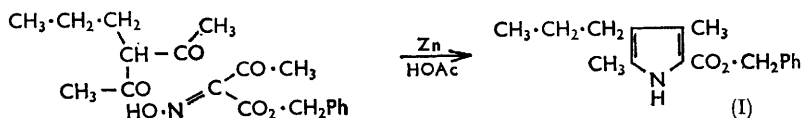


417. The Preparation of the Mixed Isomers of Tetramethyltetrapropylporphin.

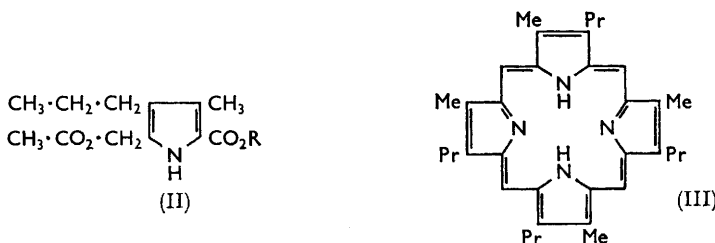
By A. H. JACKSON, P. JOHNSTON, and G. W. KENNER.

TETRAMETHYLTETRAPROPYLPORPHIN was required for investigations of ring-current effects on proton magnetic resonance (p.m.r.) spectra of porphyrins.^{1,2} We have prepared this porphyrin by a new method based on Siedel and Winkler's synthesis,³ recently improved and extended by Bullock, Johnson, Markham, and Shaw.⁴



3-Acetylhexan-2-one, prepared from n-propyl bromide and acetylacetone, was condensed with benzyl α -hydroxyiminoacetoacetate under the usual conditions of Knorr's pyrrole synthesis. Treatment of the resulting pyrrole (I) with lead tetra-acetate gave the acetoxy-derivative (II; R = CH₂Ph), from which the acid (II; R = H) was obtained by hydrogenolysis. When a solution of this acid in acetic acid was boiled and then aerated, the desired tetramethyltetrapropylporphin was formed in good yield.

It has been suggested⁴ that syntheses of this type involving polymerisation of monopyrroles under acidic conditions lead solely to "type-III"⁵ porphyrins. However, this has not been substantiated by later evidence,⁶⁻⁸ and it seems likely that our tetramethyltetrapropylporphin was a "random mixture"⁹ of type isomers (*i.e.*, approximately $\frac{1}{8}$ I, $\frac{1}{8}$ II, $\frac{1}{2}$ III, $\frac{1}{4}$ IV). This was no disadvantage in our spectroscopic studies, because we have shown that "type isomers" of octa-alkylporphyrins cannot be distinguished by n.m.r.



Experimental.—3-Acetylhexan-2-one. Acetylacetone (134 ml.), n-propyl bromide (160 g.), and anhydrous potassium carbonate (168 g.) were heated in dry acetone (148 ml.) under reflux for 24 hr. The cooled solution was filtered and the potassium carbonate was washed with acetone. Evaporation of the combined filtrates and distillation at 196—198° afforded 3-acetylhexan-2-one (90 g.; 45%), n_D^{13} 1.442 (lit.,¹⁰ n_D^{20} 1.443).

¹ Abraham, Jackson, and Kenner, *J.*, 1961, 3468.

² Abraham, *Mol. Phys.*, 1961, 4, 145.

³ Siedel and Winkler, *Annalen*, 1943, 554, 162.

⁴ Bullock, Johnson, Markham, and Shaw, *J.*, 1958, 1430.

⁵ Fischer and Stangler, *Annalen*, 1927, 459, 62.

⁶ Mauzerall, *J. Amer. Chem. Soc.*, 1960, 82, 2601.

⁷ Kay, *Proc. Nat. Acad. Sci. U.S.A.*, 1962, 48, 901.

⁸ Abraham, Burbidge, Jackson, and Kenner, *Proc. Chem. Soc.*, 1963, 134.

⁹ Cookson and Rimington, *Biochem. J.*, 1954, 57, 476.

¹⁰ von Auwers and Jacobson, *Annalen*, 1922, 426, 161.

Benzyl 3,5-Dimethyl-4-n-propylpyrrole-2-carboxylate. Sodium nitrite (7.4 g.) in water (25 ml.) was added slowly to a well-stirred ice-cold solution of benzyl acetoacetate (19.2 g.) in glacial acetic acid (30 ml.), the temperature being kept below 10°. When the addition was complete, the mixture was stirred for a further $\frac{1}{2}$ hr. and then left overnight at room temperature. Next morning it was added slowly to a well-stirred solution of 3-acetylhexan-2-one (14.2 g.) in glacial acetic acid (10 ml.), already warmed to 60°, and zinc dust (14 g.) was added simultaneously. The rate of addition of the acetylhexanone and zinc was controlled so that the temperature did not rise above 65°. Finally the whole mixture was heated on the steam-bath for a further 40 min. before being poured into ice and water (ca. 400 g.). When all the ice had melted the solid product was filtered off, washed with water, and crystallised from 90% methanol. The *pyrrole* (I) (8.1 g.; 30%) formed cream fibrous needles, m. p. 76–78°, raised to 79–80° after recrystallisation from light petroleum (b. p. 60–80°) (Found: C, 75.1; H, 7.8; N, 5.4. $C_{17}H_{21}NO_2$ requires C, 75.2; H, 7.8; N, 5.2%).

Benzyl 5-Acetoxyethyl-3-methyl-4-propylpyrrole-2-carboxylate. Lead tetra-acetate (8.9 g.) was added slowly during $\frac{1}{2}$ hr. to a well-stirred solution of the foregoing pyrrole (5.5 g.) in glacial acetic acid (150 ml.). The mixture was stirred for a further 2 hr. at room temperature before most of the acetic acid was removed under reduced pressure. The residue was poured into stirred ice-water (400 g.) and extracted with chloroform. The dried ($MgSO_4$) extracts were evaporated and the solid residue was recrystallised from methanol. The *acetoxyethylpyrrole* (II; R = CH_2Ph) (2.8 g.; 42%) crystallised as fibrous needles, m. p. 120–122°, raised to 122° by recrystallisation from petroleum (b. p. 60–80°) (Found: C, 69.2; H, 7.0; N, 4.4. $C_{19}H_{23}NO_4$ requires C, 69.3; H, 7.0; N, 4.25%).

Tetramethyltetrapropylporphin. The acetoxyethyl pyrrole (1.65 g.) in methanol (150 ml.) was hydrogenated (1 atm.) over palladium-charcoal (0.1 g.; 10%) at room temperature. Uptake of hydrogen was complete within 1 hr., and the catalyst was then filtered off and the solvent removed by evaporation under reduced pressure (nitrogen leak) at room temperature. The dark residue was taken up in ethanol (20 ml.) and glacial acetic acid (5 ml.), and then heated on the water-bath for $1\frac{1}{2}$ hr., before being aerated overnight. The deep red solution was extracted with chloroform (2×30 ml.), and the extracts were washed with sodium carbonate solution and then with water. The chloroform solution was evaporated to dryness and the residue taken up in benzene and chromatographed on alumina. The dark red band which separated from dark impurities was eluted in benzene. Recrystallisation from chloroform-methanol gave dark violet needles, m. p. 185–190° (lit.,¹¹ records m. p. 206° for the type III isomer), of tetramethyltetrapropylporphin (220 mg.; 33%) (Found: C, 81.0; H, 8.9. Calc. for $C_{36}H_{46}N_4$: C, 80.85; H, 8.7%; λ_{max} . (in benzene) 400, 498, 532, 566, and 620 (log ϵ 5.29, 4.14, 4.00, 3.84, and 3.69, respectively). The structure was confirmed by the p.m.r. spectrum of the solution in trifluoroacetic acid.¹

We thank the Nuffield Foundation for support.

THE ROBERT ROBINSON LABORATORIES,
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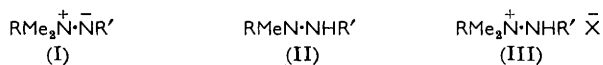
[Received, May 29th, 1963.]

¹¹ Fischer, Goldschmidt, and Nüssler, *Annalen*, 1931, **486**, 5.

418. Preparation of Some New Semipolar Surface-active Compounds.

By R. W. H. BERRY and P. BROCKLEHURST.

THE synthesis of compounds containing the $\overset{+}{N}-\bar{N}$ linkage, *N*-trimethylaminobenzimide, $\text{Me}_3\overset{+}{N}\cdot\bar{N}\cdot\text{CO}\cdot\text{Ph}$, and *N*-trimethylaminotoluene-*p*-sulphonimide, $\text{Me}_3\overset{+}{N}\cdot\bar{N}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$ has been reported by Hinman and Flores¹ and Wawzonek and Meyer,² respectively, and a suggested nomenclature for compounds of this type, has been published by Sisler.³ However, surface-active materials containing the $\overset{+}{N}-\bar{N}$ hydrophilic group were hitherto unknown, and we have prepared compounds possessing the general formula (I; R = alkyl, R' = acyl or alkanesulphonyl).



