NOTES

704. *The Effect of Sodium Tungstate Additions on the Thermal Dehydration of Silica Xerogel*

By R. A. Ross and N. Henry

Silica and silica gels are often used in mixtures with oxides or as metal " supports " in many heterogeneous catalytic rections.[1] Hence, it is interesting to see how the properties of silicas and silica gels may be influenced by inclusions of such additives. It has already been shown [2] that additions of up to 5 mole % of alkaline-earth chlorides considerably accelerates the dehydration rate of silica xerogel. These studies have been extended to examine the action of a selected transition metal anion by using sodium tugstate. Values for the rate of dehydration were supplemented by measurements of surface area and mercury density.

Experimental.—Materials. Microspheroids of silica gel were prepared by a method similar to that of Marisac.[3] They were allowed to synerise for 24 hr. and then extracted with water in a Soxhlet apparatus for 20 hr. to remove sulphate. Organic impurities were then removed by extraction with benzene for 16—24 hr., and the gel was finally washed in acetone and dried slowly at 50°. Sodium tungstate (AnalaR) was heated to above 100° on a thermal balance to remove water of crystallisation. The amount of sodium tungstate added was calculated as gram-ions % of tungstate ion on the weight of SiO_2 obtained from 1 g. of silica gel activated at 260° and subsequently calcined at 1500° for several hours.

In one set of experiments the gel and tungstate were mixed by hand-stirring and shaking for *ca.* 5 min. (This gave a degree of mixing that could not be improved on, as judged by thermo-dehydration results). In the other sets of experiments, the xerogel spheroids were bedded carefully on a layer of tungstate, or placed separately in the furnace crucible with the sodium tungstate contained in a fine-mesh platinum basket hung just below the crucible level.

Apparatus. The rate of dehydration in air was examined by means of a modified T.R. model Stanton thermobalance. The silica gel–additive charge was varied by a small amount in the region 0·9—1·1 g.; within these limits no mass effect was observed on the rate of dehydration, the values for which were converted to a mg./g. basis. The dehydration was studied by raising the furnace temperature to 260° and keeping it constant until all physically adsorbed water had been driven off from the gel spheroids. The sample was removed and kept over activated molecular sieves in a desiccator. The furnace was then raised vertically and held at the required temperature before the sample was replaced. The loss in weight was recorded until a steady value was reached, *i.e.*, less than 0·5 mg. in 10 min. In general, the

[1] F. G. Ciapetta and C. J. Plank, " Catalysis," Reinhold, New York, 1954, Vol. I, p. 315.
[2] N. Henry and R. A. Ross, *J.*, 1962, 4265.
[3] M. M. Marisac, U.S.P. 2,384,217/1945.

time taken to reach the steady value was no more than 30 min. Preliminary calibration experiments showed that the time taken for samples to reach the equilibrium temperature was, for example, 150—180 sec. at 800°.

After the samples had been cooled the mercury densities,[4] *X*-ray powder diffraction patterns, and B.E.T. surface areas (N_2; −183°) were determined for most of them.

Results and Discussion

The losses in weight of silica xerogel were examined with spheroidal and irregular particles of size ranges 2000—840 and 840—420 μ from 400—800°. There was a pronounced tendency for the irregular particles to lose more water at each temperature: for example, the steady loss for microspheroids at 750° was 40·33 mg./g., while that for the irregular hydrogel was 46·57 mg./g. at 700°. The results showed an increasing degree of dehydration with temperature for both shapes of particle.

Figure 1 illustrates the decrease in surface area with temperature for 2000—840 μ

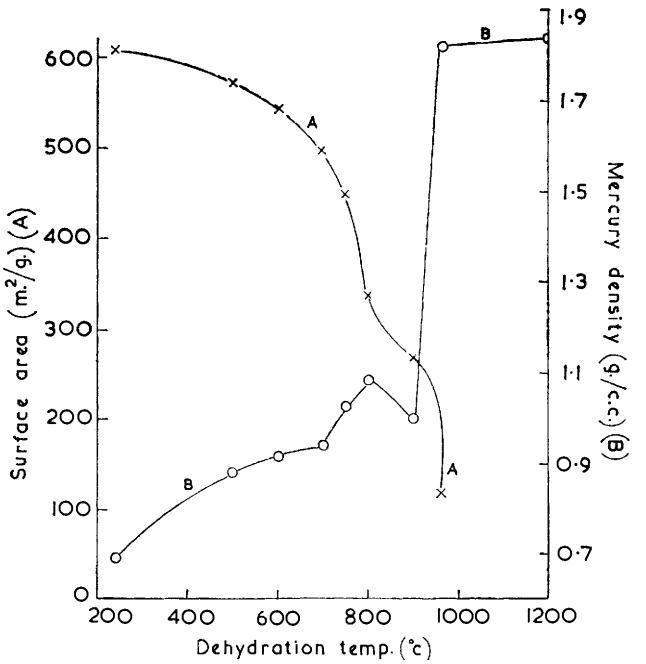


Figure 1. Variation of physical properties of xerogels with dehydration temperature:
(A), surface area
(B), mercury density

xerogel spheroids. It shows the marked decrease in surface area expected [2] around 800°. As found by Goodman and Gregg [5] for precipitated silica, the density decreases sharply around this temperature. There is a rapid increase to a high density at 900° and above, which is to be expected with the conversion of the silica to cristobalite and the corresponding elimination of pores. Pore-size distribution curves, calculated from the adsorption branch of the B.E.T. isotherm,[6] showed a maximum pore diameter at 60 Å and a secondary maximum at 35—40 Å. The height of the peak at 60 Å increased initially with the temperature of treatment, but fell rapidly at 750°, *i.e.*, around the bulk Tamman temperature (0·5 T_m). Above 750°, the distribution peaks became broader, which is consistent with the collapse of the gel framework, and samples treated at 960° ultimately showed an almost complete absence of pores.

[4] W. B. Jepson, *J. Sci. Instr.*, 1959, **36**, 319.
[5] J. F. Goodman and S. J. Gregg, *J.*, 1959, 694.
[6] C. R. Cranston and F. A. Inkley, *Adv. Catalysis*, 1957, **9**, 143.

In Figure 2, the experimental reaction rate at 500° is plotted against percentage of sodium tungstate mixed with the hydrogel. The rates were determined for losses in weight of 15, 20, 25, and 30 mg./g. from the hydrogel, and found from the tangents to the curves of weight loss *versus* time. In all cases the rate rises initially to a maximum value at around 2—3 g.-ion % WO_4^{2-} and starts to level out at 10 g.-ion %; this value for the rate lies slightly above that found in the absence of tungstate. Comparative rates of dehydration at 500° for the different methods of adding tungstate showed that the amount of dehydration achieved decreased in the series: mixed > layer > vapour > no additive.

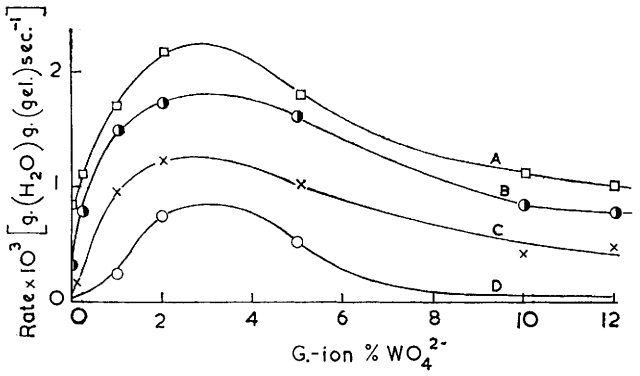


FIGURE 2. Observed rate curves showing dependence on amount of additive at 500°: loss in weight (A), 15 mg./g.; (B), 20 mg./g.; (C), 25 mg./g.; (D), 30 mg./g.

The recovery of sodium tungstate from the mixed solids was examined after separate runs at 500, 600, and 700° with additions of 5 g.-ion % WO_4^{2-}. The mixture was agitated with water and boiled, and the filtrate was evaporated to dryness. 99·5—100% of sodium tungstate was recovered and the analyses were confirmed by the oxine method. *X*-Ray powder photographs showed no interaction between the gel and the tungstate as judged by the absence of lines. The Table shows the values for the surface areas and mercury densities of xerogel samples for the three methods of tungstate addition. There was a fall in surface area, and increase in mercury density, with increase in temperature for all three types of experiment. The greatest effects were observed in the " mixed " experiments.

