show that titanium tetrachloride is not associated with methylene chloride. Cryoscopic studies demonstrate that titanium tetrachloride is not auto associated in methylene chloride at -95 °C, and in cyclohexane at + 6 °C.

50.1.21 Tazuke, Shigeo. and Okamura, Seizo.

Salt Effects on Vinyl Polymerization-A Boundary Study of Organic and Inorganic Chemistry.

Pure and Applied Chemistry, 1970,24(1),49-67

541.64:546-8

Vinyl polymerization is often affected by the addition of metal salts. A common example of metal salt effects is already seen in redox initiation

systems. In this paper the salt effects on the propagation process of vinylpyridine and N-vinylimidazole, and the direct redox initiation of vinylpyridine N-vinylimidazole and N-vinylcarbazole are discussed.

50.1.22 Mason,S.F.

Optical Activity and Molecular Dissymmetry in Coordination Chemistry.

Pure and Applied Chemistry, 1970,24(2),335-359

541.653

Classical and quantum mechanical theories of optical activity are reviewed with particular reference to the coordination compounds of the transition metal ions. The limiting cases of 'the inherently dissymmetric chromophore' and of 'the symmetric chromophore in a chiral molecular environment' are exemplified respectively by a discussion of the non-empirical exciton treatment of the tris-2,2'- bipyridyl and tris-1,10- phenanthroline complexes of the iron- group metals, and of empirical regional rules relating the position of a substituent to the optical activity of amine complexes of cobalt(III) and analogous metal ions.

542. Experimental Chemistry

50.1.23 Bolte, M. and Capestan,M.

Thermal Decomposition of Mercury-Imido-Disulphates in Air. (Fr)

Bulletin de la Societe Chimique de France, 1970,(3), 868-72

542.42:546.49-86

A thermogravimetric study of hydrothermolysis demonstrates that two different processes for the formation of mercury-imido-disulphates exist. One leads to the formation of mercury bon amido-sulphate, the other to mercury (II) monoamine sulphate.

An attempt to interpret these phenomena with a series of reactions is made.

-Hydrolysis of the mercury-imido disalphate ion, acting successively on the Hg - N bonds or on the N - S bonds.

- Recombination of the initial products.

Study of these reactions reveals the compounds obtained after mercury-imido disulphate hydrothermolysis, but the suggested mechanisms are not compatible with all of the experimental data.

50.1.24 Bolte, M. and Capestan, M.

Thermal Decomposition of Mercury-Imido Disulphates in Air. II. Barium, Strontium and Calcium Salts, $M_2Hg[N(SO_3)_2]_2$; M=Ba,Sr, or CA. (Fr)

Bulletin de la Societe Chimique de France, 1970,(3), 865-68

542.42:546.49-86

Thermal decomposition in air of mercury-imido disulphates of barium, strontium, and calcium is investigated. These products are special in that first step of decomposition (after pyrohydrolysis) leads to mercury mercury-amido sulphate formation $Hg(HgNSO_3)_2$. Under certain conditions strontium mercury-imido disulphate undergoes a second hydrolysis process which is characterized by formation of mercury (II) monoamine sulphate $HgNH_3SO_4$.

50.1.25 Queignec, R. and Wojtkowiak,B.

Comparative Infrared Absorption Spectrometry and Gas Chromatography Study of Molecular Associations by Hydrogen Bonding. (Fr)

Bulletin de la Société Chimique de France, 1970,(3), 860-864

542:543.42:541.5

The hydrogen bonding between the 1-alkynes and diethylacetamide is studied by infrared spectrometry

and gas chromatography.

The respective qualities of both methods are discussed. At the present time, gas chromatography data should still be compared with those obtained by other procedures.

50.1.26 Abdoh,Y. and Darvish, M.R.
Selective Hydrogenation of Benzalacetone.
Journal Applied Chem. 1967,17,256-285

542.941:547.542.6

Benzalacetone was hydrogenated using a Raney nickel catalyst, and various amounts of HCl,NaCl and H_3PO_4 in ethyl alcohol were added to test their inhibiting effect on catalytic activity. In the presence of HCl and H_3PO_4,Raney nickel lost its catalytic activity, and the rate of hydrogenation was decreased, but NaCl had no effect. While the hydrogenation of the ethylenic bond of benzalacetone was retarded, the decrease in hydrogen uptake by the carbonyl group was affected much more, and the amount of alcohol produced was markedly reduced.

50.1.27 Begue, J.P. et all
Réduction par lK en Solution Acétique de Composés a-Epoxycarbonyles, (2e Memoire)
Bulletin de la Societé Chimique de France, 1970,(6), 2300-2304

542.942.6

Le comportement de plusieurs epoxydes α-carbonyles en presence de IK dans l'acide acétique est étudié. II est montré que la réduction "Normalement attendue" de ces composés en esters ou cétones α-ethyléniques est conditionnée,en fait,par le sens de l'ouveture du cycle epoxydique.L'attaque par I^- du carbone en β du carbonyle conduit effectivement à la cétone α -ethylénique par l'intermédiaire d'une iodhydrine-CO - CH(I)- CH(OH) - mais celle du carbone en α de ce même groupement conduit à une iodhydrine isomère - CO - CH(OH) - CH(I) - qui selon sa structure,évolue différemment au sein du milieu réactionnel mais ne conduit pas au composé α-ethylénique cherché.

50.1.28 Hermant, G.; Dechaux J.C.; Lucquin M.
The Influence of Nitrogen Peroxide on the Low Temperature Slow Oxidation of Butane. (Fr)
Bulletin de la Société Chimique de France, 1970,(2) 473-478

542.943:542.978:547.214

A physico-chemical and analytical study is carried out on the inhibiting influence of nitrogen peroxide on the slow oxidation and low temperature stop peak of butane at 290 °C. The analytical results are:modi-

fication of the consumption, initial reagents of the important decrease of the amount of cleavage alkanes and of peroxides, accumulation of nitroalkanes. The titration of these nitroalkanes, stable at this temperature, leads to an interpretation of the experimental facts with the help of the reaction

$R^{\bullet} + NO_2 \longrightarrow RNO_2$

This inhibition stops as soon as the maximum reaction rate is reached, the consumption of nitrogen peroxide being then complete. It is shown that the measurement of the quantities of 1- nitro and 2-nitrobutane allows an approximate evaluation of the ratio of concentrations of primary and secondary butyl radicals.