Acylation of *NN*-dimethylhydrazine with dodecanoyl chloride afforded the hydrazide (II; R = Me, R' = $\text{C}_{11}\text{H}_{23}\cdot\text{CO}$). Quaternisation of this hydrazide (II) with methyl iodide gave the methiodide (III; R = Me, R' = $\text{C}_{11}\text{H}_{23}\cdot\text{CO}$), and subsequent elimination of hydrogen iodide by aqueous sodium hydroxide solution afforded *N*-trimethylaminododecanimide (I; R = Me, R' = $\text{C}_{11}\text{H}_{23}\cdot\text{CO}$) in good yield. *N*-Trimethylaminododecanesulphonimide (I; R = Me, R' = $\text{C}_{12}\text{H}_{25}\cdot\text{SO}_2$) was prepared similarly, dodecanesulphonyl bromide being used in the first step.

Materials with long-alkyl chains attached to the quaternary nitrogen were more difficult to obtain. Attempts to quaternise the substituted hydrazines (II; R = Me, R' = Ac) and (II; R = Me, R' = $\text{Me}\cdot\text{SO}_2$) with dodecyl iodide failed to give the desired quaternary iodides. The acetimide (I; R = $\text{C}_{12}\text{H}_{25}$, R' = Ac) was finally obtained by treating *N*-dodecyl-*NN*-dimethylhydrazinium bromide with acetyl chloride in benzene solution and eliminating hydrogen bromide without isolating the intermediate quaternary salt (III; R = $\text{C}_{12}\text{H}_{25}$, R' = Ac). Replacement of acetyl chloride by methanesulphonyl chloride in the above synthesis did not yield the desired *N*-(*N*-dodecyl-*NN*-dimethylamino)methanesulphonimide (I; R = $\text{C}_{12}\text{H}_{25}$, R' = $\text{Me}\cdot\text{SO}_2$). The latter was eventually obtained as the dihydrate by another route involving the quaternisation of the hydrazide (II; R = $\text{C}_{12}\text{H}_{25}$, R' = $\text{Me}\cdot\text{SO}_2$) with methyl iodide and subsequent elimination of hydrogen iodide.

For the compounds containing R = Me and R' = $\text{C}_{11}\text{H}_{23}\cdot\text{CO}$, the position of the carbonyl band in the i.r. spectra gives support for the suggested structures. Thus, for (I), (II), and (III) it occurs at 6.33, 6.02, and 5.82 μ , respectively. These shifts are expected from the influence of adjacent electron-withdrawing or electron-donating centres. The absence of an N-H band in all compounds of type (I) confirmed their structure. As expected the $\text{p}K_a$ values for compounds (I) in water were higher for the alkanoyl (R = Me, R' = $\text{C}_{11}\text{H}_{23}\cdot\text{CO}$; $\text{p}K_a = 5.3$) than the corresponding alkanesulphonyl materials (R = Me, R' = $\text{C}_{12}\text{H}_{25}\cdot\text{SO}_2$, $\text{p}K_a = 3.1$). The conductivities of aqueous solutions of (I; R = Me, R' = $\text{C}_{11}\text{H}_{23}\cdot\text{CO}$) at concentrations below the critical micelle concentration ($\sim 10^{-3}\text{M}$ at 25°) were negligibly small, confirming its non-ionic character.

Experimental.—*N*-Trimethylaminododecanimide. An ethereal solution of methyl iodide (30 g.) and *NN*-dimethyl-*N'*-dodecanoylhydrazine (46.5 g.) was refluxed for 2 hr. The cooled

¹ Hinman and Flores, *J. Org. Chem.*, 1959, **24**, 660.

² Wawzonek and Meyer, *J. Amer. Chem. Soc.*, 1954, **76**, 2918.

³ Sisler, Omietanski, and Rudner, *Chem. Rev.*, 1957, **57**, 1021.

mixture was filtered and the residue (39 g.) yielded the *N*-trimethyl-*N'*-dodecanoyl-hydrazinium iodide, m. p. 148—148.5° (needles from water) (Found: C, 47.2; H, 8.8; I, 33.0; N, 7.3. $C_{15}H_{33}IN_2O$ requires C, 46.9; H, 8.6; I, 33.1; N, 7.3%). The hydrazinium iodide (30 g.) was triturated with 3*N*-sodium hydroxide (60 ml.), and the resulting syrup extracted with chloroform. Removal of solvent gave *N*-trimethylaminododecanimide (16 g.), m. p. 35° [needles from petroleum (b. p. 40—60°)] (Found: C, 69.8; H, 12.9; N, 11.1. $C_{15}H_{32}N_2O$ requires C, 70.3; H, 12.5; N, 10.9%).

N-(*N*-Dodecyl-*NN*-dimethylamino)acetimide. A solution of *N*-dodecyl-*NN*-dimethylhydrazinium bromide (10 g.) and acetyl chloride (2.5 ml.) in benzene (150 ml.) was refluxed for 2 hr. The solvent was removed and the residual oil treated with 10% aqueous sodium hydroxide solution (28 ml.). Extraction with chloroform and removal of the solvent gave the acetimide (5.2 g.), m. p. 39—40° [from petroleum (b. p. 40—60°)] (Found: C, 69.6; H, 12.5; N, 10.6. $C_{16}H_{34}N_2O$ requires C, 71.1; H, 12.6; N, 10.4%).

N-Trimethylaminododecanesulphonimide. Dodecanesulphonyl bromide (28 g.) was added portionwise to *NN*-dimethylhydrazine (11 g.) with good stirring. Petroleum (b. p. 60—80°) was added and the mixture stirred for 30 min. Removal of the solvent gave *NN*-dimethyl-*N'*-dodecanesulphonylhydrazine (21.2 g.), m. p. 52—53° (plates, from aqueous ethanol) (Found: C, 57.1; H, 10.8; S, 11.4. $C_{14}H_{32}N_2O_2S$ requires C, 57.5; H, 11.0; S, 11.0%). A mixture of the hydrazine (5 g.) and methyl iodide (6 ml.) was refluxed for 5 hr. Removal of excess of methyl iodide and trituration with dry ether gave a solid (8.1 g.) which was triturated with 20% aqueous sodium hydroxide solution (20 ml.) at 50°. The mixture was cooled and stirred for 15 min.; the solid (5.1 g.) yielded *N*-trimethylaminododecanesulphonimide, m. p. 133—134° (needles from benzene) (Found: C, 58.9; H, 11.3; N, 9.0; S, 10.6. $C_{15}H_{34}N_2O_2S$ requires C, 58.8; H, 11.1; N, 8.9; S, 10.5%).

N-(*N*-Dodecyl-*NN*-dimethylamino)methanesulphonimide. Methanesulphonyl chloride (4.3 g.) was added slowly with stirring to a mixture of *N*-dodecyl-*N*-methylhydrazine (8.0 g.) and triethylamine (4.3 g.) with ice-cooling. The mixture was warmed to 40° and stirred at this temperature for 1 hr. Petroleum (b. p. 40—60°; 50 ml.) was added and the resulting solid gave *N*-dodecyl-*N*-methyl-*N'*-methanesulphonylhydrazine (4.25 g.), m. p. 79° (needles from aqueous methanol) (Found: C, 57.7; H, 10.7; N, 9.8; S, 10.5. $C_{14}H_{32}N_2O_2S$ requires C, 57.5; H, 11.0; N, 9.6; S, 11.0%). The hydrazine (20 g.), methyl iodide (80 ml.), and nitromethane (20 ml.) were refluxed for 3 days. The nitromethane and excess of methyl iodide were removed under reduced pressure and the residue was triturated with 20% sodium hydroxide solution (60 ml.). Extraction of the mixture with chloroform gave *N*-(*N*-dodecyl-*NN*-dimethylamino)methanesulphonimide dihydrate, m. p. 82—83° (needles from water) (Found: C, 52.8; H, 10.2; N, 8.4; S, 9.2. $C_{15}H_{38}N_2O_4S$ requires C, 52.6; H, 11.1; N, 8.2; S, 9.4%).

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419. Lithium Tetraiodide Tetrahydrate.

By G. H. CHEESEMAN and E. K. NUNN.

WITH the exception of lithium and sodium polybromides,¹ polybromides and polyiodides can be formed from all the alkali metals and ammonium at 0°. Grace² had suggested the possible formation of a lithium polyiodide but no attempt was made at its identification.

The present three-component isothermal study at 0° was performed to isolate any lithium polyiodide. Schreinemakers's wet-residue method was used in determining the composition of the pure solid phases, the best point of intersection being obtained from an algebraic treatment of the results.³

¹ Cheesman and Nunn, *J.*, 1960, 3684.

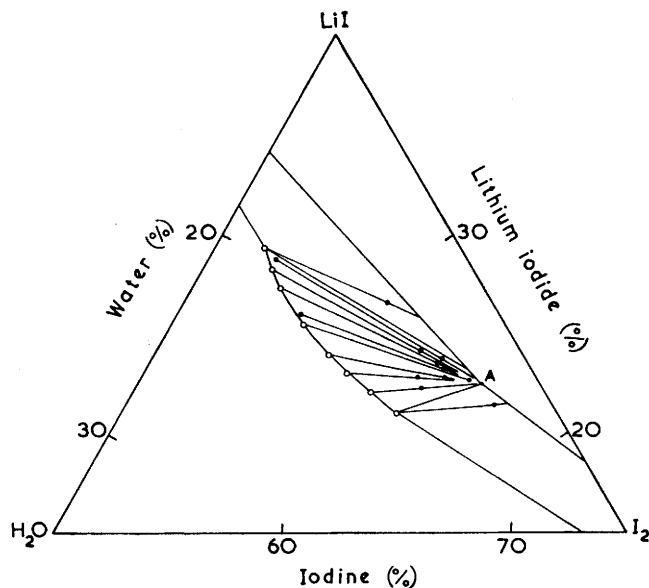
² Grace, *J. Phys. Chem.*, 1933, **37**, 347.