Physical measurements of xerogel samples treated at various temperatures

Condition	Temp.	Surface area ($m.^2/g.$)	Mercury density (g./c.c.)
Gel + WO_4^{2-} mixed (5 g.-ion %)	450°	514	0·7971
	500	489	0·8186
	550	450	0·8335
	570	483	0·8620
	600	421	0·8806
	620	395	0·9119
Gel + WO_4^{2-} layer (5 g.-ion %)	400	563	0·8200
	500	536	0·8366
	550	518	0·8417
	570	501	0·8587
	600	438	0·8753
	645	408	0·8955
Gel + WO_4^{2-} vapour	500	552	0·8207
	550	532	0·8341
	570	454	0·8705
	610	421	0·8847

From the temperature coefficients of the dehydration rates, the activation energy for 2000—840 μ xerogel was calculated to be 9·2 ± 0·4 kcal./mole. In the presence of sodium

tungstate this was lowered to 6·3 ± 0·3 kcal./mole. These values were slightly affected by particle size range and geometry.

Essentially, the dehydration may be considered as an elimination of water from neighbouring silanol groups. The latter could be in adjacent positions on the same particle surface or, at the higher temperatures, when coalescence sets in, on neighbouring particles.[2] The dehydration is catalysed in the presence of sodium tungstate vapour, as is shown specifically in the vapour experiments, which, at each temperature, resulted in less dehydration of the xerogel than was found in the solid-contact experiments. This is shown, for example, by the surface area and mercury density results. However, these differences could be accounted for by inadequate vapour–solid mixing and poor penetration of tungstate vapour through the bed of xerogel particles. Many so-called solid–solid reactions may in fact, be controlled by solid–vapour contact,[7] much as appears to be the case in the present work.

(R. A. R.) Department of Chemistry, College of Technology, Belfast.
Department of Chemistry,
University of Strathclyde, Glasgow. [*Received, November 26th*, 1964.]

[7] P. B. Weisz, *Adv. Catalysis*, 1962, **13**, 137.

---

705. *Reaction of Phosphorus Thionitride with Hydrogen, Chlorine, Hydrogen Chloride, and Aluminium Chloride*

By S. N. Nabi, (Mrs.) Safura N. Nabi, and N. K. Das

Phosphorus thionitride, $(NPS)_n$, has been prepared by Glatzel [1] and by Stock *et al.*[2] by the ammonolysis of phosphorus pentasulphide. It is an interesting compound, apparently resembling in composition the halogenophosphazenes $(NPCl_2)_n$, and more so the oxynitride $(NPO)_n$. Apart from its hydrolysis and reactions with aqueous acids, and ammonia, little is known about its chemical behaviour [2] and constitution. Thus, in view of the current interest in phosphorus–nitrogen chemistry, it was thought useful to characterise the compound.

Glatzel's method of preparation was to heat phosphorus pentasulphide with ammonium chloride, but no details of the reaction conditions were given. The reaction should be properly represented as follows:

$$n P_4S_{10} + 4n NH_4Cl \longrightarrow 4(NPS)_n + 6n H_2S + 4n HCl$$

The evolution of hydrogen chloride closely parallels the thermal decomposition of ammonium chloride.[3] This indicates that the primary step in this reaction is the dissociation of ammonium chloride into ammonia and hydrogen chloride, followed by ammonolysis of the phosphorus sulphide.

Phosphorus thionitride is an insoluble, grey-white diamagnetic solid. It does not melt, but decomposes at high temperatures (600°); its moderate refractoriness and its extreme insolubility suggest that it is macromolecular, $(NPS)_n$. Its infrared spectrum shows a diffuse band in the 1150 cm.$^{-1}$ region in the vicinity of the P–N stretching region suggested [4]

[1] E. Glatzel, *Z. anorg. Chem.*, 1893, **4**, 186.
[2] A. Stock, B. Hoffmann, F. Muller, H. Von Schonthan, and H. Kuchler, *Ber.*, 1906, **39**, 1967.
[3] D. M. Yost and H. Russel, jun., "Systematic Inorganic Chemistry of the Fifth and Sixth Group Non-metallic Elements," Prentice-Hall, New York, 1946, p. 249.
[4] N. L. Paddock, *Quart. Rev.*, 1964, **18**, 168; R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, 1962, **62**, 247.

for the phosphazenes; a weak overtone frequency occurs at 2500 cm.$^{-1}$. The P–S frequency could not be detected, probably because it lies beyond the rock-salt region.[5]

Hydrogen reacts with phosphorus thionitride causing extensive decomposition, and a complex mixture containing hydrogen sulphide, ammonia, and phosphine is obtained; the yellowish-white residual solid, which evolves phosphine on exposure to the air, is probably a lower hydride of phosphorus. It was observed that the platinum boat in which the reaction was carried out was heavily etched, probably because of the formation of platinum–phosphorus eutectics.[6]

Phosphorus thionitride reacts with chlorine at 250° giving chlorophosphazenes and disulphur dichloride, according to the equation

$$2(NPS)_n + 3nCl_2 \longrightarrow 2(NPCl_2)_n + nS_2Cl_2$$

Crystalline and semi-solid, chlorophosphazenes were formed. The crystals were trimeric cyclochlorophosphazene, the semi-solid was presumably a mixture of products of different molecular weights.

Dry hydrogen chloride attacks the phosphorus thionitride skeleton at the N–P linkage and, at relatively high temperatures (350°), ammonia is readily removed, and thiophosphoryl chloride results; this behaviour is typical of a nitride

$$(NPS)_n + 4nHCl \longrightarrow nNH_4Cl + nSPCl_3$$

Earlier reports of its reaction with hot dilute hydrochloric acid gave no details of products.

Phosphorus thionitride reacts additively with aluminium chloride at 350° in the proportion of 1 : 1, to give a product of composition $AlCl_3$,NPS; this new adduct is remarkably stable and can be heated to 700° without decomposition. It is diamagnetic, insoluble in common solvents, and unaffected by water. Dry hydrogen chloride cleaves the N–P linkage to give thiophosphoryl chloride and the ammino-complex, $AlCl_3$,NH_3. Evidently the monomer links strongly to aluminium through its nitrogen atom, but its thermal and hydrolytic stability suggest that the bonding may not be purely of the donor–acceptor type. A bis-compound, (NPS,2$AlCl_3$), could not be made, which indicates that the lone-pairs of the sulphur atom are not active.

Experimental.—Commercial phosphorus pentasulphide was purified by recrystallisation from carbon disulphide.[7]

For analysis, the solid reaction products were usually decomposed by fusion with potassium hydroxide. Sulphur was estimated gravimetrically as barium sulphate and phosphorus as phosphomolybdate. Nitrogen was determined by the Kjeldahl semi-micro method.

Preparation of phosphorus thionitride. Phosphorus pentasulphide (2·22 g., 10 mmoles) and ammonium chloride (1·07 g., 20 mmoles) were intimately mixed and heated at 300° for 2 hr. The evolved gases were led into a solution of iodine, giving the phosphorus thionitride (1·31 g., 85%) (Found: N, 18·2; P, 41·2; S, 40·6. Calc. for NPS: N, 18·3; P, 40·2; S, 41·5%). The gaseous products were identified as a mixture of hydrogen sulphide and hydrogen chloride, and their amounts were determined in solution (Found: H_2S, 0·9 g., 88%; HCl, 0·71 g., 96%). A yellow sublimate, which was deposited on the cooler parts of the reaction tube, was a mixture of unchanged phosphorus pentasulphide and ammonium chloride (0·1 g., 5%).

Thermal stability of phosphorus thionitride. Phosphorus thionitride (0·2 g.), contained in a silica boat, was heated in a tube at 600° for 2 hr. The residue was a partly decomposed product (0·185 g., 92%) (Found: N, 14·2; P, 47·0; S, 36·8%).