543. Analytical Chemistry, Generalities.

50.1.29 Courtot-Coupez, J. and L'Her,M.

Electrochemistry in Propylene Carbonate. II. Electroactivity Range and Influence of Water. (Fr)

Bulletin de la Société Chimique de France, 1970,(4), 1631-1637

543.25

The couples silver/silver (I) and ferrocene/ferrocinium can be used as reference systems in solvent. The range of electroactivity of propylene carbonate has been determined for electrodes of

smooth platinum, platinized platinum, graphite, silver and mercury, in the presence of alkali and tetraalkylammonium salts. The important influence of water on the useful practical range has been examined and attributed to its possible oxidation or reduction.

50.1.30 Ledieu, A. and Bye J.

Sine Wave Fast Polarographic Study of the Reduction Peaks of the Phosphomolybdic Complex in Water-Methylethyl Ketone a Mixed Solvent of Application to Phosphours Analysis in Very Dilute Solution. (Fr)

Bulletin de la Société Chimique de France, 1970,(2), 801-807

543.253:546.77.18-83

The factors influencing the reduction peak height of the phosphomolybdic complex in water-methylethyl ketone mixed solvent are studied systematically to determine the optimum conditions of phosphoric acid analysis in very dilute solution. The height of two of the peaks was proportional to phosphorus concentration. A reproducibility from 0.7 % for 10^{-5} M to 2.4 % for 10^{-6} M is obtained.The detection limit is 2×10^{-7} M (0.007 ppm of phosphorus).

50.1.31 Schwing-Weill, M.J. and Arnaud-Neu, F.

A Study of the Infrared Absorption Speetra of Various Molybdic Anions. (Fr)

Bulletin de la Société Chimique de France,1970,(3),853-60

543.42:546.77

Infrared absorption spectra of solid salts of normal molydates, paramolybdates, trimolybdates, tetramolybdates octamolybdates and docecamolybdates of various monovalent cations show that it is possible to characterize the different types of molybdic anions by their infrared absorption spectra, from 1,000 to 250 cm^{-1}, except for trimolybdates the spectra of which are different when associated to different cations.

In general, the spectra of the anhydrous salts are different from those of the hydrated ones, but the number of water molecules in the hydrated salts has little or no influence on the shape of the spectra.

50.1.32 Daniels, Malcolm; Hauswirth, Willam.
Fluorescence of the Purine and Pyrimidine Bases of the Nucleic Acids in Neutral Aqueous Solution at 300 K.
Science, 1971,171(3972), 675-677

543.426:547.963.32

Fluorescence of adenine, guanine, cytosine, and uracil at room temperature in neutral aqueous solution has been detected by means of a digital signal accumulation technique. Corrected emission and exci-

tation spectra are presented and compared with low-temperature data. The quantum yields are, respectively, 2.6×10^{-4}, 3.0×10^{-4}, 0.8×10^{-4}, and 0.5×10^{-4} when the bases are excited at their low-energy absorption maxima.

50.1.33 May,S. and Samadi,A.A.

Activation Analysis Determination of Germanium in High Purity Iron and Aluminium. (Fr)

Bulletin de la Société Chimique de France, 1970,(4), 1628-1631

543.53:546.289

Germanium is usually not determined in systematic analysis of high purity iron and aluminium by activation analysis.

This determination is possible if the problem is treated separately.

The nuclear reaction used is the following:
$^{70}Ge\ (n.\gamma)\ ^{71}Ge$
^{70}Ge: isotopic abundance: 20,55%,
σ: 3.4 b,
^{71}Ge : half-life : 11,4 days - X ray : 10 keV.
The experimental sensitivity is of the order of 10^{-3} µg.
The sample is irradiated in the OSIRIS reactor for 3 days in a 10^{14} n x cm^{-2} x s^{-1} flux. After

about 5 days, Ge is isolated by chemical treatment such as precipitation,ion exchange and extraction.
Ge is determined as chloride and counted with the help of a liquid scintillation counter because of the very low X- ray energy.
The analysis results show that the amounts of the Ge in Fe varies from 6×10^{-3} to 1,4 ppm according to the purity of the sample.
In Al, the results give amounts of Ge between 4×10^{-3} and 6×10^{-2} ppm.

50.1.34 Oudar,J. and Barbouth, N.

Radiochemical Method for the Determination of Sulphur on Metals. (Fr)

Bulletin de la Société Chimique de France, 1970,(3), 834-836

543.53:543.22

A new, non destructive, radiochemical method is described. Its very high sensitivity makes it possible to determine accurately fractions of 1 ppm of dissolved sulphur (1 ppm = 0.0001 % w/w).

50.1.35 Bartos, J.; Pesez,M.

A Colorimetric Study of Primary and Secondary Alkylamines and of Primary Arylamines Using 1,2 Naphthoquinone-4-Sulfonic Acid. Improvement of the Method. (Fr)

Bulletin de la Société Chimique de France,1970,(4),1627-28

543.8:545.8

The compound obtained by reacting the amine with 1,2-naphthoquinone-4-sulfonic acid is extracted with methylene chloride and the quinone is revealed by reaction with 2,4- dinitrophenylhydrazine.