³ Cheesman and Nunn, *Austral. J. Chem.*, 1964, **17**, 399.

Experimental.—Iodine was resublimed in the presence of phosphorus pentoxide. Lithium iodide was analysed as $\text{LiI}\cdot 2\text{H}_2\text{O}$.

The equilibrium mixtures, containing weighed amounts of lithium iodide, iodine, and water, to a total weight of approximately 20 g. were sealed in ampoules and shaken at regular intervals for at least 3 weeks. Glass beads were also added to assist in the attainment of equilibrium. The temperature was maintained at $0 \pm 0.02^\circ$ with a refrigerated thermostat. Liquid samples were taken with a chilled pipette incorporating a removable sleeve with a glass-wool filter. Wet solids were sampled with a chilled platinum spade. The analytical samples were weighed into 10% ammonium iodide solution. Iodine was estimated with standard ammonium thio-sulphate. The solution was then evaporated to dryness with a few drops of concentrated nitric acid, to remove the iodide as iodine, and the lithium was estimated by fuming with concentrated sulphuric acid.

Results.—The lithium tetraiodide section of the equilibrium diagram is plotted in the Figure. Qualitative tests were carried out to check the stable phases in the system. In



The lithium tetraiodide section of the lithium iodide–iodine–water equilibrium diagram. Point A corresponds to lithium tetraiodide tetrahydrate.

these tests anhydrous lithium iodide, partly dehydrated iodide, and lithium iodide trihydrate were prepared. The first two were equilibrated with iodine vapour, and the absence of absorption indicated that an anhydrous polyiodide is not formed and that an anhydrous iodide and hydrated polyiodide do not exist in stable equilibrium. The latter sample was equilibrated with iodine in the presence of water in one case and phosphorus pentoxide in the other. Absorption took place in the former only, indicating that a lower hydrate than $\text{LiI}\cdot 3\text{H}_2\text{O}$ was not in equilibrium with the polyiodide. The hydrated polyiodide formed short dark needles with a low melting point, and a sample, allowed to drain for some months over a saturated mother-liquor, had melting point $11.5\text{--}12.5^\circ$. The best point of intersection of the tie-lines connecting wet solid and saturated mother-liquor was at $22.31 \pm 0.03\%$ LiI and $65.48 \pm 0.09\%$ I_2 , the theoretical figure for $\text{LiI}_4\cdot 4\text{H}_2\text{O}$ being 22.82% LiI and 64.90% I_2 .

Magnetic susceptibility was measured for $\text{LiI}_4\cdot 4\text{H}_2\text{O}$, $\text{NaI}_2\cdot 3\text{H}_2\text{O}$, $\text{NaI}_4\cdot 2\text{H}_2\text{O}$,^{4,5} and

⁴ Briggs, Geigle, and Eaton, *J. Phys. Chem.*, 1941, **45**, 595.

⁵ Cheesman, Duncan, and Harris, *J.*, 1940, 837.

CsI_4 ,⁶ the last measurement having been reported previously.⁷ These were all diamagnetic, indicating that the simple formulæ are not applicable.

Although most of the polyhalides consist of an odd number of halogen atoms, the closely related sodium iodide system has $\text{NaI}_2 \cdot 3\text{H}_2\text{O}$ and $\text{NaI}_4 \cdot 2\text{H}_2\text{O}$ as stable solid phases. The crystal structure of the corresponding caesium compound, CsI_4 , has a structure involving I_3^- ions linked by I_2 molecules as an I_8^{2+} ion which is diamagnetic. It is probable that the lithium compound is also represented by $2\text{Li}(\text{H}_2\text{O})_4^+ \text{I}_8^{2-}$. The tetrahydrated lithium ion is known in a number of stable compounds and is apparently of sufficient size to stabilise the anion. The stabilisation of a polyhalide anion by a large cation is seen throughout the series of these compounds. The smaller cations are solvated in all cases where polyhalides can be formed.

The authors acknowledge the assistance of Dr. P. W. Smith in the measurement of magnetic susceptibilities.

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[Received, June 28th, 1963.]

⁶ Havinga, Boswijk, and Wiebenga, *Acta Cryst.*, 1954, **7**, 487.

⁷ Hubard, *J. Phys. Chem.*, 1942, **46**, 227.

420. *The Orientation of Some Methyl Esters Adsorbed on Carbon Blacks From the Vapour Phase.*

By E. H. M. WRIGHT.

IN a recent study of the adsorption of long-chain fatty acids from the vapour phase and from solution¹ on to solid adsorbents, the dangers in drawing a parallelism between orientation of the adsorbed molecules on solid and liquid surfaces have been pointed out. It has been shown² that the hydrogen bonding between the carboxyl groups is only likely to be broken if the monomer so produced can form fresh hydrogen bonds with the surface. This can readily happen on the surface of water, and it has been shown to happen on some metallic oxide and hydroxide surfaces. On these surfaces the adsorbed acid molecules assume the perpendicular orientation, with an area of about 20.5 \AA^2 per molecule. However, on the surfaces of non-porous carbon blacks such as Graphon, Spheron 6, Carbolac 1 (2400°), Sterling MT (2700°), the preferred orientation of the homologous series of fatty acids when adsorbed was shown¹ to be that with the major axes parallel to the adsorbing surface. Stearic acid, for example, occupied an area of 114 \AA^2 per molecule in the adsorbed phase. A similar behaviour for many members of the homologous series of fatty acids has been recorded.³

In the work now described, an examination has been made of some monomethyl esters adsorbed from the vapour phase on Graphon and Spheron 6, to establish the orientation of these molecules with weaker intermolecular linkages.

Experimental.—*Adsorbents.* The nature of the adsorbents has been previously described.¹

Adsorbates. Methyl butyrate and octanoate were prepared and purified as described by Markley⁴ and Vogel.⁵ "Technical" methyl acetate was purified as described by Vogel.⁵

¹ Kipling and Wright, *J.*, 1962, 855.

² Wright, Ph.D. Thesis, Hull Univ., 1961.

³ Kipling and Wright, *J.*, 1963, 3382.

⁴ Markley, "Fatty Acids," Interscience Publ., New York, 1947.

⁵ Vogel, "Practical Organic Chemistry, 3rd edn., Longmans, London, 1954.

The criterion of purity was refractive index: methyl acetate at 20°, n_D 1.3618 (lit.,⁶ 1.3619); methylbutyrate at 20°, n_D 1.3876 (lit.,⁶ 1.3879); methyl octanoate at 45° n_D 1.4066 (lit.,⁴ 1.4069).

Procedure. Adsorption was at 30°, and the vapour isotherms were determined by the flow method,⁷ which involved allowing various mixtures of ester vapour and nitrogen to come in contact with the adsorbent until equilibrium was attained.

Discussion.—The monolayer values were obtained from B.E.T. plots on results obtained for adsorption per gram of adsorbent at various corrected relative pressures of ester vapour. The area per ester molecule was calculated on the basis of the monolayer values obtained and from the known surface areas of the adsorbents. The Table gives a summary of the results for adsorption from the vapour of the three esters by Graphon and Spheron 6 at 30°, as well as the area per ester molecule thus calculated.

	Monolayer value (mmole/g.)		Area per ester molecule (Å ²)	
	Graphon	Spheron	Graphon	Spheron 6
Methyl acetate	0.404	0.484	34.5	39.0
Methyl butyrate	0.275	0.345	51.0	55.0
Methyl octanoate	0.190	0.254	73.0	75.0

The results indicate that these esters are adsorbed with their major axes parallel to the adsorbing surface, despite the weaker intermolecular linkages. If the ester molecules were adsorbed with their major axes perpendicular to the surface, the area per molecule would be expected to be about 25 Å². On the other hand for a parallel orientation the areas per molecule for the closest possible packing in the adsorbed phase, calculated from values of bond lengths and bond angles, are about 33.0, 45.0, and 67.0 Å² for the acetate, butyrate, and octanoate, respectively. If, however, the packing of the adsorbed molecules, oriented parallel to the surface, were determined by the size of the ester grouping, and so not the closest possible packing, the areas per molecule would be 42.0, 56.0, and 87.0 Å², respectively.

It seems clear that these esters when adsorbed on Graphon and Spheron 6 assume a parallel orientation although the packing of the molecules seems to be slightly neater on Graphon. This is not surprising in view of the heterogeneous nature of the Spheron 6 surface.⁸

I am grateful to the Science Research and Equipment Fund of the College for providing grants to purchase equipment, and to the Chemistry Department for necessary facilities.

UNIVERSITY COLLEGE OF SIERRA LEONE, FREETOWN.

[Received, July 26th, 1963.]

⁶ Weissberger, Proskauer, Riddick, and Toops, "Technique of Organic Chemistry—Organic Solvents," 2nd edn., Interscience Publ., New York, Vol. 7, 1955.