Reaction of phosphorus thionitride with hydrogen. Phosphorus thionitride (0·385 g.), contained in a platinum boat, was heated at 450° in a Pyrex tube through which dry hydrogen was passed for 2 hr.; this procedure caused a heavy attack on the platinum boat. The issuing gases were condensed in a trap cooled in liquid air, and, after the reaction was over the contents

[5] L. J. Bellamy, " Infra-red Spectra of Complex Molecules," Methuen, London, 1958, p. 322.
[6] M. C. Miller, D. W. Rhys, and R. A. Shaw, *Ind. Chemist*, 1964, **40**, 183.
[7] Ref. 3, p. 188.

of the trap were fractionated through traps at −63° and −200°. The small fraction condensing at −63° was ammonia (0·036 g., 42%) (Found: *M*, 19; Calc. for NH_3: *M*, 17). The fraction condensing at −200° was a mixture of hydrogen sulphide and phosphine; this was treated with a 10% solution of sodium hydroxide which absorbed the hydrogen sulphide (0·102 g., 60%), and the undissolved fraction was identified as phosphine (*ca.* 0·06 g.) (Found: *M*, 30; Calc. for PH_3: *M*, 34). A yellow-white sublimate, which condensed on the cooler parts of the tube, decomposed in contact with the atmosphere giving off phosphine and was probably a lower hydride of phosphorus. Some colourless droplets of a heavy liquid condensed on the sides of the reaction tube and were also found in small amounts in the boat, but were not characterised. If glass or fused-silica boats were used for the reaction, they also were heavily etched.

Reaction of phosphorus thionitride with chlorine. Phosphorus thionitride (0·257 g.) contained in a fused-silica boat, was heated at 250° in a Pyrex tube, through which dry chlorine was passed for 2 hr. The residue in the boat was of a buttery consistency, and had the composition of chlorophosphazene, ($NPCl_2$) (0·27 g., 70%) (Found: Cl, 62·0; N, 11·6; P, 27·1. Cl_2NP requires Cl, 61·3; N, 12·0; P, 26·1%). Some white crystals, which sublimed on to the cooler parts of the tube (80 mg., 20%), and melted at 114—115°, were soluble in petroleum ether; and were probably the trimeric chlorocylophosphazene, $N_3P_3Cl_6$ (Found: Cl, 61·6; P, 26·3%). A yellow liquid which condensed in a cold-finger (−22°) attached to the reaction tube was identified as disulphur dichloride (0·2 g., 91%) (Found: Cl, 52·8; S, 46·9. Calc. for S_2Cl_2: Cl, 52·6; S, 47·4%).

Reaction of phosphorus thionitride with hydrogen chloride. Dry hydrogen chloride was passed for 2½ hr. over phosphorus thionitride (0·116 g.), contained in a fused-silica boat, and heated to 250°. The white sublimate which collected on the cooler parts of the tube was identified as ammonium chloride (Found: Cl, 66·5; N, 26·2. Calc. for NH_4Cl: Cl, 66·3; N, 26·1%). A transparent liquid condensed in a cold-finger (−22°) and was also found in small amounts in the boat and was identified as thiophosphoryl chloride, $SPCl_3$ (0·203 g., 80%) (Found: Cl, 63·6; P, 18·8; S, 18·1. Calc. for $SPCl_3$: Cl, 63·0; P, 18·2; S, 18·8%). At 200°, reaction was incomplete.

Reaction of phosphorus thionitride with aluminium chloride. (i) *Reaction in equimolar ratio.* An intimate mixture of phosphorus thionitride (0·385 g., 5 mmoles) and aluminium chloride (0·67 g., 5 mmoles), contained in a fused-silica boat in a closed tube, was heated at 350° for 2 hr. The solid product was washed with water and had the composition of the 1 : 1 *adduct*, $AlCl_3$,NPS (1 g., 95%) (Found: Al, 13·2; Cl, 49·7; N, 6·9; P, 15·2; S, 15·6. $AlCl_3NPS$ requires Al, 12·8; Cl, 50·5; N, 6·6; P, 14·7; S, 15·4%). At 250° and at 300°, reaction was incomplete and the products contained free aluminium chloride.

(ii) *Reaction in the molar ratio of* 1 : 2. Phosphorus thionitride (0·385 g., 5 mmoles) and aluminium chloride (1·336 g., 10 mmoles) were heated together for 2 hr. at 350°, and the product was treated with water. The aqueous extract contained aluminium chloride (0·62 g., 46%) (Found: Al, 20·8; Cl, 79·2. Calc. for $AlCl_3$: Al, 20·2; Cl, 79·8%). The residue that remained after extraction with water was washed with ethanol and dried. Analyses showed it to be the 1 : 1 adduct, $AlCl_3$,NPS (0·93 g., 80·7%) (Found: Al, 13·3; Cl, 50·1; N, 7·1; P, 15·1; S, 14·8%).

Thermal stability of the adduct. When 0·1 g. portions of the adduct were heated in sealed tubes at 500, 600, and 700° for 1 hr., no decomposition and no loss in weight were observed, and the residues were shown by analysis to be the unchanged adduct.

Reaction of the adduct with hydrogen chloride. The adduct (0·194 g.), contained in a fused-silica boat, was heated at 300° in a Pyrex tube, through which dry hydrogen chloride was passed for 2 hr. The liquid that condensed in an attached cold-finger (−45°) was thiophosphoryl chloride (0·146 g., 93·3%) (Found: Cl, 64·1; P, 17·5; S, 18·3. Calc. for $SPCl_3$: Cl, 63·0; P, 18·2; S, 18·8%). The white solid residue in the boat was identified as the 1 : 1 aluminium chloride–ammonia addition complex, $AlCl_3,NH_3$ (0·116 g., 90·6%) (Found: Al, 16·9; Cl, 70·8; N, 10·0. Calc. for $AlCl_3H_3N$: Al, 17·1; Cl, 70·7; N, 9·3%). The slight condensate that appeared on the cooler parts of the tube was a mixture containing traces of thiophosphoryl chloride.

Magnetic susceptibilities. The magnetic susceptibilities of phosphorus thionitride and its adduct with aluminium chloride were measured on a Curie–Cheneveau magnetic balance, Mohr's salt being used as a standard. The susceptibilities (30°) were (NPS), $-1{\cdot}06 \times 10^{-6}$ and $AlCl_3$,NPS, $-0{\cdot}5 \times 10^{-6}$.

Infrared spectra. Infrared spectra were measured on mulls, with a Perkin-Elmer model 21 double-beam spectrometer, with rock-salt optics, in the range 4000—650 cm.$^{-1}$.

The authors thank Dr. R. A. Shaw for helpful criticism and Professor M. H. Khundkar for his interest.

CHEMICAL LABORATORY, UNIVERSITY OF DACCA, DACCA-2, EAST PAKISTAN.
(MRS. S. N. N.) EAST REGIONAL LABORATORIES,
PAKISTAN COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH,
DACCA-2, EAST PAKISTAN. [*Received, October 5th*, 1964.]

---

706. *The* $[Me_2Tl\ py]^+$ *Ion*

By I. R. BEATTIE and P. A. COCKING

WE report here an attempt to prepare a planar T-shaped complex ion in which all the electrons closely associated with the central atom are either in closed inner shells or involved in σ-bond formation. To produce such an ion we would require an acceptor (AB_2) with stereochemistry dictated by linear (presumably *sp*) hybridisation, but able to take on (weakly) one monodentate ligand. We selected the dimethylthallium ion as acceptor (remembering the relatively large *s*–*p* separation in this region of the Periodic Table [1]). Dimethylthallium chloride contains the linear C–Tl–C skeleton [2] and is frequently [3] considered to be an ionic compound. We prefer to think of it as an analogue of dimethyltin difluoride [4] with bridging halogens.* Thus, it is well known [5] that trimethylthallium is a rather poor acceptor, forming weak adducts such as Me_3Tl,NMe_3 (melting near 0°). It is unreasonable to assume that the Me_2Tl^+ ion is a very poor acceptor (it is formed by removing methyl ion from trimethylthallium) unless some exceptional stabilisation is achieved due to the linearity of the C–Tl–C group. As dimethylthallium chloride crystallises unchanged from pyridine solution we decided to avoid the potential donor chloride ion and to carry out our experiments with dimethylthallium perchlorate.