546. Inorganic Chemistry

50.1.36 Sinicki, Chr.

Solvation Coefficients of Trihalides, Halides and Halogens in Dimethylformamide. (Fr)

Bulletin de la Société Chimique de France, 1970,(4), 1643-1648

546.12.04

The solvation coefficients of halide, trihalide ions and halogens were determined in dimethyl-formamide by applying Strehlow's hypothesis to the REDOX systems I^-/I_3^--I_3^-/I_2 Br^-/Br_3^- Br_3^-/Br_2, Cl^-/Cl_2. The predictions made from these coefficients are in good agreement with the literature, particularly with reference to solubility data.

50.1.37 Palumbo, Francis J. and Fraas Foster.

Note on the Removal of Sulfur From Stack Gases by an Electrical Discharge.

Air Pollution Control Association, 1971,21(3),143-144

546.22:537.52:628.15

50.1.38 Avinens, MM.C;Cot,L.et Maurin,M.

Etude Thermique et Cristallographique Comparée de Quelques Sulfates et Fluoroberyllates.

Annales de Chimie, 1970,5(6),423-434

546.226:546.46-86:548:541.11

L'étude cristallographique et thermique de quelques sulfates et fluoroberyllates nous a permis de relever de nombreux cas d'isotypie entre ces deux familles de sels. Pour toutes les phases hydratées isotypes que nous avons rencontrées, les paramètres de la maille sont systématiquement plus grands dans le cas des sulfates, bien que l'anion fluoroberyllate soit plus volumineux. D'autre part les températures de debut de déshydratation sont toujours plus élevées pour les fluoroberyllates que pour les sulfates correspondants. Nous pensons que ces propriétés sont dues a de nombreuses liaisons hydrogène plus solides dans les fluoroberyllates.

L'évolution thermique différnte des sels anhydres montre la fragilité de l'anion BeF_4^{2-}.

50.1.39 Foss, Olav.

Stereochemistry of Tellurium(II) Complexes and Related Compounds.

Pure and Applied Chemistry,1970,24(1),31-49

46.243.2-86:541.63

Linear three-centre systems of sixth-group atoms occur in the triselenocyanate ion and in a series of tellurium(II complexes.

In the triselenocyanate ion, the Se-Se bonds are about 0.32 Å longer than covalent single bonds. In centrosymmetric square-planar tellurium(II) complexes, the tellurium-ligand bonds are about 0.27 Å longer than covalent single bonds. In tellurium(II) complexes where the linear three-centre systems are not symmetrical, pronounced relative trans bond-lengthening effects of ligands are observed. The phenyl group has a particularly large trans bond-lengthening effect.

The transition state in nucleophilic substitutions at divalent sulphur, selenium and tellurium is discussed.

50.1.40 Feraud, P.F. and Gerbier, G.
A Sensitive and Fast Method for Measuring the Corrodability of Magnesium Rich Alloy. (Fr)
Bulletin de la Societe Chimique de France, 1970,(3) 832-834

546.3-1-46:620.193:542.3

The ponderal variations due to liquid displacement induced by gaseous evolution accompanying corro-

sion can be followed automatically with a recording balance.This very sensitive method follows the reaction kinetics and can be applied to all low temperature gas producing phenomena.

50.1.41 Fischer, E.O.

Structure, Bonding and Reactivity of (Stable) Transition Metal Carbonyl Carbene Complexes.

Pure and Applied Chemistry,1970,24(2),407-423

546.75/.78:541.49

The generally applicable method for the preparation of stable metal carbonyl carbene complexes by nucleophilic addition of a carbanion from an organolithium reagent to a carbonyl group with subsequent methylation of the resulting acylcarbonyl metallate by diazomethane or trimethyloxonium-tetrafluoroborate is described. The i.r. and ^{1}H-n.m.r. spectra of new cyclopentadienyl carbonyl nitrosyl carbene complexes of chromium, molybdenum and tungsten confirm the idea of the bonding of methoxyorganylcarbene ligands as being predominantly a donation of electron density from the ligand to the rest of the molecule, with only a very much weaker π-acceptance of electrons.

Five types of reaction of carbonyl carbene comp lexes, CO substitution,carbene substitution,ester cleavage, addition and rearrangement, and H substitution are described with representative examples.

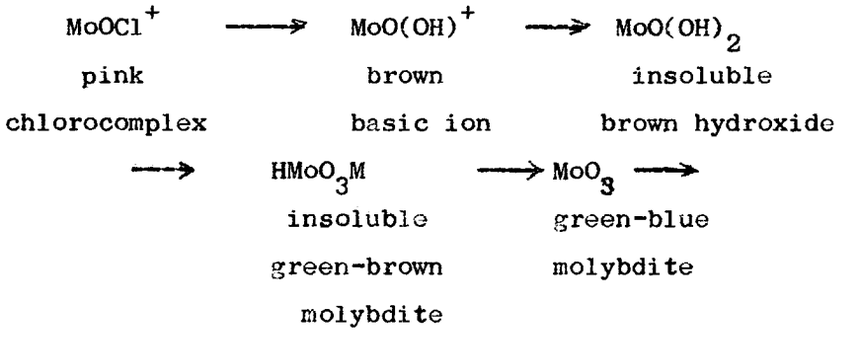
The kinetic results on the aminolysis of phenyl-methoxycarbene pentacarbonyl chromium, and the conclusions which can be drawn from the i.r. and ^{1}H-n.m.r. spectra of some o-,m- and p-substituted derivatives and arene chromium dicarbonyl carbene complexes are discussed. Results obtained from the analogous ion carbonyl system are briefly given. Some of the general features of bonding of this type of compound are summarized by the x-ray results obtained for six carbene complexes.

Finally, an account of the secondary reactions of cleaved carbene ligands with themselves and olefins close this survey of this new field of organometallic chemistry.