⁷ Blackburn, Ph.D. Thesis, London Univ., 1954.

⁸ Beebe, Biscoe, Smith, and Wendell, *J. Amer. Chem. Soc.*, 1947, **69**, 95.

421. Synthesis of 2,5-Diaryl-1,4-benzoquinones.

By EIRWYN THOMAS.

A NUMBER of 2,5-(*ortho*-substituted)diphenyl-1,4-benzoquinones have been prepared according to published methods.¹

Experimental.—2,5-Dichloro-3,6-di-*o*-methoxyphenyl-1,4-benzoquinone. *o*-Anisidine (12.3 g.) was diazotised in dilute hydrochloric acid with sodium nitrite (6.9 g.), and the diazonium solution added during 1 hr. to a solution of 2,5-dichloroquinol (8.9 g.) and sodium hydrogen carbonate (25.2 g.) in water (5 l.). After a further 2 hr., the precipitate was coagulated (NaCl), filtered off, and treated with acetone (25 ml.). The residue was crystallised from acetic acid, and the *benzoquinone* (35% yield) then had m. p. 267° (Found: C, 61.85; H, 3.9; Cl, 18.3. C₂₀H₁₄Cl₂O₄ requires C, 61.7; H, 3.6; Cl, 18.25%).

The 2,5-diaryl-3,6-dichloro-1,4-benzoquinones listed in Table 1 were similarly prepared.

TABLE 1.

Aryl group	Solv.	M. p.	Found (%)				Formula	Requires (%)			
			C	H	Cl	N		C	H	Cl	N
<i>o</i> -Chlorophenyl	AcOH	244°	54.2	1.85	35.6	—	C ₁₆ H ₈ Cl ₄ O ₂	54.3	2.0	35.7	—
2,6-Dichlorophenyl	EtOH	283	45.9	1.5	45.6	—	C ₁₈ H ₆ Cl ₆ O ₂	46.3	1.3	45.6	—
2-Naphthyl	C ₆ H ₆	302	72.5	3.5	16.3	—	C ₂₈ H ₁₄ Cl ₂ O ₂	72.7	3.3	16.55	—
<i>o</i> -Nitrophenyl	AcOH	280	51.75	2.0	16.95	7.0	C ₁₆ H ₈ Cl ₂ N ₂ O ₆	51.55	1.9	16.95	6.7
<i>o</i> -Cyanophenyl	AcOH	308	63.65	2.45	18.5	7.0	C ₂₀ H ₈ Cl ₂ N ₂ O ₂	63.3	2.1	18.75	7.4

2,5-Dihydroxy-3,6-di-*o*-methoxyphenyl-1,4-benzoquinone. The dichloro-compound (2 g.), 2*N*-sodium hydroxide (100 ml.), and ethanol (100 ml.) were refluxed for 2 hr. Acidification and dilution gave a precipitate of the *dihydroxy-compound* (85% yield), m. p. 282° (from ethanol) (Found: C, 68.1; H, 4.8. C₂₀H₁₆O₆ requires C, 68.2; H, 4.55%).

2,5-Di-*o*-tolylazo-1,4-benzoquinone. A solution of *o*-toluidine (from 42.8 g.), at pH 6.9, was added during 1 hr. to 2,5-dichloroquinol (17.9 g.) in water (4 l.). The aerated solution was kept for 2 hr., the resin deposited was transferred to a column of alumina, and then eluted with acetone. The purple product was crystallised from acetone and then oxidised

TABLE 2.

Terphenyls.

Substituent			Solv.	M. p.	Found (%)				Formula	Required (%)			
2,2''-	2',5'-	3',6'-			C	H	Cl	N		C	H	Cl	N
OMe	Cl	OAc	EtOH	319°	60.55	4.2	14.2	—	C ₂₄ H ₂₀ Cl ₂ O ₆	60.6	4.2	14.95	—
Me	Cl	OAc	EtOH	244	64.7	4.7	16.7	—	C ₂₄ H ₂₀ Cl ₂ O ₄	65.0	4.5	16.0	—
Cl	Cl	OAc	EtOH	272	54.2	3.1	29.8	—	C ₂₅ H ₁₄ Cl ₄ O ₄	54.5	2.9	29.35	—
CN	Cl	OAc	EtOAc	291	61.6	3.2	15.7	5.85	C ₂₄ H ₁₄ Cl ₂ N ₂ O ₄	61.95	3.0	15.3	6.0
Me	Cl	OH	EtOH	244	66.55	4.85	19.3	—	C ₂₀ H ₁₆ Cl ₂ O ₂	66.85	5.0	19.8	—
Cl	Cl	OH	EtOH	272	54.4	2.7	34.95	—	C ₁₈ H ₁₀ Cl ₄ O ₂	54.0	2.5	35.5	—
Me	OAc	OAc	EtOH	245	68.75	5.5	—	—	C ₂₈ H ₂₆ O ₈	68.55	5.3	—	—

with sodium nitrite (5 g.) in acetic acid (50 ml.). Dilution gave the azo-compound (10% yield), m. p. 216° (from acetic acid), as orange needles (Found: C, 69.45; H, 5.7; N, 15.75. C₂₀H₁₆O₂N₄ requires C, 69.75; H, 5.9; N, 16.3%).

¹ Browning and Adams, *J. Amer. Chem. Soc.*, 1930, **52**, 4098; Kvalnes, *J. Amer. Chem. Soc.*, 1934, **56**, 2478; Schimmelschmidt, *Annalen*, 1950, **566**, 184; Nilsson and Erdtmann, *Acta Chem. Scand.*, 1956, **10**, 735; Nilsson, *Acta Chem. Scand.*, 1956, **10**, 1377; Bohlmann, *Chem. Ber.*, 1957, **90**, 1519; Edwards and Lewis, *J.*, 1959, 3250; Cain, *J.*, 1961, 936; 1963, 356; Bennett and Uri, *J.*, 1962, 2753.

1,4-Diacetoxy-2,5-dichloro-3,6-di-2'-naphthylbenzene. This was prepared by reductive acetylation of the corresponding quinone (0.5 g.) with zinc dust (0.2 g.) and acetic anhydride (50 ml.). The product (80% yield) had m. p. 272° (from ethyl acetate) (Found: C, 69.6; H, 4.1; Cl, 14.3. $C_{30}H_{20}O_4Cl_2$ requires C, 69.9; H, 3.9; Cl, 13.8%).

By similar reactions the terphenyls listed in Table 2 were prepared.

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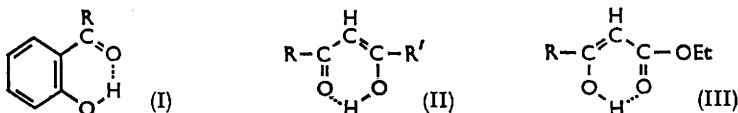
[Received, August 16th, 1963.]

422. Proton Magnetic Resonance of Hydrogen-bonded Chelate Rings.

By R. W. HAY and P. P. WILLIAMS.

THE marked effect of hydrogen-bonding on the resonance frequencies of protons was established very early in the development of nuclear magnetic resonance.¹ Hydrogen-bonding causes a very large paramagnetic shift, the origin of which has been discussed by Pople, Schneider, and Bernstein.²

o-Hydroxy-aldehydes, hydroxy-ketones and hydroxy-esters (I), the enol forms of β -diketones (II), and β -keto-esters (III) readily form intramolecular hydrogen-bonded chelate rings (I—III).



Rasmussen³ and Bellamy⁴ have discussed the effect of hydrogen-bonding on the infrared absorption of the carbonyl group involved in the chelate ring and have shown that chelation leads to a considerable reduction in the carbonyl stretching frequency. Correlations have also been noted between the carbonyl stretching frequency of certain enols⁵ and *o*-hydroxy-ketones and their derivatives⁶ and the location of the hydroxylic proton resonance signal. Displacement of the proton resonance signal towards lower field appears to indicate a stronger hydrogen bond. In certain natural products such as usnic acid⁷ and ceroptene,⁵ the proton resonance occurs around 19 δ and the chelated carbonyl absorption as low as 1515 cm^{-1} , indicating very strong intramolecular hydrogen-bonding.

The present aim was the location of the hydroxylic proton resonance signal in the following compounds: salicylaldehyde (I; R = H), methyl salicylate (I; R = OMe), *o*-hydroxyacetophenone (I; R = Me), acetylacetone (II; R = R' = Me), benzoylacetone (II; R = Ph, R' = Me), dibenzoylmethane (II; R = R' = Ph), diethyl oxaloacetate (III; R = CO₂Et), and ethyl acetoacetate (III; R = Me) in order to determine if a relationship exists between the hydroxylic proton resonance signal and the infrared stretching frequency of the carbonyl group involved in the chelate ring. Although the keto-enol equilibria of compounds of type (II) and (III) were not studied in detail the percentage of enol in these compounds has been roughly determined.

¹ Arnold and Packard, *J. Chem. Phys.*, 1951, **19**, 1608.

² Pople, Schneider, and Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, p. 400.

³ Rasmussen, Tunnicliffe, and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1068, 1073.

⁴ Bellamy and Beecher, *J.*, 1954, 4487.

⁵ Nilsson, *Svensk kem. Tidskr.*, 1961, **9**, 460.