Dimethylthallium perchlorate recrystallises unchanged from water or tetrahydrofuran. However, it is extremely soluble in pyridine, from which the compound Me_2TlClO_4,py can be obtained. This adduct can be recovered unchanged from acetonitrile solution suggesting co-ordination rather than simple solvation by the pyridine. This, as far as we are aware, would be the first co-ordination compound of the dimethylthallium ion with a monodentate ligand. ν_3 and ν_4 of the perchlorate ion in this compound (although observed by infrared spectroscopy of Nujol mulls) are effectively single apart from a shoulder on ν_3 at about 1125 cm.$^{-1}$ and do not show the gross changes found for a number of (co-ordinated) perchlorate spectra.[6] Similarly weak bands at 925 and 465 cm.$^{-1}$ indicate only slight distortion of the ClO_4^- tetrahedron to allow these Raman active modes (ν_1 and ν_2, respectively, of ClO_4^-) to appear in the infrared region. These results suggest, but do not prove, that the adduct is to be formulated as $[Me_2Tl\ py]^+ClO_4^-$.

* G. E. Coates and R. N. Mukherjee (*J.*, 1963, 229) report that dimethylthallium cyanide decomposes at 275° and is insoluble in benzene. The corresponding aluminium, gallium, and indium compounds are tetrameric in benzene. It is reasonable to suppose that the thallium compound does not form a tetramer because the preferred linearity of TlC_2 is more compatible with an extended polymer.

[1] See, *e.g.*, R. S. Nyholm, *Proc. Chem. Soc.*, 1961, 2731.
[2] H. M. Powell and D. M. Crowfoot, *Nature*, 1932, **130**, 131; *Z. Krist.*, 1934, **87**, 370.
[3] N. V. Sidgwick, " The Chemical Elements and their Compounds," Clarendon Press, Oxford, 1950.
[4] I. R. Beattie and T. Gilson, *J.*, 1961, 2585.
[5] G. E. Coates, " Organometallic Compounds," Methuen, London, 1960.
[6] See, *e.g.*, B. J. Hathaway and A. E. Underhill, *J.*, 1961, 3091.

The Raman and infrared spectra of several relevant compounds are given in the Table (for the range 650—400 cm.$^{-1}$). The Raman spectra in all cases show a very strong band at approximately 500 cm.$^{-1}$ (the Me–Tl–Me symmetric stretch [7]). In none of these spectra

Raman and infrared spectra (650—400 cm.$^{-1}$) of some dimethylthallium compounds

Compound	Technique	Frequencies [ν or $\Delta\nu$ (cm.$^{-1}$)]				
Me_2TlClO_4,py	i.r. mull (Nujol or py)	621s ‡	555m	492w	467w ‡	413m §
Me_2TlClO_4,py	R. solid			495vs †		
Me_2TlClO_4	i.r. soln. in py	obscured	546s	484wsh	469w ‡	obscured
Me_2TlClO_4	i.r. soln. in MeCN + py	626s ‡	550m	487wsh	~460wbr ‡	complex obscured
Me_2TlClO_4	i.r. soln. in MeCN	626s ‡	558m		466w ‡	
Me_2TlClO_4	i.r. Nujol mull *	623vs ‡	555m			
Me_2TlClO_4	R. solid			497vs †		
Me_2TlClO_4, 1-10-phen.	i.r. Nujol mull	631s ‡	551m	496w	465w ‡	462w § 416m §
Me_2TlCl	i.r. Nujol mull		550m			
Me_2TlCl	R. solid			493vs		

* Difficult to mull (tends to explode during mulling). † No other strong bands in this region—symmetric Me_2Tl stretch about five times as intense as ν_1 of ClO_4^- at 930 cm.$^{-1}$ (no band at 550 cm.$^{-1}$). ‡ Probably ClO_4^- vibrations. § Probably ligand vibrations.

were we able to observe the appearance of the antisymmetric Me–Tl–Me stretch at about 550 cm.$^{-1}$. It is tempting from this evidence to assign a linear C–Tl–C skeleton. However, although dimethylthallium chloride and perchlorate show no band in the infrared spectrum near 490 cm.$^{-1}$, helping to confirm the supposed linearity, the adduct Me_2TlClO_4,py shows a weak band at 491 cm.$^{-1}$ close to that at 495 cm.$^{-1}$ in the Raman spectrum and suggesting that the Me–Tl–Me symmetric stretch is weakly infrared active (as indeed it should be even for the T-shaped ion).

Our spectral results suggest that the compound Me_2TlClO_4,py consists essentially of the ion $[Me_2Tlpy]^+$ approximately T-shaped but with a slightly bent C–Tl–C unit, together with the free perchlorate ion. It is clear that an *X*-ray examination of this species is necessary.* In the case of the adduct Me_2TlClO_4,1,10-phenathroline similar arguments lead to the suggested ion $[Me_2Tlphen]^+$, containing a nearly linear C–Tl–C grouping.

Experimental.—CAUTION: Dimethylthallium perchlorate and its adducts may behave as explosives.

Dimethylthallium perchlorate was prepared from dimethylthallium hydroxide and perchloric acid.[8] The dimethylthallium perchlorate was dissolved in pyridine and the 1 : 1 adduct obtained as a precipitate by successive treatments with benzene. (Benzene and a concentrated solution of dimethylthallium perchlorate in pyridine give two immiscible layers.) The adduct was analysed for pyridine (using 255 mμ absorption), thallium [by digestion with concentrated nitric acid, reduction with sulphur dioxide to thallium(I) and titration with iodate by Andrew's method], perchlorate (using nitron to precipitate nitron perchlorate) (Found: pyridine, 18·9, 19·6, 19·0, 19·7; Tl, 50·2, 50·5, 50·7; perchlorate 24·2, 23·5. $C_7H_{11}ClNO_4Tl$ requires pyridine, 19·1$_5$; Tl, 49·5; perchlorate, 24·1%). This product dissolved in acetonitrile, decanted from a small residue, and pumped to dryness, led to a crystalline residue (Found: pyridine, 19·6, 20·1, 20·1, 20·2. $C_7H_{11}ClNO_4$ requires pyridine, 19·1$_5$%). Similarly solutions of dimethylthallium perchlorate and 1,10-phenanthroline in acetonitrile yielded a crystalline precipitate. The adduct was analysed for 1,10-phenanthroline (using 270 mμ absorption) and thallium (as described above) (Found: 1,10-phenanthroline, 35·8, 34·9, 35·5; Tl, 39·7, 41·2. $C_{14}H_{14}ClN_2O_4Tl$ requires 1,10-phenanthroline, 35·4; Tl, 39·8%).

* Mr. R. Hulme of this department is kindly looking at crystals of this compound.

[7] P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, 1960, **56**, 1591.
[8] J. R. Cook and D. F. Morten, *J. Inorg. Nuclear Chem.*, 1964, **26**, 1249.

Raman spectra were taken on a model 81 Cary Raman spectrophotometer; infrared spectra on a Perkin-Elmer 221 spectrometer equipped with rock-salt grating–cæsium bromide optics.

We thank Dr. Glen Deacon for very helpful discussions, including a suggestion for the method of analysis, and for gifts of certain dimethylthallium compounds. We also thank the D.S.I.R. for generous financial support.

DEPARTMENT OF CHEMISTRY, KING'S COLLEGE,
LONDON W.C.2.

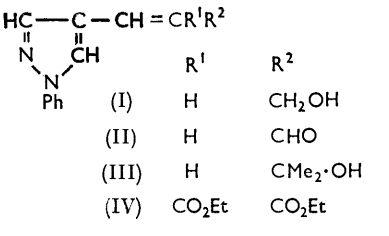
[*Received, October 15th*, 1964.]

---

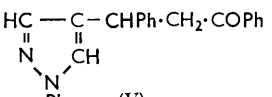
707. *Reactions of Some Unsaturated Pyrazole Compounds*

By I. L. FINAR and K. J. SAUNDERS

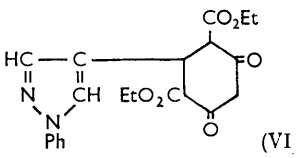
β-(1-PHENYL-4-PYRAZOLYL)ACRYLIC ACID [1] and its ethyl ester [2] have been treated with lithium aluminium hydride to give 3-(1-phenyl-4-pyrazolyl)prop-2-en-1-ol (I). The structure of the alcohol was confirmed by oxidation with manganese dioxide (cf. Mildner Weedon [3]) to β-(1-phenyl-4-pyrazolyl)acraldehyde (II) which was then oxidised with and ammoniacal silver nitrate to the acrylic acid.