50.1.42 Souchay,P.,Cadiot, M.; and Viossat, B.
Some New Properties of Mo^{iv} and Mo^{v} Hydroxides. (Fr)
Bulletin de la Société Chimique de France,1970,(3), 892-898

546.774/.775:543.422

In the acidity range between 2N HCl and 8N NaOH, Mo^{iv} can exist in the following forms (increasing alkalinity):



Addition of bases to solutions of Mo^{v} in the form of $Mo_4O_8^{4+}$ causes precipitation of a hydroxide which, contrarily to that of Mo^{iv}, has cationic exchange properties. An excess of base transforms this hydroxide into Mo^{vi} (MoO_4--) and Mo^{iv} (molybdite $HMoO_3M$ or MoO_3--).

547. *Organic Chemistry*

50.1.43 Agami,C.

Aprotic Solvents.IV. Use of N,N.N,N-Tetramethylethylenediamine as Solvent in the Chemistry of Organometallic Compounds. (Fr)

Bulletin de la Société Chimique de France, 1970,(4), 1619-1624

Ref: 73

547:542.61

50.1.44 Hildbrand,J. and Kaufmann,G.

Electronic Structure of 1-Methyl-4 Phospha-3,5,8-Trioxabicyclo- [2,2,2] Octane. (Fr)

Bulletin de la Société Chimique de France, 1970,(3)876-81

547.002

A complete assignment is proposed for the spectra of 1-methyl-4-phospha-3,5,8- trioxabicyclo-[2.2.2] octane. Normal coordinate analysis allows interpretation of the phosphite electronic structure. Comparision with the corresponding phosphate shows the influence of the terminal oxygen atom on the molecule.

50.1.45 Le Berre, A.; Etienne, A. and Dumaitre, B.
Sulfoethylation. II. Sulfoethylbetaines from Tertiary Amines. (Fr)
Bulletin de la Société Chimique de France, 1970, (3), 954-58

547.233.3:542.954.6

Many tertiary amines (mostly heterocyclic), react with ethylenesulfonylchloride, $CH_2=CHSO_2Cl$ in aqueous, ethanol or acetic solutions to give sulfoethylbetaines,

$\geq \overset{+}{N}CH_2CH_2SO_3^-$

The reaction probably proceeds by three principal steps: nucleophilic addition of tertiary nitrogen to the actived double bond of the sulfochloride, hydration by the solvent, then dehydrochlorination of the resulting compound. The first two steps are fast in the cold, the third one needs slight heating or the presence of a weak base such as dimethylformamide.

30.1.46 Rabesiaka, J.

Studies on Organomagnesium Compounds in Tertiary Amines.V. Reaction of Benzonitrile. (Fr)

Bulletin de la Société Chimique de France,1970,(4), 1440-1445

547.25

The reaction of benzonitrile with organomagnesium compounds in tertiary amines leads to a phenylated imine,thus preventing the formation of a ketene-imine as in nitrile of type RCH_2CN.

If an equimolecular ratio of reagents is used, the imine leads to normal ketones in almost quantitative yield.

If the ratio of nitrile to organomagnesium compound is 2, three types of compounds can be isolated.
a β-diketone,
a triphenylalkylpyrimidine,
a triazine.

The relative amounts of these products vary with the nature of the reagents (organomagnesium compound, solvent, nitrile) and with the experimental conditions (temperature and method of addition).

This reaction allows easy synthesis of some β-diketones.

50.1.47 Ucciani,E., Pierri,F. and Naudet,M.

Photobromination of Aliphatic Chains. III.Aliphatic Acids with 6 to 18 Carbon Atoms* (Fr)

Bulletin de la Société Chimique de France,1970,(2), 791-795

547.29:541.14:542.944

The substitution of aliphatic acids (from C_6 to C_{18}) by bromine under UV irradiation takes place at a rate which varies exponentially with the inverse of the chain length.

This reaction leads to complex mixtures including noticeable amounts of threo and erythro -CHBr - CHBr- systems. These α-dibromo derivatives never appear at the end of the chain or next to the carboxyl group. In the case of the C_{12}, C_{14}, C_{16} and C_{18} acids, the α-dibromo derivatives are statistically distributed on the other carbons, and in the case of shorter acids (C_6, C_8, C_{10}) they are preferentially formed in anteterminal positions; the CH_3 - CHBr - CHBr- $(CH_2)_n COOH$ isomer is then the most important one.

The results obtained are in agreement with the radical mechanism already assumed which implies a transition state and a bridged radical.

50.1.48 Rio,G. and Berthelot, J.

Photoxidation of Acyclic Dienes: 1,1,4,4-Tetraphenyl Butadiene and Benzalazine. (Fr)

Bulletin de la Société Chimique de France,1970,(4), 1509-1511

547.315.24:541.14

The existence of an unstable photoxidation product of 1,1,4,4-tetraphenyl butadiene is postulated; its decomposition is claimed to follow two different pathways: one regenerates the starting material and the other yields benzophenone and acetylene. The photoxidation of benzalazine produces benzaldehyde and nitrogen.

50.1.49 Simonet, J.

Electroreduction of α,β-Unsaturated Ketones(III). A Comparison of the Electrolytic Reductions of Aliphatic Unsaturated Ketones in Organic and Non-Acidic Aqueous Media. (Fr)

Bulletin de la Société Chimique de France,1970,(4), 1533-1539

547.384:541.13

Aliphatic, α,β-unsaturated ketones of the type

$$R_1R_2C = CHCOR_3,$$

and acetophenone, are electrochemically reduced on a mercury electrode in organic and aqueous-organic media.

In an aprotic organic medium, two monoelectronic steps are generally observed. The influence of an added proton donor on the second step, and on the reversibility of the first step, is studied. The results obtained in an aqueous-organic medium are compared to those obtained in a highly protic medium.

50.1.50 Gautier, Jean-Claude. et all

Préparation de Crotonaldimines et Leur Reduction par le Couple Magnésium-Acide Acétique.

