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SPECTROSCOPIC STUDIES OF ORGANOPHOSPHORUS COMPOUNDS Part VII. IR Spectra of Alkyltriphenylphosphonium Compounds*

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(Received September 25, 1972)

Abstract. A detailed study of the IR spectra of triphenylphosphine and alkyltriphenylphosphonium iodides and bromides having methyl, *n*-propyl or *n*-butyl as the alkyl group is reported for the 4000–250 cm^{-1} region. Integrated intensity of a number of bands besides the X-sensitive ones shows that the changes in intensity are related to quaternization in the case of the k, m, o, c and q, and to the length of the alkyl chain for n, a, b, d and p. A characteristic feature of the spectra is the splitting of the band in the 750 cm^{-1} region corresponding to the C—H out-of-plane bending. The changes in intensity and splitting of the bands are both interpreted on the basis of induced polarization whereby the formal positive charge on the phosphorus atom creates a polarity in the ring by attracting their π -electron density. The positive inductive effect of the alkyl group is responsible for the increase in the polarity and hence a dependence of the intensity is observed on the alkyl chain-length. The amount of splitting and the intensity of mode n is also found related to the bulk of the alkyl group. The intensity of the P—C (aliphatic) absorption, however, decreases with chain-length. The X-sensitive modes q, y, t and u shift their positions on quaternization of the phosphine.

For the phosphonium bromides the intensity enhancement is at least three times that of the iodides. There is a further shift in the band position and splitting is more pronounced. The P—C stretching frequency is shifted to slightly lower frequencies from $780 \pm 10 \text{ cm}^{-1}$ in the iodides to 765 ± 5 in the bromides.

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SPECTROSCOPIC STUDIES OF ORGANOPHOSPHORUS COMPOUNDS

Part VIII. IR Spectra of Tri-*m*-tolylphosphine and Alkyltri-*m*-tolylphosphonium Iodides*

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(Received December 27, 1972)

Abstract. The spectra of tri-*m*-tolylphosphine and alkyltri-*m*-tolylphosphonium iodides, where the alkyl group is methyl, ethyl, *n*-propyl and *n*-butyl have been reported and assignments have been made for the 1600–250 cm^{-1} region.

Integrated intensity measurement of a number of bands shows that the same is related to the length of the alkyl chain and/or quaternization. The intensity of the *m*-tolyl phosphorus compounds is on the whole lower than the phenyl and *p*-tolyl compounds which is explained in terms of induced polarization of the formal positive charge. The intensity variation of quite a few modes and particularly those in the 1600–1400 cm^{-1} region has also been interpreted similarly. The high intensity of mode *n* here again suggests that this is due to steric overcrowding. Splitting of the $\nu(\text{C—H})$ modes is the characteristic feature of *m*-tolylphosphonium compounds also. The $\nu_{\text{as}} \text{P—C}_{\text{aliphatic}}$ is noted at 790 cm^{-1} .

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MASS SPECTRAL STUDIES OF SOME CYCLOHEXENE-DERIVED POLYHALOGENOALKANES

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(Received November 21, 1972)

Abstract. The mass spectral studies of dichloromethylcyclohexane (I), 1-dichloromethyl-2-chlorocyclohexane (II) and dichloromethylcyclohexane (III) have been described. The pattern of mass fragmentation of the above compounds show a regular order.

1,1-SUBSTITUTED DICHLOROMETHYLENE COMPOUNDS

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(Received December 7, 1972; revised February 13, 1973)

Abstract. 1,1-Substituted dichloromethylene compounds are produced in the reaction of carbon tetrachloride or bromotrichloromethane with primary and secondary aliphatic amines containing at least two α -hydrogens on the alkyl group of the amine. The mass spectra of these compounds are reported. A mechanism which depicts the product formation is proposed.

REACTION OF THIONYL BROMIDE WITH SUBSTITUTED PHENOLS

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(Received April 14, 1972; revised October 14, 1972)

Abstract: This paper deals with the reaction of thionyl bromide and some substituted phenols. In case of *o*, *m* and *p*-cresols, 4-bromo-*o*-cresol, 4-bromo-*m*-cresol and 2-bromo-*p*-cresols were isolated. Similarly 2-chlorophenol and 4-chlorophenol gave 4-bromo and 2-bromochlorophenols in moderate yields.

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THE DECARBOXYLATION OF OXALIC ACID IN RESORCINOL AND CATECHOL

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(Received November 15, 1972)

Abstract. Kinetic study of the decarboxylation of oxalic acid in resorcinol and catechol has been made for the first time. The reaction is of first order. The observations support the view that all the five decompositions proceed through an intermediate complex.

SOLVENT EFFECTS IN THE OXIDATION OF TRIPHENYLPHOSPHINE

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(Received November 21, 1972; revised January 13, 1973)

Abstract. Oxidation of triphenylphosphine with peroxybenzoic acid has been studied kinetically in various polar solvents. It has been observed that this reaction follows second order kinetics and its rate constant is directly proportional to the dielectric constant of the solvent employed. Activation energies and entropies of activation of this reaction have also been calculated.