	R^1	R^2
(I)	H	CH_2OH
(II)	H	CHO
(III)	H	$CMe_2 \cdot OH$
(IV)	CO_2Et	CO_2Et



(V)



(VI)

Ethyl β-(1-phenyl-4-pyrazolyl)acrylate [2] has been treated with methylmagnesium iodide and phenylmagnesium bromide to give 2-methyl-4-(1-phenyl-4-pyrazolyl)but-3-en-2-ol (III) and 1,3-diphenyl-3-(1-phenyl-4-pyrazolyl)propan-1-one (V), respectively.

1-Phenyl-4-vinylpyrazole [4] has been polymerised by heating with azobisisobutyronitrile.

Ethyl 1-phenyl-4-pyrazolylmethylidenemalonate (IV) has been prepared by treating 4-formyl-1-phenylpyrazole [5] with diethyl malonate.

Michael condensations have been attempted between ethyl acetoacetate and various 1-phenyl-4-pyrazolyl compounds with an α,β-unsaturated carbonyl side-chain, *viz.*, ethyl β-(1-phenyl-4-pyrazolyl)acrylate,[2] 4-(1-phenyl-4-pyrazolyl)but-3-en-2-one,[1] 1-phenyl-3-(1-phenyl-4-pyrazolyl)prop-2-en-1-one,[6] and ethyl 1-phenyl-4-pyrazolylmethylidenemalonate. With the first three pyrazoles only starting material was recovered, but with the last condensation occurred to give ethyl 4,6-dioxo-2-(1-phenyl-4-pyrazolyl)cyclohexane-1,3-dicarboxylate (VI).

Experimental.—*3-(1-Phenyl-4-pyrazolyl)prop-2-en-1-ol* (I). β-(1-Phenyl-4-pyrazolyl)acrylic acid (2·1 g., 0·01 mole) was placed in the thimble of a continuous extractor with lithium aluminium hydride (0·38 g., 0·01 mole) and dry (Na) ether (25 c.c.) in the receiver. The solvent was refluxed until the acid was completely removed from the thimble (4 hr.). The receiver was

[1] I. L. Finar and K. E. Godfrey, *J.*, 1954, 2293.
[2] I. L. Finar and K. Utting, *J.*, 1959, 4015.
[3] P. Mildner and B. C. L. Weedon, *J.*, 1953, 3294.
[4] I. L. Finar and K. J. Saunders, *J.*, 1963, 3967.
[5] I. L. Finar and G. H. Lord, *J.*, 1957, 3314.
[6] I. L. Finar and G. H. Lord, *J.*, 1959, 1819.

cooled and water (5 c.c.) and 2N-sulphuric acid (20 c.c.) were cautiously added. The ethereal layer was washed with 0·2N-sodium hydroxide and then water, dried, and evaporated. Recrystallisation of the residue from benzene–light petroleum (b. p. 60—80°) gave the *alcohol* (0·25 g., 13%) as white needles, m. p. 83—85° (Found: C, 72·1; H, 6·0; N, 13·7. $C_{12}H_{12}N_2O$ requires C, 72·0; H, 6·05; N, 14·0%). Ethyl β-(1-phenyl-4-pyrazolyl)acrylate (2·4 g., 0·01 mole) was treated with lithium aluminium hydride (0·38 g., 0·01 mole) and ether (25 c.c.) in the same way (ester removed after 0·5 hr.) to give the alcohol (1·0 g., 50%).

β-(1-*Phenyl*-4-*pyrazolyl*)*acraldehyde* (II). The alcohol (I) (1·5 g., 0·0075 mole) in acetone (75 c.c.) was shaken with manganese dioxide (15·0 g., 0·17 mole) for 6 hr. and then set aside overnight. The mixture was filtered and water added to the filtrate to give a precipitate. Recrystallisation from aqueous ethanol gave the *aldehyde* as pale yellow needles, m. p. 87—89° (Found: C, 73·1; H, 4·8; N, 14·0. $C_{12}H_{10}N_2O$ requires C, 72·7; H, 5·1; N, 14·1%). The aldehyde (0·1 g.) was heated at 50° for 0·5 hr. with ammoniacal silver nitrate. The mixture was filtered and the filtrate acidified to give β-(1-phenyl-4-pyrazolyl)acrylic acid, m. p. and mixed m. p. 184—186° (from aqueous acetic acid).

2-*Methyl*-4-(1-*phenyl*-4-*pyrazolyl*)*but*-3-*en*-2-*ol* (III). To methylmagnesium iodide (magnesium, 2·4 g., 0·1 g. atom; methyl iodide, 14·2 g., 0·1 mole) in ether (20 c.c.) was added dropwise ethyl β-(1-phenyl-4-pyrazolyl)acrylate (4·8 g., 0·02 mole) in ether (250 c.c.) during 2 hr. The mixture was refluxed for 1 hr. and the ethereal solution decanted from a yellow tar. This tar was shaken with saturated aqueous ammonium chloride (60 c.c.) and extracted with ether (3 × 50 c.c.). The combined ethereal extracts were washed with water, dried, and evaporated. The residue was recrystallised from light petroleum (b. p. 80—100°) to give the *alcohol* (0·23 g., 5%) as white needles, m. p. 80—81·5° (Found: C, 73·9; H, 7·0; N, 12·0. $C_{14}H_{16}N_2O$ requires C, 73·7; H, 7·1; N, 12·3%).

1,3-*Diphenyl*-3-(1-*phenyl*-4-*pyrazolyl*)*propan*-1-*one* (V). To phenylmagnesium bromide (magnesium, 0·61 g., 0·025 g. atom; bromobenzene, 3·9 g., 0·025 mole) in ether (5 c.c.) was added dropwise ethyl β-(1-phenyl-4-pyrazolyl)acrylate (1·2 g., 0·005 mole) in ether (70 c.c.) during 1·5 hr. The mixture was refluxed for 1 hr. The ethereal solution was decanted from a tar and shaken with crushed ice (100 g.) and then with 25% aqueous ammonium chloride (25 c.c.). The ethereal layer was separated and retained; the aqueous layer was extracted with ether (2 × 25 c.c.), and the ethereal extracts were added to the previously retained ethereal layer. The solution was washed with water, dried, and evaporated. The residue was recrystallised three times from ethanol to give the *ketone* (0·44 g., 25%) as white needles, m. p. 117—118·5° (Found: C, 81·3; H, 5·7; N, 7·6. $C_{24}H_{20}N_2O$ requires C, 81·8; H, 5·7; N, 7·95%).

Polymerisation of 1-*phenyl*-4-*vinylpyrazole*. The pyrazole (0·50 g., 0·0029 mole) and azobisisobutyronitrile (0·01 g.) were cautiously heated on a steam-bath. A vigorous reaction occurred to give a solid which was dissolved in benzene (2 c.c.). Addition of ether gave the *polymer* (0·40 g., 80%) as a white powder, m. p. 120—155° (Found: C, 77·6; H, 5·9; N, 16·6. $C_{11}H_{10}N_2$ requires C, 77·6; H, 5·9; N, 16·5%).

Ethyl 1-*phenyl*-4-*pyrazolylmethylidenemalonate* (IV). 4-Formyl-1-phenylpyrazole (1·7 g., 0·01 mole) and diethyl malonate (1·6 g., 0·01 mole) were dissolved in benzene, and piperidine (4 drops) was added. The solution was refluxed for 6 hr., dried, and evaporated. Recrystallisation of the residue from light petroleum (b. p. 80—100°) gave the *ester* (1·7 g., 55%) as white needles, m. p. 63—65° (Found: C, 64·9; H, 5·8; N, 8·8. $C_{17}H_{18}N_2O_4$ requires C, 65·0; H, 5·8; N, 8·9%).

Michael condensations. Ethyl 1-phenyl-4-pyrazolylmethylidenemalonate (1·05 g., 0·0033 mole), ethyl acetoacetate (0·53 g., 0·0041 mole), ethanol (10 c.c.), and piperidine (4 drops) were heated at 50° in a closed vessel for 72 hr. (cf. Finar [7]). Partial removal of solvent gave *ethyl* 4,6-*dioxo*-2-(1-*phenyl*-4-*pyrazolyl*)*cyclohexane*-1,3-*dicarboxylate* (VI) (0·012 g., 1%), m. p. 163—167°. Recrystallisation from ethanol gave white needles, m. p. 171—173° (Found: C, 63·5; H, 6·15; N, 7·0. $C_{21}H_{22}N_2O_6$ requires C, 63·3; H, 5·6; N, 7·0%). When the reactants were stored at room temperature, the yield of the cyclohexane-1,3-dicarboxylate, m. p. 171—173°, was 0·25 g. (19%). The unsuccessful condensations were attempted under similar conditions, *viz.*, 72 hr. at 50°.