⁶ Porte, Gutowsky, and Hunsberger, *J. Amer. Chem. Soc.*, 1960, **82**, 5057.

⁷ Forsen, Nilsson, and Wachtmeister, *Acta Chem. Scand.*, 1962, **16**, 583.

The chemical shifts relative to tetramethylsilane observed in the various hydrogen bonded chelates are listed in the Table.

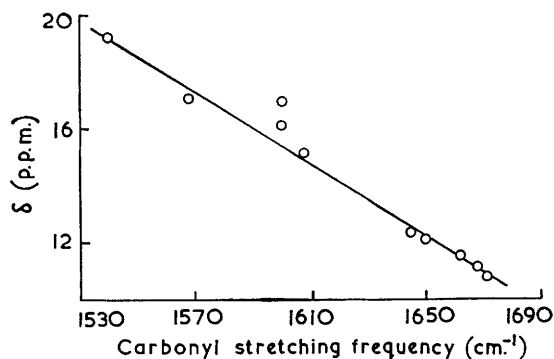
The hydroxylic proton chemical shifts δ in p.p.m. and the perturbed carbonyl stretching frequency, in cm^{-1} , of compounds containing hydrogen-bonded chelate rings.

	c.p.s.*	δ	ν_s (C-O)	Enol* (%)
Salicylaldehyde	670	11.17	1668	—
Methylsalicylate	650	10.83	1671	—
<i>o</i> -Hydroxyacetophenone	740	12.33	1645	—
Acetylacetone	904	15.07	1608	83
Dibenzoylmethane	1018 †	16.97	1600	100 †
Benzoylacetone	965 †	16.08	1600	93 †
Ethylacetoacetate	728	12.13	1650	10
Diethyloxaloacetate	690	11.50	1662	77
<i>NN'</i> -Di- <i>o</i> -hydroxybenzylidene ethylenediamine ...	790 †	13.17	—	—
<i>N</i> - <i>o</i> -Hydroxybenzylideneaniline	796 †	13.27	—	—
"Selenium acetylacetonate"	1021 †‡	17.02	1568	—
Usnic acid †	—	19.20	1540	—

* Pure liquids. † In deuteriochloroform. ‡ $\text{Se}_2(\text{acac})_2$; selenium is bonded to carbon not oxygen.

A plot of the chemical shift against the carbonyl stretching frequency, is approximately linear (Figure). The β -triketone configuration in usnic acid gives very strong hydrogen bonds presumably because proton transfer can occur between a number of similar structures. A similar effect is observed in the chelate ring of acetylacetone. Proton transfer

Relationship between the chemical shift of the hydroxylic proton and the carbonyl stretching frequency.



between two equivalent structures leads to the formation of a moderately strong hydrogen bond.



The anomalous positions of the points for benzoylacetone and dibenzoylmethane are presumably due to the deshielding effects of the additional phenyl groups, resulting in a shift of the resonance to lower fields relative to acetylacetone. In salicylaldehyde and *o*-hydroxyacetophenone, the aromatic ring is directly involved in the conjugate chelate (IV), and the strength of the hydrogen bond has been related to the double-bond character of the bond common to the conjugate chelate and the aromatic ring.⁶ The low-field shift of the hydroxyl proton resonance induced by the ring-currents in the benzene ring is

evidently compensated by the reduced stretching frequency of the carbonyl group conjugated with the aromatic ring. Hydrogen bonds in these compounds are probably even weaker than those found in β -keto-esters.

Freedman⁸ has recently suggested on the basis of infrared evidence that contrary to accepted views, the strength of the OH \cdots N hydrogen bond is comparable to the strength of the OH \cdots O hydrogen bond. In compounds such as *NN'*-di-*o*-hydroxybenzylideneethylenediamine and *N-o*-hydroxybenzylideneaniline the hydroxylic proton shifts support this view.

Experimental.—Most of the compounds were commercial samples, and some were purified by distillation or recrystallisation until they had the correct melting or boiling points. The n.m.r. spectra were recorded at 60 Mc, on a Varian Associates, H.R. 60 spectrometer. The substances were studied at room temperature either as pure liquids or in solution in deuteriochloroform. Tetramethylsilane present in *ca.* 2 vol.-% was used as internal standard.

Infrared spectra were measured in chloroform solution with a Perkin-Elmer 221 spectrometer.

Financial assistance by the Victoria University of Wellington Research Fund is gratefully acknowledged. Thanks are due to Dr. C. J. Wilkins for the sample of "selenium acetylacetone."

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⁸ Freedman, *J. Amer. Chem. Soc.*, 1961, **83**, 2900.

423. *Charge-transfer Spectra and the Ionization Energy of Azulene.*

By A. C. M. FINCH.

THE ionization energy of azulene has not hitherto been measured, but its value has been calculated: (a) 8.30 eV with all exchange-integrals equal;¹ (b) 8.32 eV by the " ω -technique" of Wheland and Mann;² (c) 8.29 eV by simple molecular-orbital theory;² (d) 7.43 eV by re-minimization of the ionized state;³ (e) 7.52 eV from ground-state orbitals and integral-correction;³ (f) 9.59 eV from Koopman's theorem.³

The ionization energy of azulene is now estimated from the frequency of the charge-transfer absorption bands in the spectra of its complexes with 1,3,5-trinitrobenzene, chloranil, and iodine, by using the parameters and quadratic equation given by Briegleb and Czekalla.⁴ The results are quite consistent at 7.4–7.5 eV, in agreement with the values in (d) and (e), above, of Hoyland and Goodman. The three equations proposed by Platt and his collaborators⁵ for complexes between iodine and donors of higher ionization energy gave widely discrepant results with azulene; only their equation (2) gives a concordant value for the ionization energy. All these results are in Table I.

In order to get a fourth estimate by using the acceptor 2,3-dicyanoquinone, the equation proposed⁶ on the basis of its charge-transfer spectra with polymethylbenzenes in

¹ Streitwieser and Nair, *Tetrahedron*, 1959, **5**, 165.

² Streitwieser, *J. Amer. Chem. Soc.*, 1960, **82**, 4125.

³ Hoyland and Goodman, *J. Chem. Phys.*, 1962, **36**, 12.

⁴ Briegleb and Czekalla, *Z. Elektrochem.*, 1959, **63**, 6.

⁵ McConnell, Ham, and Platt, *J. Chem. Phys.*, 1953, **21**, 66.

⁶ Hammond, *J.*, 1963, 3113.

methylene chloride or carbon tetrachloride is shown to be applicable also to the complexes of more ready donors. The spectra of complexes between dicyanoquinone and polynuclear aromatic hydrocarbons were measured, and Hammond's equation⁶ gives values

TABLE 1.

Charge-transfer bands of some complexes of azulene, and its ionization energy calculated therefrom.

Acceptor	Solvent	Charge-transfer peak		Ref. for eqn.	<i>I</i> (ev)
		$\bar{\nu}$ (μ^{-1})	$h\nu$ (ev)		
1,3,5-Trinitobenzene	CH ₂ Cl ₂	2.18	2.70	4	7.4
Chloranil	CH ₂ Cl ₂	1.55	1.92	4	7.4
Iodine	CCl ₄	2.45	3.04	4	7.5
1,3,5-Trinitrobenzene	solid	2.08 *	2.58	5	7.5, 6.6, 8.1
Chloranil	solid	1.48	1.84	—	—
2,3-Dicyanoquinone	PhH	1.62	2.01	—	—
	(CH ₂ Cl ₂)	(1.56)	(1.93)	6	(7.5)
2,4,7-Trinitro-9-fluorenone	CHCl ₃	1.84—1.91	2.28—2.36	†	7.4—7.5

* Appears to be a double band with components of maxima *ca.* 2.0 and 2.2 μ^{-1} . † $h\nu = 0.92I - 4.56$; this slope matches well the ratio (0.93) between the slopes of the plots (see ref. 9) of $E_{t(\text{ox})}$ against *I* (0.68) and $E_{t(\text{ox})}$ against $h\nu$ (0.73).

in fair agreement with the previously known⁴ ionization energies of these donors (Table 2). However, scatter throughout the plot of $h\nu$ against *I* suggest Foster's rule⁷ may not apply rigorously to complexes of such a strong acceptor even in non-ionizing solvents.

TABLE 2.

Charge-transfer spectra of some complexes with 2,3-dicyanoquinone, and ionization energies calculated therefrom.

Donor	<i>a</i>	$\bar{\nu}$ (μ^{-1})	$h\nu$ (ev)	Concn. (mm)		<i>I</i> ^b (ev)	<i>I</i> ^c (ev)
				Donor	Acceptor		
Pyrene	B {	2.52	1.88	25	12	7.55	{ 7.31
		2.12 ^g	2.63				
	M {	1.46	1.81	25	2	7.55	{ 8.35
		2.09	2.60				
Anthracene	B	1.46	1.81	35	20	7.4	7.2
	M	1.41	1.75	2	2		
Dimethylaniline	B	1.41	1.75	24	20	7.3	7.2
	M	1.40	1.74	18	2		
Perylene	B	1.25 ^g	1.55	1.5	20	7.15	6.85
	M	1.19 ^g	1.48	2	3		
Tetramethyl- <i>p</i> -phenylenediamine	B	1.18—1.20 ^d	1.47	1	2	6.6	6.9
	M	1.20 ^e	1.49	1	2		
Azulene	B	1.62	2.01	3	12	—	7.5
	M	1.56 ^f	1.93	—	—		

^a Solvent: B = benzene, M = methylene chloride. ^b From charge-transfer to other acceptors (ref. 4). ^c From values of $h\nu$ in methylene chloride by the equation in ref. 6. ^d Supersaturated solution measured within 1 min. of mixing. ^e Measured within 20 sec. of mixing; later the solution had gone cloudy white. ^f Hypothetical value (see text). ^g Complex was chemically stable in solution.