Annales de Chimie, 1970,5(6), 435-451

547.415.3:542.942.3

Les crotonaldimines sont réduites a O° par le couple magnésium-acide acétique en milieu eau-ether. Il se forme principalement des di-aldimines qui, par un mécanisme d'aldolisation interne suivi d'une élimination d'amine, conduisent à des aldimines cyclopenténiques substituées cis et trans. Une etude chimique et spectroscopique confirme la structure de ces imines.Enfin,une réduction par le borohydrure de sodium des imines cyclopenténiques donne des amines secondaires cyclopenténiques.

Les differentes crotonaldimines étudiées sont préparées par échange aldehyde-cétone entre le crotonal et la méthyl isobutyl cétone dans des N-diméthyl-1,3 butylidène amines. Ces dernières

sont formées par action de l'amine sur la méthyl isobutyl cétone, soit à froid en présence d'un catalyseur acide ($ZnCl_2$), soit à chaud en présence d'un agent azéotropique pour enlever l'eau formée. A chaud, à côté de la cétimine attendue, il se forme des cétimines éthyléniques provenant de la condensation de la cétimine simple sur elle-même.

50.1.51 Maffrand, J.P. and Maroni,P.
Stereochemistry of Diols and Their Cyclic Derivatives. I. Secondary Tertiary Diols and the Corresponding 1,3-Dioxanes.(Fr)
Bulletin de la Société Chimique de France, 1970,(4), 1408-1412

547.841:541.63:547.42

Synthesis and separation of the diastereoisomers of a diol series was carried out. Configurations were determined by an NMR study of the corresponding 1,3-dioxanes whose spectra have several similarities with diol spectra.This analogy seems to indicate that diols generally have a chelated pseudo-chair conformation. The results obtained by infrared spectroscopy reinforce this hypothesis.

50.1.52 Le Berre, A.; Etienne,A.; Dumaitre, B.
Sulfoethylation.I.Taurines and Taurobetaines from Primary and Secondary Amines. (Fr)
Bulletin de la Société Chimique de France,1970,(3)946-53

547.536:547.466.1:542.954.6

The alkyl ethenesulfonates, $CH_2 = CHSO_3R$, have two functional groups which are very sensitive to nucleophilic attack. These compounds react first at the activated double bond, then at the ester group when treated in the cold with a non-aromatic primary or secondary amine. They give alkyl 2-alkylamino-or 2-dialkylaminoethane- sulfonates,

$R(H)NCH_2CH_2SO_3R'$ and $R_2NCH_2CH_2SO_3R'$

usually of low stability, which are transformed either by hydrolysis or aminolysis to taurines,

$R(H)_2\overset{+}{N}CH_2CH_2SO_3^-$ and $R_2(H)\overset{+}{N}CH_2CH_2SO_3^-$,

or by intra-or inter-molecular alkylation to sulfoethylbetaines,

$R(R)_2\overset{+}{N}CH_2CH_2SO_3^-$ and $R_2(R)\overset{+}{N}CH_2CH_2SO_3^-$

A convenient synthesis for taurines and related betaines results.

50.1.53 Chiron,R. and Graff,Y.

Study of χ-Ketonic Acid Amides. (Fr)

Bulletin de la Société Chimique de France,1970,(2), 575-82

547.484.4

By reaction of organomagnesium compounds with succinimides, or by reaction of primary amines with β,γ-unsaturated δ-lactones, amides of γ-ketonic acids are generally obtained. However, in some cases

an isomeric hydroxy-pyrrolidinone is isolated. The structure of the compound obtained is unambigously determined by a chemical and spectrographic study. A hypothesis is put forward to explain the formation of these compounds.

50.1.54 Pierre, J.L.; Perraud, R. and Arnaud, P.
Nuclear Magnetic Resonance of Small Rings.XII.Conformational Study of the cis and Trans Chrysantemic Esters and Primary Alcohols. (Fr)
Bulletin de la Société Chimique de France,1970,(4), 1539-1544

547.5:543.42

Preferred conformations are demonstrated for the title compounds by solvent effects on the NMR spectrum (esters groups), and the convenient vicinal coupling constant (isopropenyl and hydroxymethyl groups). The intramolecular hydrogen bond between the hydroxyl and the isopropenyl groups of the cis-alcohol is demonstrated by infrared spectroscopy, and confirmed by NMR.

50.1.55 Pierre, J.L.;Vidal,M. and Arnaud, P.
Nuclear Magnetic Resonance in Small Rings. XIII. Cycloprpylidenes. (Fr)
Bulletin de la Société Chimique de France, 1970,(4), 1544-1550

547.5:543.42

N M R spectral analysis of several cyclopropylidene derivatives with an ester function on the ring is carried out by double resonance experiments. Chemical shifts, coupling constants an solvent effects are discussed.

50.1.56 Linstrumelle, G.

Note on Cycloheptatriene Carboxylic Acids and the Rearrangement of Their Esters. Preparation of Four Isomers of Acetyl Cycloheptatriene. (Fr)

Bulletin de la Société Chimique de France, 1970,(3) 920-926

547.518

The photochemical decomposition of ethyl diazoacetate in benzene gives mainly a mixture of ethyl-7-cycloheptatriene carboxylate 2 b and its ester 3 b, while the thermal decomposition gives a mixture of the esters 2 b and 4 b. Each isomer of the esters and of the Buchner acids are prepared in a pure state from the ester 2 b: the procedures described in the literature were improved. In particular, the action of heat on these esters in decalin under reflux leads to an equilibrium mixture of 50% of the ester 5 b, 25% 3 b and 25% 4 b.

Several photochemical isomerisations are studied:

the ester 2 b gives rise to esters 3 b and 4 b. The ester 5 b rearranges very rapidly to the ester 3 b.

The four isomers of acetyl cycloheptatriene are prepared.

50.1.57 Mousseron,M.; [illegible]enka,J.M.; Darvich, M.R.
Obtention de Dérivés de la Phényl-1 Cyclohexylamine Comportant un Groupe Phényle en Axial, (Fr)
Bulletin de la Société Chimique de France, 1970,(4), 1435-39

547.551:542.91

1-phenyl cyclohexylamine derivatives, substituted in the 4-position of the cyclohexane ring and with the phenylgroup axial, are prepared. The products are identified by NMR spectroscopy.