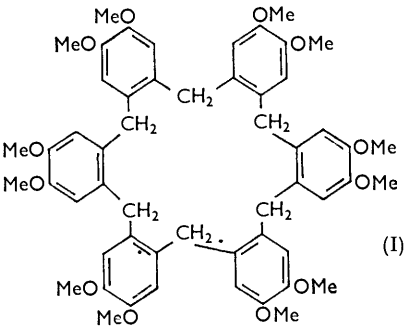
THE NORTHERN POLYTECHNIC, HOLLOWAY ROAD, LONDON N.7. [*Received, October 15th*, 1964.]

[7] I. L. Finar, *J.*, 1961, 674.

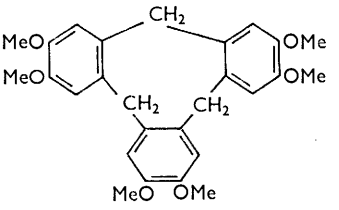
708. *The Structure of Cycloveratril*

By A. Goldup, A. B. Morrison, and G. W. Smith

Although cycloveratril has excited some interest because of its ability to form inclusion compounds [1] its structure appears to have been only very briefly examined. It is commonly believed to have the structure (I) assigned to it by Oliverio *et al.*[2] and supported by Liquori *et al.*[3] We have recently synthesised a sample of cycloveratril and find that the molecular weight is exactly one-half of that required by structure (I).*



(I)



(II)

Cycloveratril appears to have been first synthesised from veratrole (1,2-dimethoxybenzene) and formaldehyde by Robinson [4] who assigned it the structure 2,3,6,7-tetramethoxydihydroanthracene. She did not report any inclusion compounds although Bhagwat,[5] who obtained a product of similar melting point by oxidation of laudanosine, reported it to crystallise with benzene of crystallisation. The first suggestion that the structure proposed by Robinson was incorrect was made by Oliverio *et al.*[2] who attempted to obtain 2,3,6,7-tetramethoxyanthraquinone from cycloveratril by oxidation. Despite experiments under varying conditions they were only able to obtain the anthraquinone in poor yield but did succeed in isolating the lactone α,α-dioxy-4,4′,5,5′-tetramethoxydiphenylmethane-2,2′-dicarboxylic acid. This product could not arise from 2,3,6,7-tetramethoxydihydroanthracene and led Oliverio and his co-workers to investigate the structure of the condensation product in greater detail. By carrying out the reaction under mild conditions they obtained a series of intermediate products, one of which was identified as 4,5-bis-(3,4-dimethoxybenzyl)-1,2-dimethoxybenzene. This, on condensation with formaldehyde, gave cycloveratril. It had also been reported by Robinson that the same condensation product as that obtained from veratrole and formaldehyde could be obtained by condensation of 3,3′,4,4′-tetramethoxydiphenylmethane and formaldehyde. This suggested that cycloveratril contained an even number of benzene rings, and when taken in conjunction with the other evidence, led Oliverio *et al.*, to propose the cyclic structure (I). However, Friedel–Crafts condensations are known to be reversible [6] and under the reaction conditions employed by Robinson cleavage of some 3,3′,4,4′-tetramethoxydiphenylmethane could well occur. Rearrangements giving products containing odd numbers of benzene rings cannot be ruled out.

* Since this Paper was submitted for publication the authors' attention has been drawn to similar findings by J. S. Lindsey (*Chem. and Ind.*, 1963, 823).

[1] V. Caglioti, A. M. Liquori, N. Gallo, E. Giglio, and M. Scrocco, *J. Inorg. Nuclear Chem.*, 1958, **8**, 572.
[2] A. Oliverio and C. Casinovi, *Ann. Chim.* (*Italy*), 1952, **42**, 168.
[3] A. M. Liquori, F. Bertinotti, V. Carrelli, and A. M. Nardi, *Ricerca sci., Suppl.*, 1952, **22**, 65.
[4] M. G. Robinson, *J.*, 1915, **107**, 267.
[5] V. K. Bhagwat, D. K. Moore, and F. L. Pyman, *J.*, 1931, 443.
[6] C. F. Woodward, G. T. Borcherdt, and R. C. Fuson, *J. Amer. Chem. Soc.*, 1934, **56**, 2103.

Because of the poor solubility of cycloveratril in cryoscopic solvents no molecular-weight determinations were carried out to confirm this structure. Liquori *et al.*,[3] on the basis of *X*-ray-diffraction studies, concluded that the molecular weight was 900 in support of structure (I). They chose the non-centrosymmetric space group (*Ic*) requiring four molecules per unit cell but gave no evidence for the correctness of their structure determination (no *R* value quoted). The alternative space group (*I*2/*c*) requiring eight molecules per unit cell appears to have been rejected largely as a result of a statistical analysis of the *h*0*l* intensities which indicated the *b*-axis projection to be non-centrosymmetric. However, the Patterson projections given by Liquori *et al.* show vector peaks along the *a* and *c* directions, from which the presence of a two-fold rotation axis can be inferred. The correct choice of space groups would therefore seem to be (*I*2/*c*) corresponding to a molecular weight of 450.

We have recently repeated the preparation of cycloveratril as described by Oliverio *et al.*, and also Robinson's synthesis. Both gave the same product, as shown by melting points and mixed melting points, infrared and mass spectrometry, unit-cell dimensions, and uptake of benzene on crystallisation from this solvent, and were identical with those reported by the original workers (Table). The yield obtained by Robinson's procedure

Comparison of reported data on cycloveratril

	Oliverio's method		Robinson's method	
	Oliverio	Authors	Robinson	Authors
C (%) (Calc. 71·96)	—	71·25	72·0	—
H (%) (Calc. 6·72)	—	6·67	6·7	—
M. p.	232—233°	230·5—231 (corr.)	227	230·5—231 (corr.)
Molecular weight (Calc. 450·2)				
(*a*) Mass spectrometer	—	450·2		450·2
(*b*) Vapour-pressure osmometer	—	447 ± 5	—	452 ± 5
Cell parameters (Benzene complex)				
a (Å)	24·5	24·5	—	24·5
b (Å)	9·61	9·6	—	9·6
c (Å)	22·65	22·6	—	22·6
β	92°	92°	—	92°

is however considerably higher (*ca.* 70%) and this is the recommended method of preparation. The highest peak observed on examination of the products on a high-resolution mass spectrometer (Associated Electrical Industries Limited, model MS9) occurred at 450·2 although scanned to mass number 1200. Molecular-weight determinations in benzene solution using a vapour pressure osmometer (Mechrolab Incorporated) gave values for both products.

The only structure tenable having a molecular weight of 450 and yielding the lactone referred to above on oxidation is the cyclic structure 2,3,7,8,12,13-hexamethoxy-5,10-dihydro-15*H*-tribenzo(*adg*)cyclononene (II). This structure would also be expected to give the same products on nitric acid treatment, namely 6,6′-dinitro-3,3′,4,4′-tetramethoxydiphenylmethane, 4,5-dinitroveratrole, and 6-nitroveratric acid as reported by Robinson. Further support is given by the n.m.r. spectrum which shows the correct band intensities and magnetically non-equivalent protons on each methylene group. Courtauld models of this molecule show that two forms are possible. Of these only one, the symmetrical umbrella-shaped structure, is consistent with the observed n.m.r. spectrum. It is interesting to note that the structure of cycloveratril is somewhat similar to that of tri-*o*-thymotide, which also forms inclusion compounds.

The British Petroleum Company Limited,
B.P. Research Centre, Sunbury, Middlesex. [*Received, November 18th*, 1964.]