The spectrum of the complex with azulene could be observed only in benzene and not in the usual methylene chloride where reaction was too rapid. Whereas this change of solvent little affected the charge-transfer energies of the tertiary amines, those of the

⁷ Foster, *Nature*, 1958, **181**, 337.

aromatic hydrocarbons were increased by 0.07 eV. When the transition energy of azulene-dicyanoquinone in benzene is corrected by this much, Hammond's equation⁶ gives a fourth consonant estimate for the ionization energy of azulene, 7.5 eV.

Lepley⁸ reported the spectra of complexes between 2,4,7-trinitro-9-fluorenone in chloroform and many aromatic hydrocarbons including azulene. The already known⁴ ionization energies of some of the donors can be fitted to the charge-transfer energies by a linear equation from which a fifth consistent estimate of the ionization energy of azulene is obtained (Table I).

Pysh and Yang⁹ concluded that the ionization energy of azulene or acenaphthylene could not be estimated from their polarographic oxidation potentials, since the data did not fit the general linear correlation with the charge-transfer energies⁸ of the complexes between trinitrofluorenone and the compounds studied. They attributed this divergence to anomalous solvation energies of these cations. An additional reason might be the probable irreversibility of the electrode-reaction with azulene. This instability of the azulene radical-cation is suggested by the formation of dark oxidation products on the anode,⁹ and by the very weak paramagnetism of the strongly conducting solution in molten antimony trichloride from which little azulene can be recovered,¹⁰ in contrast with the conducting solutions of other aromatic hydrocarbons.^{10,11}

Although *p*-benzoquinone is an acceptor slightly stronger than trinitrobenzene,^{12a} it would not form a complex with azulene.

The charge-transfer transitions of azulene-trinitrobenzene and azulene-chloranil both occurred at lower energy in the solid phase, as measured by diffuse reflectance, than in solution. These provide two more examples of an ostensibly general phenomenon which may also be discerned in the data reported by Foster and Thomson¹³ for the complexes between *NNN'*-tetramethyl-*p*-phenylenediamine and the acceptors 2,4-dinitrotoluene, *m*-dinitrobenzene, 1,3,5-trinitrobenzene, and chloro-*p*-benzoquinone; 2,4,6-trinitrotoluene seems to be exceptional.

The transition wave-number reported here, $2.18 \mu^{-1}$, for azulene-trinitrobenzene in solution is exactly the same as that found previously for the complex in a solid disc of potassium bromide.¹⁴

Experimental.—Melting points are corrected.

Materials. 1,3,5-Trinitrobenzene was recrystallized several times from ethanol, m. p. 122.5—123.5°. Chloranil had m. p. 296.5—297° (sealed tube) (from benzene). *p*-Benzoquinone was recrystallized twice from petroleum ether and sublimed, m. p. 114—115°. 2,3-Dicyanoquinone, kindly supplied by Dr. P. R. Hammond, iodine "resublimed," AnalaR carbon tetrachloride, anthracene (B.D.H. microanalytical reagent, m. p. 216—217.5°), pyrene (B.D.H., m. p. 147.5—149°), AnalaR *NN*-dimethylaniline, and *NNN'*-tetramethyl-*p*-phenylenediamine, kindly supplied by Dr. K. M. C. Davis, were not further purified. Azulene was purified by formation, recrystallization, and decomposition of its trinitrobenzene complex;¹⁵ it was sublimed at 80°/7 mm., m. p. 100—101°. Perylene (Aldrich) had m. p. 279—279.5° (rapidly heated to 275°) (from toluene). Methylene chloride (May and Baker) and benzene (Hopkin and Williams M.F.C.) were dried over calcium sulphate.

The dull blue azulene-chloranil complex crystallized from a concentrated solution in benzene of equimolar weights of the components, did not melt below 405°.

Measurements. Diffuse reflectance spectra of the solids diluted with lithium fluoride were measured in a Unicam S.P. 500 spectrophotometer with the S.P. 540 attachment and the RSV

⁸ Lepley, *J. Amer. Chem. Soc.*, 1962, **84**, 3577.

⁹ Pysh and Yang, *J. Amer. Chem. Soc.*, 1963, **85**, 2124.

¹⁰ Baughan, Finch, and Stoodley, unpublished results.

¹¹ Baughan, Jones, and Stoodley, *Proc. Chem. Soc.*, 1963, 274.

¹² Beukers and Szent-Györgyi, *Rec. Trav. chim.*, 1962, **81**, 255, (a) Table I; (b) Table III.

¹³ Foster and Thomson, *Trans. Faraday Soc.*, 1962, **58**, 860; 1963, **59**, 296.

¹⁴ Dewar and Lepley, *J. Amer. Chem. Soc.*, 1961, **83**, 4560.

¹⁵ Plattner and Pfau, *Helv. Chim. Acta*, 1937, **20**, 224.

SZG500 photomultiplier. Transmission spectra of solutions were measured with a Unicam S.P. 700 recording spectrophotometer. The solutions of azulene and electron-acceptor (0.5—5mm), contained separately in two 5-mm. path-length cells, were placed in the reference beam, and a mixture of equal volumes (1.3 ml.) of the same solutions, in a 10-mm. path-length cell, in the sample beam. Spectra were first observed about 2 min. after mixing. The concentrations of the stock solutions were adjusted until a fairly intense charge-transfer band was observed. If the absorption of one of the components overlapped this band, its concentration was kept as low as possible. Solutions of the complexes of dicyanoquinone often had to be more concentrated than those of azulene (Table 2). The slit-width was never more than 0.06 mm., corresponding to a maximum band-width of $0.005 \mu^{-1}$.

The chemical stability of the complexes increased, but the intensity of their absorption decreased in order in the series of solvents: carbon tetrachloride, methylene chloride, benzene. The second solvent was preferred but could not always be used. Chloroform was avoided because the stabilizing ethanol might interfere. No unambiguous charge-transfer absorption could be detected in solutions of azulene and iodine in methylene chloride or benzene, but only in carbon tetrachloride. Both azulene and the complex were unstable in this solvent; the peak of the absorption band shifted slowly $0.1 \mu^{-1}$ to higher energy and increased 60% in height during 1 hr. After 24 hr. the solution of this complex had deposited a reflective film. The initial frequency was used in the calculation. The change of solvent is unlikely to cause an appreciable discrepancy, for the charge-transfer band of pyrene-chloranil, for example, shifts only $0.01 \mu^{-1}$ when the solvent is altered from methylene chloride to carbon tetrachloride.^{12b}

When solutions in methylene chloride of azulene and dicyanoquinone were mixed, intense bands quickly grew at 1.27 and $1.67 \mu^{-1}$, and a black paramagnetic solid (which is being further investigated) was slowly precipitated.

Mixtures of azulene and *p*-benzoquinone in methanol, benzene, or methylene chloride showed no charge-transfer absorption, even when the solution was so concentrated as 10mm. Indeed, on evaporation of the solution in benzene, the components crystallized out separately. The mixture reacted slowly in methanol or benzene, and more rapidly in methylene chloride; the peak of a weak band trebled its height and shifted from 1.67 to $1.80 \mu^{-1}$ in 20 min.

The author gratefully acknowledges a Fellowship financed by the D.S.I.R. and made available by Professor M. C. R. Symons.

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424. *Pyrolytic and Photolytic Decomposition of Trityl p-Toluate.*¹

By K. DARRELL BERLIN and GENE P. STURM.

PYROLYSIS of certain alkyl esters is well recognized as a valuable method for the synthesis of unsaturated hydrocarbons^{2,3} but elegant work in recent years has shown that the decomposition is complex for certain esters, notably the alkenyl (*e.g.*, vinyl) esters of both aliphatic and aromatic acids.⁴ In view of the availability of trityl esters,⁵ and since trityl benzoate had been reported to decompose at 500° to yield tetraphenylmethane,⁶ an investigation was undertaken to explore the utility of the reaction in the synthesis of 1,1,1-triphenylmethyl hydrocarbons. Trityl alkylcarboxylates decomposed to give

¹ Previous paper in the series, *J. Org. Chem.*, 1963, **28**, 2039.

² Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., New York, 1929.

³ De Puy and King, *Chem. Rev.*, 1960, **60**, 431.

⁴ See the recent papers of Ritchie and his co-workers, *J.*, 1955, 2717; 1957, 4700; 1963, 2678, 2688, 2692, 2697.

⁵ Berlin, Gower, White, Gibbs, and Sturm, *J. Org. Chem.*, 1962, **27**, 3595.