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ADSORPTION ON HOMOGENEOUS SURFACE

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Abstract. Piezogravimetric method has been used to study the adsorption of H_2O , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, $n\text{-C}_3\text{H}_7\text{OH}$ and $n\text{-C}_4\text{H}_9\text{OH}$ on polished quartz crystal surface, at 26.7°C . The isotherms of type II, tending to meet the saturation pressure line. The BET equation was found to be valid up to $p/p^\circ = 0.4$. The values of the molecular cross-sectional areas of the alcohols showed a horizontal orientation on the quartz crystal surface.

A MNEMONIC APPROACH TO THE CLAUSIUS AND MAXWELL DIFFERENTIAL THERMODYNAMIC RELATIONSHIPS

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(Received November 22, 1972; revised March 1, 1973)

Abstract. A simple and explicit mnemonic procedure for the derivation of the set of Maxwell's first order partial derivatives and the Clausius relationships, in terms of fundamental thermodynamic parameters (V, T, P and S), is described with illustrative examples. The procedure has been applied, in the first instance, to thermodynamic systems of constant and variable composition and, later, extended to cover cases of constant volume, temperature, pressure and entropy. All this has been taken up with the aid of a computational procedure based on an instructive logic rather than on a mathematical operational logic.

Biological Sciences Section

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SOME ASPECTS OF MATING AND OVIPOSITION BEHAVIOUR OF THE SPOTTED BOLLWORM OF COTTON, *EARIAS VITTELLA* (F.)

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(Received August 19, 1972; revised January 2, 1973)

Abstract. Investigations were made on the mating and oviposition behaviour of the spotted bollworm of cotton, *Earias vittella* (F.) in the laboratory. The field-collected larvae when reared on natural diet showed a sex ratio of 49 males to 51 females. The females generally mated once and the maximum mating was observed on the fourth night after emergence. The mating was maximum between 2-3 a.m. and the duration of mating ranged from 30-105 min. It was also observed that males mate more often when confined with several females than with one.

The females started laying eggs on the second night after emergence or the first night following mating. The most active oviposition period was in the range of 2-7 days post-emergence. A mated female laid on an average 159 eggs. The majority of oviposition occurred during night hours.

STUDIES ON THE PHENOTYPIC POLYMORPHISM OF MUSCA DOMESTICA L.

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(Received October 23, 1972; revised February 20, 1973)

Abstract. Phenotypic polymorphism in *Musca domestica* L. was studied. Laboratory cultures and field collected flies were examined under the binocular microscope but no aberrant forms could be found. Breeding of single pairs, however, yielded a large number of variants, in the F₂ generation.

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THE GENERA OF LYGAEINAE (HETEROPTERA:LYGAEIDAE) IN WEST PAKISTAN

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(Received August 19, 1972; revised December 20, 1972)

Abstract. Only four genera of Lygaeinae were previously known from West Pakistan. Present study records seven more to bring the total to eleven. A key to these genera and brief diagnostic characters are given. The subfamily Lygaeinae is credited to Schilling 1829, contrary to an earlier practice of crediting to Stål 1862.

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FURTHER CONTRIBUTIONS TO THE CELLULOSE DESTROYING FUNGI OF PAKISTAN

(Miss) FATIMA ASAD, AHMEDUNNISA, S. SHAHID HUSAIN and S. IFTIKHAR AHMED

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(Received June 2, 1972; revised November 24, 1972)

Abstract. Fungi causing deterioration of cellulosic materials such as paper, cloth, straw and cotton in nature were collected and examined. A total number of 35 fungi belonging to the *Myxomycetes*, *Phycomycetes*, *Ascomycetes* and *Fungi imperfecti* were isolated. Fungi belonging to *Ascomycetes* and *Fungi imperfecti* were predominant and species of *Chaetomium* and *Aspergillus* were most frequent in their respective groups.

Present investigation was carried out in an effort to further the work of previous investigators and hence certain cellulolytic materials like paper, cotton, cloth and straw were examined to isolate microorganisms colonizing these materials.

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STUDIES ON THE BACTERIOSTATIC PROPERTIES OF HIGHER PLANTS OF KARACHI REGION

Part II

(Miss) MARYAM SALEH ATTIA, (Miss) SHAHNAZ AHMAD and S.A.H. ZAIDI

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(Received April 1, 1972; revised January 30, 1973)

Abstract. Radial diffusion assay of ethanolic extracts of 68 higher plants against 14 human pathogenic bacteria have been described. The extracts of 15 plants showed bacteriostatic activity against all the 14 test organisms; 42 plants exhibited varied degree of activity while the rest were found to be inactive.

STUDIES ON SOME ASPECTS OF DEHYDRATION OF BITTER GOURD (KRELA)

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(Received September 7, 1972; revised November 29, 1972)

Abstract. Results of the effects of different pretreatments on the quality of dried bitter gourd (krela) have been presented. Blanching in alkaline medium was found to preserve the colour and ascorbic acid. Salting improved the taste by removing most of the bitterness, but affected the rehydration properties adversely. Drying without any pretreatment produced products of poor quality.