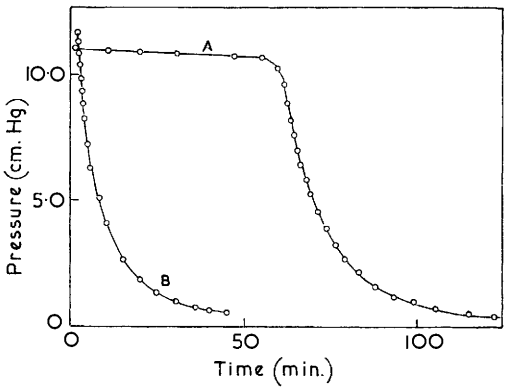
709. *The Thermal Polymerisation of Carbon Suboxide*

By A. R. Blake

Carbon suboxide polymerises at elevated temperatures to form a red solid [1,2] the structure and properties of which have been recently described.[3-5] No precise information is yet available on the rate and conditions of polymerisation, although it has been reported [3] that the reaction is preceded by an induction period of unpredictable length, is sensitive to surface, and proceeds at a rate which increases with temperature and pressure. In this Note, observations on the rate of the polymerisation reaction over a wide range of conditions are reported.

Carbon suboxide was prepared as previously described.[4] The rate of polymerisation was followed in the absence of mercury, by observing the pressure fall on a spiral glass manometer; this was possible as the solid polymer was the only reaction product. The temperature of the reaction cell (70 ml. capacity) was product-controlled to within $\pm 1°$. The volume of the system external to the furnace was less than 2 ml. Before each run the cell was evacuated to 10^{-5} mm. Hg and held for 16 hours at the reaction temperature.

An induction period was observed whenever the reaction took place in a new vessel, but not in all reactions carried out subsequently (Figure). This effect was clearly connected



The fall of monomer pressure with time: A, unconditioned vessel; B, conditioned vessel

with the surface condition of the reaction vessel and suggested that the polymerisation was surface-initiated although inhibited in the early stages by a surface poison, probably adsorbed water. Treatment of a conditioned reaction vessel with water vapour for 2 hours at 1 cm. pressure and evacuation at 10^{-5} mm. Hg for 3 hours resulted in the return of the induction period, confirming that the presence of surface water was responsible for the effect. The length of the induction period was reproducible and increased with decreasing temperature and pressure, consistent with a chain-initiating species reacting with a surface poison during this period. Induction periods ranged from 8·2 minutes at 200° and 33 cm. Hg to several days at 10 cm. Hg and room temperature.

The rate of polymerisation is proportional to the suboxide pressure over the range of conditions studied (50—200°, 1—50 cm. Hg, in Pyrex and in silica reaction vessels). First-order rate constants are given in the Table. Arrhenius plots yielded good straight lines

[1] A. Klemenc, G. Wechsberg, and G. Wagner, *Z. phys. Chem.* (*Frankfurt*), 1934, **170**, 97.
[2] L. Schmidt, H. P. Boehm, and U. Hofmann, *Proc. Conf. Carbon*, 3rd Conf., Buffalo, 1959, p. 235.
[3] R. N. Smith, D. A. Young, E. N. Smith, and C. C. Carter, *Inorg. Chem.*, 1963, **2**, 829.
[4] A. R. Blake, W. T. Eeles, and P. P. Jennings, *Trans. Faraday Soc.*, 1964, **60**, 691.
[5] A. R. Blake and A. F. Hyde, *Trans. Faraday Soc.*, 1964, **60**, 1775.

and activation energies of 6·3 and 8·0 kcal. mole^{-1} have been obtained in Pyrex and in silica reaction vessels, respectively.

The effect of a comprehensive range of additives on the rate of polymerisation at 12 cm. Hg pressure has been observed. Additions of carbon monoxide, carbon dioxide, oxygen, nitric oxide, and ethylene had no effect on the reaction rate. Addition of isobutane (17 cm. Hg) reduced the rate slightly and carbon tetrachloride at 7·4 cm. Hg caused a considerable reduction and departure from first-order kinetics. It is significant that in these cases there was a high probability of surface adsorption taking place.

First-order rate constants for the polymerisation of carbon suboxide

Pyrex vessel (Geometric surface area/volume = 1·9 cm.$^{-1}$)		Silica vessel (Geometric surface area/volume = 1·9 cm.$^{-1}$)	
Temp.	Rate constant (min.$^{-1}$ × 10^3)	Temp.	Rate constant (min.$^{-1}$ × 10^3)
70°	3·04	55·5°	4·5
81	4·3	79·0	9·2
100	9·5	45·5	16·8
122·5	14·8	134	28·9
144	22·4	142	54·7
185	67·6	156	67·6
62·5	10 *	179	136·8
94	24 *	218	210·2
145	63 *		

* Surface to volume ratio = 19 cm.$^{-1}$.

Change of surface to volume ratio of the vessel affects the reaction rate, but this has not been studied in sufficient detail to warrant quantitative interpretation. Polymer deposition surprisingly has no effect on the reaction rate although it has been shown [5] to be a material of high surface area. After carbonisation, however, the polymer has a very marked effect on the reaction, polymerisation proceeding rapidly at low temperatures. This may be connected with the formation of a large concentration of centres with unpaired electron spins,[6] which are effective in initiating a polymerisation chain.

The presence of an induction period and the observations on gas additions suggest that the reaction is a surface process, this being qualitatively confirmed by variation in rate constant with change in surface area of the reaction vessel. In particular, the lack of sensitivity to free-radical scavengers (O_2, NO) suggests that no gas-phase free-radical process is involved, although it does not rule out the possibility of a surface free-radical mechanism. The observation on the effect of carbonised polymer is consistent with this latter view.

CENTRAL ELECTRICITY GENERATING BOARD, BERKELEY NUCLEAR LABORATORIES,
BERKELEY, GLOUCESTERSHIRE. [*Received, October 23rd*, 1964.]

[6] S. Mrozowski and D. Wobschall, *J. Chim. phys.*, 1960, **57**, 915.

710. *Some Rate Constants from Calculated Equilibrium Constants*

By K. N. Bascombe, M. Cowperthwaite, and R. Shaw

The rate constants of many formally simple chemical reactions are not readily accessible experimentally. An alternative approach is possible if data are already available for the reverse reaction, since the equilibrium constant can be calculated by use of statistical mechanics.[1] Thus for reaction (1)

$$HO_2 + Ar \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H + O_2 + Ar \qquad (1)$$

we have $K_c = k_1/k_{-1}$, *i.e.*, $k_1 = K_c k_{-1}$.

In the same way k_2 and k_3 below, the absolute values of which have not been measured, can be evaluated from the known rate constants k_{-2} and k_{-3} and calculated equilibrium constants.

$$CH_3O + NO \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CH_3ONO \qquad (2)$$

$$CH_3O + NO_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CH_3ONO_2 \qquad (3)$$

We report the results of such calculations for reactions (1—3). The equilibrium constant for reaction (1) was calculated by using the following values of parameters: $\Delta H_0^\circ = 45{\cdot}9$ kcal. mole^{-1} (ref. 2), angle $\widehat{HOO} = 105°$ (as in H_2O), O–O bond length 1·42 Å, O–H bond length 1·02 Å, H–O–O bending frequency 1370 cm.$^{-1}$, O–O stretch frequency 1010 cm.$^{-1}$ and O–H stretch frequency 2700 cm.$^{-1}$. No experimental data are available for these molecular dimensions and vibration frequencies of HO_2, and the values used were derived from data for H_2O, O_2, and H_2O_2 by interpolation and extrapolation procedures, which are necessarily to some extent arbitrary. However, the translational contribution to the free energy function for HO_2 is much the largest, and plausible alterations in the vibrational and rotational parameters will not affect the conclusion that reaction (1) is unlikely to be important for the removal of HO_2 in combustion reactions. The values for k_{-1} were obtained by extrapolation from the results of Clyne and Thrush.[3]

The free-energy functions for methyl nitrite were calculated by using the structural data and frequencies given by Gray and Pratt,[4] except that the methyl group was considered to be fixed, as suggested by Ray and Gershon.[5] The free-energy functions for the methoxyl radical CH_3O were calculated by using the following structural parameters and frequencies: angle $\widehat{OCH} = 109° 28'$, angle $\widehat{HCH} = 109° 28'$, C–O bond length 1·44 Å, C–H bond length 1·09 Å, C–H antisymmetrical stretch frequency 2837 cm.$^{-1}$, C–O stretch frequency 950 cm.$^{-1}$, H–C–H bending frequencies (2) 1056 cm.$^{-1}$, –C– rocking frequencies (2) 1458 cm.$^{-1}$ and C–H bending frequency 1458 cm.$^{-1}$. The free-energy functions found for methoxyl were in good agreement with those obtained by Jain and Kapoor.[6] The free-energy functions for nitric oxide were calculated by using N–O bond length 1·15 Å and $\nu_0 = 1889{\cdot}9$ cm.$^{-1}$. The results were similar to the values given in the JANAF tables.[7]

[1] G. S. Rushbrooke, " Introduction to Statistical Mechanics," Clarendon Press, Oxford, 1949.
[2] S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, 1962, **36**, 2681.
[3] M. A. A. Clyne and B. A. Thrush, *Proc. Roy. Soc.*, 1963, *A*, **275**, 559.
[4] P. Gray and M. W. T. Pratt, *J.*, 1958, 3406.
[5] J. D. Ray and A. A. Gershon, *J. Phys. Chem.*, 1962, **66**, 1750.
[6] D. V. S. Jain and M. M. Kapoor, *Proc. Inst. Sci. India*, 1961, *A*, **27**, 105.
[7] JANAF Interim Thermochemical Tables, The Dow Chemical Company, Midland, Michigan, U.S.A.