⁶ Jones and Ritchie, *J.*, 1960, 4141.

complex pyrolysates, a radical mechanism being postulated to explain the formation of triphenylmethane, benzophenone, and the corresponding acid.¹ Oxidation of the melt of an ester resulted in a marked increase in the yield of benzophenone, the suggested product from decomposition of the triphenylmethoxy-radical. In the present study, trityl *p*-toluate was synthesized by condensation of trityl bromide with sodium *p*-toluate in benzene. It had been prepared previously,⁷ in unspecified yield, by the interaction of di-*p*-toluoyl peroxide and the trityl radical. Purification was tedious, with only a 52% return from the crude material (95%).

Thermal decomposition of trityl *p*-toluate in both a static-flow (340°) and rapid-flow (425°) system yielded nearly identical results. An increase in the amount of decarboxylation at the higher temperature suggested decay of the *p*-toluoyloxy-radical. Carbon dioxide probably does not have a *p*-toluic acid as a precursor, since the acid had been produced (98.7%) in the pyrolysis of cyclohexyl *p*-toluate at 464°.⁸ Indeed, *p*-toluic acid and triphenylmethane were isolated in yields of 78 and 73% in the static-flow pyrolysis, compared to 48 and 79%, respectively, in the rapid-flow experiment. The detection of 9-phenylfluorene in the pyrolysate of trityl *p*-toluate (static system) is further evidence for homolytic alkyl-oxygen bond cleavage, as trityl radicals disproportionate in the presence of light to give triphenylmethane and the dimer of 9-phenylfluorene.⁹ Irradiation of the trityl radical had been shown to produce both 9-phenylfluorene and its dimer.¹⁰ Minor products in the pyrolysis of trityl *p*-toluate (rapid flow) included benzophenone, triphenylmethanol, biphenyl, and carbon monoxide. In the static decomposition, traces of benzene and toluene were also noted. Rapid abstraction of hydrogen by the trityl radical was anticipated.¹ However, trityl peroxide was isolated in rapid-flow thermolysis, which suggested that the trityl radical was present in the pyrolysate and was oxidized upon standing in solution exposed to the atmosphere.

All compounds were identified by infrared analysis and gas chromatography. An acidic polymeric material was also obtained whose ultraviolet spectrum resembled that of *p*-toluic acid. However, it resisted purification and appeared to form tars with several solvents.

When oxygen was passed through a melt of trityl *p*-toluate at 340°, or when a solution (12%) in boiling benzene was irradiated in the presence of oxygen, nearly identical reaction mixtures resulted. However, as noted with the trityl alkylcarboxylates,¹ the quantity of benzophenone increased. Triphenylmethoxy-radicals were readily produced by oxidation of trityl radicals, and the former collapsed to benzophenone and phenyl radicals.¹¹ Photolysis of a solution of triphenylmethane in benzene under nearly identical conditions resulted in recovery of the hydrocarbon in 98% yield. Since triphenylmethane is not significantly decomposed, it is probably not a precursor of triphenylmethyl radicals in the photolysis of trityl *p*-toluate. The results reported herein support a radical mechanism for the decompositions.

Neither *p*-tolyltriphenylmethane nor tetraphenylmethane was detected in the rapid-flow pyrolysis conducted on a benzene solution of trityl *p*-toluate. Similarly, the pyrolysate from the static decomposition did not contain either hydrocarbon. Consequently, simple elimination of carbon dioxide and coupling of *p*-tolyl radicals with trityl radicals does not occur in this example, or the quantities of such compounds, if formed, are outside the limits of our detection methods. Several unidentified trace products were present below the level of 1%. Trityl benzoate may be a truly exceptional case since the trityl radical is known to induce the decomposition of diacyl peroxides but the yield is quite dependent on the nature of the peroxide.¹² The stability of the benzyloxy-radical

⁷ Wieland and Meyer, *Annalen*, 1942, 551, 249.

⁸ Smith and Wetzel, *J. Amer. Chem. Soc.*, 1957, 79, 875.

⁹ Schmidlin and Banus, *Ber.*, 1912, 45, 1344.

¹⁰ Letsinger, Collat, and Magnusson, *J. Amer. Chem. Soc.*, 1954, 76, 4185.

¹¹ Wieland, *Ber.*, 1911, 44, 2550.

¹² Denney and Weiss, *J. Org. Chem.*, 1963, 28, 1415.

is recorded.¹³ A π -complex formed between the trityl radical and the benzoyloxy-radical (and perhaps solvent), was postulated to collapse to tetraphenylmethane.¹⁴ Stability of such a complex may well be influenced by small changes in the structure of the acyloxy-radical. Moreover, at the pyrolysis temperatures employed with trityl *p*-toluate, existence of a similar complex would be less probable.

Experimental.—Preparation. The trityl esters were prepared by the general procedure reported previously.⁵ Sodium *p*-toluate (37.6 g., 0.238 mole) was added to trityl bromide (64.6 g., 0.200 mole) in dry reagent benzene (250 ml.). The mixture was stirred and heated under reflux for 2 hr. Sodium bromide was filtered off, and the filtrate concentrated, to yield a solid (95%), m. p. 191—193° (from butan-2-one) (39 g., 52%) (lit.,⁷ m. p. 187—189°). Infrared and n.m.r. spectra were consistent with the assigned structure.

Apparatus and procedure. The apparatus has been described previously.¹ The ester, as a 15% solution in benzene, was introduced into the pyrolysis column from an addition funnel having a helium inlet tube. Static pyrolyses were run in a 50-ml. Pyrex round-bottom flask fitted with a gas inlet tube and a water condenser. Volatile components were captured in a trap containing solid carbon dioxide. Photolyses were conducted on 12% solutions of trityl *p*-toluate in benzene, in a 100-ml. quartz round-bottom flask with a 140 w, 3.9 A Hanovia ultraviolet lamp.

Analytical methods. An Aerograph Hy-Fi Model A-550 gas chromatograph with a flame ionization detector (Wilkins Instrument and Research, Inc.) was used for qualitative and quantitative analyses. The internal-standard method was used for the quantitative analysis of compounds obtained in lower yields. *p*-Toluic acid was extracted with sodium hydrogen carbonate, precipitated with 12*N*-hydrochloric acid, washed, dried, and weighed. It was identified from m. p., mixed m. p., and infrared analysis. Triphenylmethane was separated by chromatography on alumina, and weighed. Infrared analysis, m. p., and mixed m. p. determinations verified the gas-chromatographic identification of triphenylmethane, and products obtained in lower yields where possible. Carbon dioxide was absorbed by Ascarite and weighed. Carbon monoxide was identified by the palladium chloride test.¹⁵ Both carbon oxides were identified by infrared analysis also. Trityl peroxide was identified in the rapid-flow pyrolysate by infrared analysis, m. p., and mixed m. p. with the authentic compound prepared as reported by Gomberg.¹⁶

Results from pyrolysis runs. (1) The rapid-flow pyrolysis of trityl *p*-toluate at 425° gave the following yields of products [based on starting ester (0.028 mole)]: triphenylmethane (79%), *p*-toluic acid (48%), carbon dioxide (26%), triphenylmethanol (4%), trityl peroxide (2%), unknown A (0.14 g.), and traces of carbon monoxide, benzophenone, and biphenyl. The yields were comparable in a second run. (2) Static pyrolysis of trityl *p*-toluate (7.81 g., 0.020 mole), under helium, at 340° for 1 hr. gave the following compounds: triphenylmethane (73%), *p*-toluic acid and anhydride (78% as acid), carbon dioxide (7%), 9-phenylfluorene (13%), benzophenone (5%), toluene (2%), benzene (trace), carbon monoxide (trace), and acidic polymeric material (0.17 g.). (3) Static pyrolysis for 1 hr. at 340°, while bubbling oxygen through the melt, of trityl *p*-toluate (0.02 mole) gave: triphenylmethane (60%), *p*-toluic acid and anhydride (95% as acid), benzophenone (10%), carbon dioxide (3.9%), benzene (1.3%), toluene (2.6%), triphenylmethanol (1.0%), traces of phenol, carbon monoxide, biphenyl, and two unknowns, and 1.0 g. of acidic polymeric material. (4) Photolysis of trityl *p*-toluate in benzene (12% solution; 0.013 mole), under a nitrogen atmosphere, for 72 hr. at 60° gave *p*-toluic acid (9%), triphenylmethane (1%), benzophenone (1.6%), unknown A (0.018 g.), a small undetermined amount of triphenylmethanol, and a large quantity of recovered ester. (5) Photolysis in benzene (12% solution, 0.014 mole) for 73 hr. at 70°, while bubbling oxygen through the solution, gave *p*-toluic acid (55%), triphenylmethane (0.5%), benzophenone (6.0%), unknown A (0.013 g.), an appreciable but undetermined amount of triphenylmethanol, and a large amount of recovered ester. (6) Photolysis of triphenylmethane (0.005 mole) in benzene (25 ml.) at 80° for 61 hr., while bubbling oxygen through the solution, gave traces of biphenyl, benzophenone,

¹³ Hammond and Soffer, *J. Amer. Chem. Soc.*, 1950, **72**, 4711.

¹⁴ Benkeser and Schroeder, *J. Amer. Chem. Soc.*, 1958, **80**, 3314.

¹⁵ Altieri, "Gas Analysis," American Gas Association, New York, 1945, 257.