50.1.58 Grammaticakis, P.
Ultraviolet and Visible Absorption Spectra of Aryl- and Aroyl-Hydrazones. VII. Nitrobenzoylhydrazones. (o,m and p). Part II. (Fr)
Bulletin de la Société Chimique de France, 1970,(3), 933-45

547.556.9:543.42

A study of the UV and visible absorption spectra of the o, m and p - nitrobenzoylhydrazones of some

aromatic carbonyl compounds, mostly substituted acetophenones, shows that the o, m and p-nitration of benzoylhydrazones does not alter their main qualitative spectral relations. A steric effect has been suggested to account for the differences between the benzoylhydrazones of substituted benzaldehydes and the same derivatives of the corresponding substituted acetophenones. This effect is increased by o-nitration of the benzoyl group and decreased by p-nitration; m-nitration has little effect.

50.1.59 Mamont, P.

Condensation of Styrene and 1,1-Diphenyl Ethylene with Ubiquinones in Acidic Media. (Fr)

Bulletin de la Société Chimique de France, 1970,(4), 1557-1564

547.567.3

Acid treatment of the ubiquinone 4 in the presence of 1,1-diphenyl ethylene or styrene leads respectively to the tetrahydrofuran derivative 5 or the bicyclic derivative 15.The formation of dichromanes of type 3 was not observed.These could have resulted from 1,4- addition of the olefin on an intermediate methylene quinone of type 2.

50.1.60 Mamont,P.

Acid Treatment of Tocoquinones.III.Acidic Condensation of Styrene with Tocoquinone-1. (Fr)

Bulletin de la Société Chimique de France, 1970,(4), 1564-1568

547.567.3

Acid treatment of tocoquinones in the presence of styrene yields a bicyclic compound of type 4 which results from the condensation of the olefin with carbons 2 and 6 of the quinone nucleus. A type 3 dichroman derivatives is not formed. This is in contrast to previous results obtained in this series with 1,1-diphenyl ethylene.

50.1.61 Mamont, P.

Acid Isomerization Mechanism of Menaquinones, Tocoquinones and Unbiquinones. (Fr)

Bulletin de la Société Chimique de France, 1970,(4), 1568-1571

547.567.3

The results of the acid catalysed condensation between an olefin (like styrene or 1,1-diphenyl ethylene) and a quinone (menaquinone, ubiquinone or tocoquinone) are summarized . The formation mechanism of the different products is discussed and a tentative general explanation for the observed reactivity di-

fferences is proposed.

50.1.62 Beslin,P. and Conia, J.M.

Thermolysis and Photolysis of Unsaturated Ketones. XVIII. Application of the Thermocyclisation of 3-(but-3-enyl) Cyclohexanoes to the Total Synthesis of 12-Oxosteroids. (Fr)

Bulletin de la Société Chimique de France,1970,(3), 959-964

547.572.6:542.92:547.92:54.07

By heating at 350°, 1-(but-3-enyl)-7-methoxy-1, 2,3,4,4 a, 9,10,10 a- octahydro-3- phenanthrone 19 is cyclised to give 3-methyl-17 -methyl-18-nor-1, 3,5(10)-estratien-12-one 25 in 70% yield.

3-(but-3-enyl)-7-methoxy-2-methyl-1,2,3,4,4a, 9,10,10a octahydro-3-phenanthrone 23 leads to a mixture of two isomers: 3-methoxy-17b-methyl-13-iso-1,3,5(10)-estratrien-12-one 28 and 3-methoxy-17-methyl-iso-1,3,5,(10)-estratrien - 12 - one 29

The stereochemistry of the cyclised products has been elucidated by NMR (including solvent shifts), and IR spectroscopy.

50.1.63 Wylde, R. and Teulon,J.M.

The Epoxides of Limonene: Synthesis and Reactivity.(Fr)

Bulletin de la Société Chimique de France, 1970,(2), 758

547.596.7:542.943.6

The two limonene epoxides are prepared in a pure state,by a method which provides sufficient quantities of each isomer.

The p-nitrobenzoate of 1-chloro neodihydrocarveol leads to the cis-epoxide, while the 2-chloro-8-p menthene-1-ol leads to the trans-epoxide.

From a study of physicochemical properties, mostly N M R, and the reactivity towards lithium aluminium hydride and dimethylamine, a mechanism for the cleavage is proposed.

50.1.64 **Chalvet,O.**,Royer, R. and Demerseman,P

Studies in the Benzofuran Series XLI. Tentative Theoretical Interpretation of the Chemical Behaviour of Benzofuran, Compared to Benso [b] Thiophene. (Fr)

Bulletin de la Société Chimique de France, 1970,(4) 1483-1490

547.72

The differences between benzofuran and benzo[b] thiophene, as observed from their physical properties, are fully verified with their respective sensitivities towards electrophilic substitution and their ability to undergo addition reactions on the heterocyclic ring.

Differences are also observed in the behaviour towards nucleophiles of their derivatives which contain an electron-withdrawing group at the 3 position.

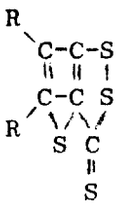
The charge and the potential barrier diagrams of benzofuran calculated using the Pariser-Parr and Pople method (taking into account configuration interactions or not), and also the total charge (π and σ) diagrams obtained by the CNDO method, do not explain the observed chemical reactivity of the compound as well as an approach involving bond orders and delocalisation energies.

The theroretical data explain in part the experimental differences between benzofuran and benzo b thiophene.