Short Communications

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A NEW RECORD OF OCHTERUS MARGINATUS (LATR.) (HETEROPTERA: OCHTERIDAE) FROM SIND PROVINCE, PAKISTAN

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ABNORMAL FORMATIONS OF LEAF, FLOWER AND FRUIT OF PAPAYA SUFFERING FROM VIRUS INFECTION

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Technology Section

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EFFECT OF AGGREGATE SIZE ON LEACHING OF SALTS FROM SOIL AGGREGATES*

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(Received November 24, 1972)

Abstract. The effect of size of aggregates on leaching of salts from aggregates was studied by making the soil aggregates with 10% CaCl_2 solution. The aggregates were graded into different sizes, packed in columns and leached under constant water head. The size of aggregates influenced the leaching pattern, salt being removed more rapidly from smaller aggregates.

A CUMULATIVE EFFECT OF PHOSPHATIC FERTILIZERS ON THE 'A' VALUE OF SOILS UNDER RICE CULTIVATION

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(Received August 18, 1972; revised February 3, 1973)

Abstract. Residual availability of P was investigated in three soils using rice plant for three consecutive years under greenhouse conditions. The 'A' values of the three soils measured in different years were significantly higher than their respective preceding years and that of the first year (1964) compared to Olsen's NaHCO_3 -P extracted from the original soils. Comparatively larger amounts of residual P were available in the Kala Shah Kaku loamy soil during all the years. A reverse tendency was observed in the Tando Mohammad Khan clay loam soil having the highest content of clay and carbonates.

The fractions of P derived from the added P and per cent of superphosphate fertilizer utilized by the rice plants decreased as the availability of residual P in soils increased. Only slight fixation of P occurred in Tando Mohammad Khan soil in the first as well as the second year and in Dokri soil during the second year only otherwise large additional amounts of P released from all the soils over and above the P applied. This indicates a very negligible fixation of P in soils particularly the loamy ones grown to rice.

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CHEMOSTERILIZATION OF THE LABORATORY-REARED YELLOW-FEVER MOSQUITO, *Aedes Aegypti*(L) BY SUBSTITUTED PHOSPHINE OXIDES AND METHYLMELAMINES

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(Received November 7, 1972; revised March 2, 1973)

Abstract. Test with 5 substituted bis-(1-aziridinyl)-phosphine oxides indicated that they were active sterilants for third instar larvae of laboratory-reared *Aedes aegypti* (L.) inducing 100% sterility at 2.5 p.p.m. Methylmelamines proved ineffective even up to 10 p.p.m. concentration and are not active chemosterilants for mosquitoes. Toxicity of substituted-phosphine oxides was much higher as compared to methylmelamines. Isopropoxy and butoxy phosphine oxides induced 100 and 91.7% sterility at 1 p.p.m. dose respectively. At higher concentrations phosphine oxides produced abnormal pattern of adult emergence terminating into death.

INCIDENCE OF MEDULLATION IN CARPET WOOLS

Part II. Extent of Medullation in Heterotypical Fibres

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(Received July 5, 1972; revised November 22, 1972)

Abstract. Fibre diameter and the diameter, length and frequency of medullated fragments were determined in the case of 20 heterotypical fibres of 10 different carpet wools. The various relationships between these characteristics were examined statistically and, where necessary, fully medullated fibres were also included in the studies. It appears that the role of diameter is two-fold: in addition to its effect on the proportion of medullated fibres in a sample as reported earlier,³ the diameter affects the extent of medullation in individual fibres. As the diameter of heterotypical fibres increases, the medulla diameter also increases rather rapidly till it reaches its maximum at a fibre diameter of about 100 μ , when the medulla occupies more than 85% of the fibre volume.

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MECHANICAL CONSTANTS OF SINGLE WOOL FIBRES

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(Received October 4, 1972; revised January 30, 1973)

Abstract. Mechanical constants of single fibres from wools of widely different dimensional attributes have been determined after stretching to 30%. No relationship was found between area of cross-section and the stress at 30% strain. The work done in stretching to 30% exhibited a significant correlation with the cross-sectional area and the linear regression of the former on the latter was also found significant at 5% level and accounted for some 27% of the variation.

EVALUATION OF KATTHA BAUXITES FOR INDUSTRIAL UTILIZATION

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(Received August 28, 1972; revised February 6, 1973)

Abstract. Attempts have been made to evaluate twenty representative bauxite samples of the Kattha area and their chemical, mineralogical and physical properties such as bulk density, shrinkage after firing, thermal expansion and pyrometric cone equivalent were determined. Silica and alumina contents of bauxites vary from 7.5 to 42% and 37.6 to 75.45% respectively. Most of the samples are rich in boehmite while a few contain considerable amount of kaolinite. The bauxites may be utilized for the production of alumina and aluminous chemicals, low and high grade refractories, high alumina cement, abrasives and in the purification of oils, waxes and petroleum.