¹⁶ Gomberg, *J. Amer. Chem. Soc.*, 1900, **22**, 757.

triphenylmethanol, and unchanged starting material (>98%). (7) A solution of the ester (4.95 g.) in benzene (40 ml.) was heated at 65° in the dark for 72 hr., under a nitrogen atmosphere. Extraction of the solution gave no acid, and the gas chromatogram was identical with that of the pure ester.

We gratefully acknowledge support of this research by the National Science Foundation.

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[Received, September 30th, 1963.]

425. Isomerisation Accompanying Friedel-Crafts Alkylation with Propyl and Butyl Ethers, Alcohols, and Bromides.

By P. G. NIELD.

DURING work on the action of aluminium chloride on alkyl ethers, alcohols, and halides^{1,2} the nature of the products of monoalkylation of benzene with a number of these reagents was investigated, with the results shown in the Table.

Alkylating agent	AlCl ₃ (moles)	Temp./Time	Monoalkylbenzenes	
			Yield %	Composition
Di-n-propyl ether ...	2	80°/5 hr.	33	n-(37%) and iso-(63%)PrPh
Di-n-butyl ether	2:3	60/5 hr.	7.5	n-, s-, and iso-BuPh
Di-s-butyl ether	2:3	75°/6 hr.	33	s-, and iso-BuPh
Di-isobutyl ether ...	2:3	50°/7 hr.	16	iso-, s-, and t-BuPh
Ethyl t-butyl ether	2:5	15°	71	t-BuPh
n-Propyl alcohol ...	2:5	80°/6½ hr.	38	n-(47%) and iso-(53%)PrPh
n-Butyl alcohol	2	50°/5½ hr.	11	n-, s-, and iso-BuPh
s-Butyl alcohol	1:4	15°	77.5	s-BuPh
Isobutyl alcohol ...	1:4	60°/6 hr.	17	t-BuPh (+ small amounts of s- and iso-BuPh)
n-Butyl bromide ...	0:7	0/8 hr.	50	n-(38%) and s-(62%)BuPh
s-Butyl bromide ...	0:7	0/5½ hr.	33	s-BuPh
Isobutyl bromide ...	0:7	0/6 hr.	30	t-BuPh
t-Butyl chloride	0:8	0/4½ hr.	77	t-BuPh
n-Propyl formate ...	0:8	25—60°/4 hr.	36	n- and iso-PrPh

The composition of the monoalkylbenzenes was determined by infrared spectroscopy, the following characteristic bands serving to differentiate the propyl- and butyl-benzenes in mixtures of isomers:

n-Propylbenzene	1380, 1360, 1340, 1260, 1205, 1095, 1050, 1030, 960, 890, 815 cm. ⁻¹
Isopropylbenzene	1385, 1365, 1325, 1300, 1280, 1255, 1215, 1080, 1050, 1030, 925, 815 cm. ⁻¹
n-Butylbenzene	1390, 910, 1110, 940 cm. ⁻¹
s-Butylbenzene	1310, 1090, 1030, 1020, 1010, 1000, 960 cm. ⁻¹
Isobutylbenzene	1380, 1370, 1350, 1290, 1120, 1110, 1100, 930 cm. ⁻¹
t-Butylbenzene	1490, 1460, 1450, 1400, 1390, 1270, 1250, 1210, 1060, 1040, 840 cm. ⁻¹

The proportion of the isomers present in the binary mixtures was calculated from their infrared spectra. For the propylbenzenes the optical intensities at 1365 and 1095 cm.⁻¹ were compared with those of authentic n- and iso-propylbenzene at the same frequencies. For the mixture of n- and s-butylbenzene the two bands selected were those at 1110 and 960 cm.⁻¹

The ternary mixtures could not be analysed quantitatively in this way owing to the overlap of the strongest characteristic bands of the isomers, but the qualitative picture is quite clear.

The qualitative composition of the propylbenzenes obtained by alkylation with n-propyl formate was determined by the perbromination method of Hennion and Anderson,³

¹ Baddeley and Pickles, *J.*, 1953, 3726.

² Baddeley and Nield, *J.*, 1954, 4684.

³ Hennion and Anderson, *J. Amer. Chem. Soc.*, 1946, 68, 424.

pentabromo-n-propylbenzene, m. p. 95°, and hexabromobenzene, m. p. 320°, being isolated.

Searles⁴ reported that alkylation with di-n-propyl ether (6 hours at reflux temperature) gave a mixture of 17.33% of n- and 82.66% of iso-propylbenzene. He also referred to an alkylation with di-n-butyl ether⁵ which it was stated gave only s-butylbenzene (16% yield).

The alkylations with n-propyl alcohol and its formate serve to disprove two claims of complete retention of configuration in alkylation with agents containing n-alkyl groups^{6,7} (apart from intramolecular alkylation⁸); the sole remaining exception is alkylation with cyclopropane.⁹

The results above can be compared with the subsequent findings of Roberts and Shienghong¹⁰ in alkylation with propyl and butyl chlorides at 80°. A difference occurs in the products derived from reagents containing the isobutyl group. Whereas alkylation with isobutyl chloride at all temperatures between -18 and 80° gives t-butylbenzene only, with di-isobutyl ether, and to a lesser extent isobutyl alcohol, iso- and s-butylbenzene occur also.

The theoretical implications of these results, together with subsequent findings, will be discussed in a further communication.

The author thanks Dr. Meakins for the infrared spectra.

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[Received, November 7th, 1963.]

⁴ Searles, *J. Amer. Chem. Soc.*, 1954, **76**, 2313.

⁵ Prindle, Ph.D. Thesis, Washington University, St. Louis, Missouri, 1942.

⁶ Tsukervanik and Vikhrova, *J. Gen. Chem., U.S.S.R.*, 1937, **7**, 632; Ipatieff, Pines, and Schmerling, *J. Org. Chem.*, 1940, **5**, 253.

⁷ Bowden, *J. Amer. Chem. Soc.*, 1938, **60**, 645.

⁸ Baddeley and Williamson, *J.*, 1956, 4647.

⁹ Grosse and Ipatieff, *J. Org. Chem.*, 1937, **2**, 447.

¹⁰ Roberts and Shienghong, *J. Amer. Chem. Soc.*, 1960, **82**, 732.

426. Organosilicon Compounds. Part XXIX.¹ The Stereochemical Course of the Reaction of a Silicon Hydride with Chlorotriphenylmethane.

By J. D. AUSTIN and C. EABORN.

TRIORGANOSILANES react with chlorotriphenylmethane to give chlorotriorganosilanes and triphenylmethane, and a recent kinetic study by Corey and West showed that in fairly polar or weakly polar solvents, such as nitromethane and benzene, the reaction probably involves the silane and a trityl-carbonium ion-chloride ion pair, possibly in a four-centre process (I).²

We have studied the stereochemistry of this type of reaction by treating (+)-methyl-1-naphthylphenylsilane³ with chlorotriphenylmethane in benzene. Little, if any, optical activity was lost, and (-)-(chloro)methyl-1-naphthylphenylsilane was obtained in 71% yield. From assignments of configuration made by Sommer and Frye and their colleagues^{3,4} it can be concluded that the reaction takes place with retention of configuration at the silicon atom, which is consistent with the four-centre mechanism proposed by Corey and West.

¹ Part XXVIII, Bott, Eaborn, and Leyshon, *J.*, 1964, 1971.

² Corey and West, *J. Amer. Chem. Soc.*, 1963, **85**, 2430.

³ Sommer and Frye, U.S.P. 3,024,262 (1962).

⁴ Sommer and Frye, *J. Amer. Chem. Soc.*, 1959, **81**, 1013; 1960, **82**, 4118; Sommer, Frye, Musoff, Parker, Rodewald, Michael, Okaya, and Pepinsky, *ibid.*, 1961, **83**, 2210; Sommer, *Angew. Chem. Internat. Edn.*, 1962, **1**, 143.

Experimental.—Sommer and Frye's method³ was used to make (+)-methyl-1-naphthylphenylsilane, m. p. 62·5—63·5°, $[\alpha]_D^{20} + 33\cdot0^\circ$ (*c* 4·28 in cyclohexane) [lit.,³ m. p. 63·5—64·5°, $[\alpha]_D^{20} + 33\cdot7$ (*c* 4·00 in cyclohexane)].

A solution of (+)-methyl-1-naphthylphenylsilane (0·54 g., 22 mmoles) and chlorotriphenylmethane (0·61 g., 22 mmoles) in anhydrous benzene (15 ml.) was refluxed in an atmosphere of dry nitrogen for 4 hr. Benzene was then distilled off under reduced pressure until the residual volume was *ca.* 3 ml., and triphenylmethane was filtered off from the cold solution. The remaining benzene was evaporated from the filtrate under reduced pressure, and the residue was recrystallized from pentane, to give (–)-(chloro)methyl-1-naphthylphenylsilane (0·44 g., 71%), m. p. 62·5—63·5°, $[\alpha]_D^{20} - 6\cdot03$ (*c* 4·4 in cyclohexane) [lit.,³ m. p. 63·5—64·0°, $[\alpha]_D^{20} - 6\cdot28$ (*c* 10·5 in cyclohexane)].

We thank Albright and Wilson Ltd. for supporting this research, and Mr. J. S. Hughes of Midland Silicones Ltd. for his interest and encouragement.

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[Received, December 4th, 1963.]