50.1.65 Appriou, P., Brelivet and Teste, J.

Sulphur Containing Heterocyclic Compounds. V. Synthesis of Thieno [3-2-c] 1,2- Dithiol-3- Thiones. (Fr)

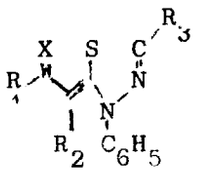
Bulletin de la Société Chimique de France, 1970,(4) 1497-1502



547.73

The reaction of sulphur with variously substituted 5-vinyl-1,2-dithiol-3-thiones provides a convenient synthesis of thieno[3,2-c]1,2-dithiol-3-thiones. Several of the latter compounds are described.

50.1.66 Maguet, M., Poirer, Y. and Tests, J.
Heterocyclic Sulphur Compounds (VI). Syntheses of Some Derivatives of 1,3,4 Thiadiazoline. (Fr)
Bulletin de la Société Chimique de France, 1970,(4), 1503-1509



X= S,O,N

547.73

∝-Chlorobenzylidene phenyl hydrazine and ethyl bromo (phenylhydrazono) acetate condense with 5-aryl-1,2-dithiol-3-thiones with opening of the dithiol ring. The products obtained are (Δ 4-1,3,4-thiadiazoline-2-ylidine) thioacetophenones, whose structures have been established by desulphurisation and by independent synthesis involving condensation of diazoacetophenone with 3,5-diphenyl- Δ 4-1,3,4-thiadiazoline-2-thione. On treatment with methyliodide, the thioacetophenones give compounds which can be consi-

dered as iodides of 2-(2-vinyl-methylthio)-3,5-diphenyl-1,3,4- thiadiazolium. The latter compounds react with primary aliphatic and aromatic amines. Some properties of the N-aryl amines thus obtained are described.

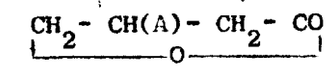
50.1.67 Ducher Suzanne et Peyronnet Jacques.
Réactivité de L'expoxy-3-4 Butanoate D'éthyle en Milieu Acide.
Annales de Chimie,1970,5(6),415-422

547.717:547.294-26

Traiter l'epoxy-3-4 butanoate d'éthyle par un réactif AH(HCl, CH_3COOH, ROH) entraîne l'ouveture du cycle epoxyde. Cetter rupture est toujours favorisée:

- d'une part par l'emploi de catalyseurs acides protoniques minéraux ou acides de Lewis,
- d'autre part, par le reflux de l'ensemble réactionnel durant plusieurs heures.

Le produit essentiel de la transformation est toujours l'alcool secondaire $CH_2(A) - CH(OH) - CH_2 - COOC_2H_5$. Lorsquil se forme une petite quantité d'alcool primaire isomère $CH_2(OH) - CH(A) - CH_2 - COOC_2H_5$, celui-ci se cyclise en butanolide



isolable.

L'epoxy-ester est remarquablement stable à la chaleur et ne se prête pas à l'isomérisation en dérivé carbonylé.

50.1.68 Buu-Hoi,N.P., Jacquignon,P. and Ledesert, L.
The Chemistry of Carbazoles. IV.Synthesis and Roarrangement of Benzo-and Dibenzo-Carbazolenines. ((Fr)
Bulletin de la Société Chimique de France,1970,(2), 628-631

547.756.32

One tetracyclic and two pentacyclic carbazolenines are synthesized from 2-methyl-1-tetralone for testing their potential carcinogenic activity; treated with palladized charcoal, these compounds underwent demethylation and rearrangement to give 11 H-benzo [a]carbazole and 13-H-dibenzo [a, i] - and dibenzo [a, g]-carbazole respectively. An investigation of their NMR spectra and of their electronolysis pattern is undertaken.

50.1.69 Barascut, J.L., Elguero, J. and Jacquier, R.
Studies in the Azole Series.LXV. Aminopyrazoline Tautomerism. Part. 1.General Considerations and Synthesis of Fixed- Structure Compounds.5-Amino Pyrazoline Tautomerism. (Fr)
Bulletin de la Société Chimique de France, 1970,(4), 1571-1576

547.77

Tautomerism of 5-amino- and 3-amino- pyrazolines was studied by N M R . A 5-imino pyrazolidine form was demonstrated in the first case. 3-Amino-2-pyrazoline and 3-imino-pyrazolidine are the only two forms possible for 3-amino-pyrazolines in the second case.

The synthesis of model compounds was undertaken to completely solve this last problem. 1,2-Dimethyl-3-imino-pyrazolidine was prepared and the synthesis of 3-dialkyl- amino-2-pyrazolines was attempted. The structure of 1-phenyl-5-imino-pyrazolidine dihydrochloride was established.

50.1.70 Elguero,J.; Jacquier, R. and Mondon,S.
Studies in the Azole Series. LXVI.Aminopyrazoline Tautomerism. Part 2. Synthesis of Compounds of Partially Fixed Structure; 3-Dialkylamino Pyrazolines. (Fr)
Bulletin de la Société Chimique de France, 1970,(4), 1576-1581

547.77

Several syntheses for 3-dialkylamino-pyrazolines were tried. Only sodium/alcohol reduction of 1-phenyl-3-dimethylamino pyrazole sulfomethylate products 1-phenyl-3-dimethylamino pyrazoline. The N M R spectrum

of the formylated 1-phenyl-3-amino pyrazoline derivative is discussed.

50.1.71 Coispeau, G., Elguero J.; Jacquier, R.
Studies in the Azole Series. LXVII. Reaction Mechanism of α,β-Unsaturated Carbonyl Compounds with Hydrazines. The Stereochemistry of 4 and 5 Positions in 2-Pyrazoline and the 2-pyrazoline ion. (Fr)
Bulletin de la Société Chimique de France, 1970,(4), 1581-1585

547.77

A mechanism is proposed for the reaction of mono or 1,2-disubstituted hydrazines with α β-unsaturated carbonyl compounds. The C-protonation of an intermediate 3-pyrazoline determines the stereochemistry of the 2-pyrazoline obtained. This mechanism explains the acid catalyzed proton exchange of the 3-and 4-positions and the 4-position deuterium incorporation results.

50.1.72 Elguero,J.,Jacquier,R. and Shimizu,B.
Studies in the Azole Series. LXVIII. Attempted Synthesis of 3-Acyl Pyrroles, Preparation of 3-Acyl-4-Pyrrolidinones. (Fr)
Bulletin de la Société Chimique de France ,1970,(4), 1585-1590

547.77

The synthesis and spectral characteristics (IR and NMR of 3-acyl-4-pyrrolidinones are described. The 3-acylpyrroles could not be obtained from these compounds.Several other synthetic methods were tried without success.

50.1.73 Pesson,M. and Antoine, M.

Studies in the 1,2,4-Triazole Series.VI. Tautomers of 5,6-Dioxo-4-Methyl-3-Thioxo Hexahydro-1,2,4-Triazine. (Fr)

Bulletin de la Société Chimique de France, 1970,(4), 1599-1606

547.792

5,6-Dioxo-4-methyl-3-thioxo-hexahydro-1,2,4-triazine **1** has two acid protons and is capable of having several tautomeric forms in solution. Preparation of the N-and S-methyl and the dimethyl derivatives of I is by direct methylation with diazomethane or by independent synthesis. Among the compounds described, 5,6-dioxo-2,4-dimethyl-3-thioxo-hexahydro-1,2,4-triazine undergoes ring regression into a 1,2,4-triazole derivative as previously described for related compounds. A UV study of alcohol solutions of 5,6-dioxo-4-methyl-3-thioxo-hexahydro-1,2,4-triazine and its methyl derivatives strongly suggests that a 6-enolized form exists.

50.1.74 Pesson,M. and Antone,M.

Studies in the 1,2,4-Triazole Series. V.N,N-Dialkyl Amides Derived From 1,2,4-Triazol-5-yl Carboxylic Acids. (Fr)

Bulletin de la Société Chimique de France, 1970,(4), 1590-1599

547.792

Preparation of N,N-dialkyl amides (derivatives of 1,2,4-triazol-5-yl carboxylic acids) from N,N-dialkyl semioxamazides is described. Reaction conditions and the nature of the cyclizing reagent determine whether the cyclization of 1-(N,N-dialkyl oxamoyl)-4-methyl thiosemicarbazides leads to 5-(N,N-dialkyl carbamoyl)-3-mercapto-4-methyl-1,2,4-triazoles or to 5,6-dioxo-4-methyl-3-thioxo hexahydro-1,2,4-triazine. Their structure and chemical properties are discussed. The latter compound and several of its derivatives are unstable in alkaline media where they undergo ring regression into derivatives of 1,2,4-triazole.

50.1.75 Eliel,E.

Conformational Analysis of Saturated Heterocyclic Compounds. (Fr)

Bulletin de la Société Chimique de France, 1970,(2), 517-524

Ref : 54

547.84:541.6

50.1.76 Ishibe, N. et all.
Photosensitized Oxygenation of 4H-Pyran-4-Thiones and 4H- Thiopyran-4-Thiones.
Chemical Communications, 1971,(2),118-119

547.818

50.1.77 Friedmann, Nadav. and Miller, Stanley L.
Primitive Earth Synthesis of Nicotinic Acid Derivatives.
Science,1971,171(3975),1026-1027

547.826.1:54.07

Nicotinonitrile, 2-cyanopyridine, and 4-cyanopyridine can be synthesized under primitive earth conditions by the action of electric discharges on ethylene and ammonia. The electric discharge first synthesized pyridine and hydrogen cyanide, which react in the discharge to form the cyanopyridines. Nicotinonitrile would have hydrolyzed in the primitive ocean to nicotinamide and nicotinic acid.

50.1.78 Daunis, J. et all
Studies in the as - Triazine Series.V. Synthesis of 1,6-Dihydro-1,2,4-Triazine (Fr)
Bulletin de la Société Chimique de France, 1970,(4), 1606-1611

547.873

Several 3,5-disubstituted (by OH, SH and $NH-NH_2$) 1,6-dihydro-1,2,4-triazine derivatives are described.

50.1.79 Nicaise, A.M. and Bourdon,R.

Oxidation of Δ^5- 7-Oxo Steroids by Means of Trifluoroperacetic Acid. (Fr)

Bulletin de la Société Chimique de France, 1970,(4), 1552-1557

547.92

Trifluoroperacetic acid reacts with Δ^5 -7-oxosteroids to give complex mixtures. Two distinct series of compounds can be isolated: diacids of similar structural type which are weakly soluble in aliphatic hydrocarbons, and a soluble fraction containing several differents types of compound. The structures of the latter products are described.

50.1.80 Wrzeciono,U. et all

Syntheses of Labelled Tetracyclic Triterpenes. I. 14 C-25 and D6-26,27 Lanosterol, Cycloartenol, Parkeol and 31-Norcycloartenol; II. T-2 Lanosterol and Cycloartenol. (Fr)

Bulletin de la Société Chimique de France, 1970,(3),966-74

547.92:54.07

(25-^{14}C)- and (26,27-D_6)- lanosterol, cycloartenol and 31-norcycloartenol are obtained by the same sequence starting from the unlabelled triterpenes: ozone cleavage of the side-chain, reduction to the trinor-24-alcohols, formation of the 24-iodo derivatives, of the 24-triphenyl-phosphonium iodides, of the 24-ylides, and finally reaction with ^{14}C- or D-labelled acetone. (25-^{14}C) and (26,27-D)-parkeol are obtained by the same method, after isomerisation of the double bond from 8 to 9 (11), in the trinor-24-alcohol obtained from lanosterol. The degradation of cycloeucalenol to 31-norcycloartenol is described in detail. (2-T)-Lanosterol and cycloartenol are obtained by exchange of the 3-ketones with THO, followed by reduction.