The following heats of formation at 298°K, in kcal. mole^{-1}, were used: CH_3O 3·1 (ref. 8), NO 21·6 (ref. 9) and CH_3ONO −15·6 (ref. 5). The values for k_{-2} were calculated from the equation $\log k_{-2} = 13{\cdot}03 - 36{,}600/2{\cdot}303\ RT$, derived from the work of Phillips.[10]

As k_2 was found to vary so little with temperature, the rate constant for the formally analogous reaction (3) was calculated for one temperature only. The free-energy function for methyl nitrate was evaluated from the work of Brand and Cawthon.[11] Their results

TABLE 1

T °K	800	900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
$-\log_{10} K_c$	12·70	11·29	10·16	9·23	8·47	7·82	7·26	6·78	6·36	5·99	5·67	5·38	5·11
$\log_{10} k_{-1}$	15·10	15·06	15·02	14·99	14·96	14·94	14·92	14·90	14·89	14·88	14·86	14·85	14·82
$\log k_1$	2·40	3·77	4·86	5·76	6·49	7·12	7·66	8·12	8·53	8·89	9·19	9·47	9·71

Units K_c, mole c.c.$^{-1}$; k_{-1}, mole^{-2} c.c.^{2} sec.$^{-1}$; k_1 mole^{-1} c.c. sec.$^{-1}$.

TABLE 2

T °K	300	400	500	600
$\log_{10} K_c$	24·80	17·79	13·59	10·75
$\log_{10} k_{-2}$	−13·63	−6·97	−2·97	−0·30
$\log_{10} k_2$	11·17	10·82	10·62	10·45

Units: K_c, mole^{-1} c.c.; k_{-2}, sec.$^{-1}$; k_2, mole^{-1} c.c. sec.$^{-1}$.

TABLE 3

T °K	$\log_{10} K_c$	$\log_{10} k_{-3}$	$\log_{10} k_3$
300	24·73	−14·37	10·36

Units: K_c, mole^{-1} c.c.; k_{-3}, sec.$^{-1}$; k_3, mole^{-1} c.c. sec.$^{-1}$.

were preferred to those of Dixon and Wilson,[12] because the former led to better agreement between statistically calculated and third-law values for the entropy of methyl nitrate. The free-energy function for nitrogen dioxide was calculated by using data from the JANAF tables.[7] The following heats of formation at 298°K, in kcal. mole^{-1}, were used: NO_2 8·0 (ref. 9) and CH_3ONO_2 −29·0 (ref. 13). The value for k_{-3} was extrapolated from the results of Appin, Chariton, and Todes.[14]

The results show that k_2 is greater than k_3, which is in line with recent experimental work [15] on the relative rates of the two reactions. We cannot explain why k_2 and k_3 are one or two powers of ten smaller than the rate constants of the apparently analogous reactions [15] (4) and (5).

$$CH_3 + NO \rightleftharpoons CH_3NO \quad (4)$$

$$CH_3 + NO_2 \rightleftharpoons CH_3NO_2 \quad (5)$$

MINISTRY OF AVIATION, E.R.D.E., WALTHAM ABBEY, ESSEX.

[Present address (M. C.): STANFORD RESEARCH INSTITUTE, MENLO PARK, CALIFORNIA.]

[*Received, November 26th*, 1964.]

[8] R. Shaw, unpublished results.
[9] NBS Circular 500, Washington, 1952.
[10] L. Phillips, *J.*, 1961, 3082.
[11] J. C. D. Brand and T. M. Cawthon, *J. Amer. Chem. Soc.*, 1955, **77**, 319.
[12] W. B. Dixon and E. B. Wilson, *J. Chem. Phys.*, 1961, **35**, 191.
[13] D. M. Fairbrother, H. A. Skinner, and E. W. Evans, *Trans. Faraday Soc.*, 1957, **53**, 779.
[14] A. Appin, J. Chariton, and O. Todes, *Acta Physiochim. U.R.S.S.*, 1936, **5**, 655.
[15] L. Phillips and R. Shaw, Tenth Symposium (International) on Combustion, Cambridge, 1964.

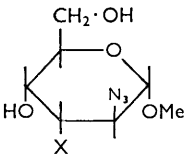
711. *Periodate Oxidation. Part IX.*[1] *Azido-sugars*

By C. B. Barlow, R. D. Guthrie, and (in part) D. Murphy

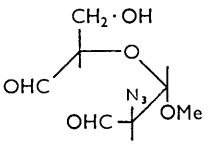
Periodate oxidation of azido-sugars can lead to anomalous results, because of reaction of the initial oxidation product with iodine.

During an investigation into the ring-opening of epimino-sugars[2] it became necessary to examine the periodate oxidation of sugar derivatives containing an azido-group. There appears to be no references in the literature to such oxidation.

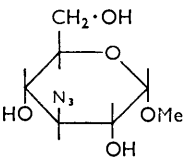
Methyl 2-azido-2-deoxy-α-D-altroside (I) was oxidised with aqueous sodium metaperiodate at pH 4 and 7. The periodate uptake was determined by iodometric titration with sodium arsenite.[3] Oxidation was extremely rapid and about 2 mols. of oxidant were apparently consumed in under three minutes, as opposed to the one mol. uptake expected. It was noted that when the iodine liberated from the unchanged periodate was allowed to stand in the dark for 15 minutes, the iodine colour faded, suggesting that iodine was reacting in some way, therefore giving a low titre and hence an apparently high uptake of periodate. Similar results were obtained with methyl 3-amino-2-azido-2,3-dideoxy-α-D-altroside (II) hydrochloride at pH 7.



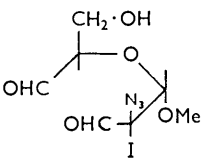
(I: X = OH)
(II: X = NH_2)



(III)



(IV)



(V)

One possible explanation is that the azido-group is being attacked. This was disproved as methyl 3-azido-3-deoxy-α-D-glucoside (IV) when treated under the same conditions showed no periodate uptake over a long period.

It would therefore appear that the apparent over-oxidation is due to the reaction of iodine with the α-azido-aldehyde (III) formed initially. Similar "over-oxidations" have been reported previously.[4]

This explanation was shown to be correct by several experiments. First, determination of the periodate uptake by ultraviolet spectrophotometry,[5] in which the system is not interfered with chemically, showed that only one mol. of oxidant was reduced for both compounds (I) and (II). Secondly, a solution of the azido-altroside (I), which had been first allowed to react with exactly one mol. of periodate reacted with 0·8 mol. of iodine in 15 minutes. Investigation of the possibility of using the back-titration method in which an excess of sodium arsenite solution was added to the oxidation solution before the potassium iodide[6] showed the method to be unsatisfactory because of a badly fading end-point.

As yet no study of the products either before or after reaction with iodine have been made. By analogy with previous work[4] it is tentatively suggested that the iodinated product has structure (V). These experiments have shown that care must be taken if the results of periodate oxidation are used in the structural study of azido-sugars.

[1] Part VIII, G. J. F. Chittenden and R. D. Guthrie, *J.*, 1965, 2271.
[2] R. D. Guthrie and D. Murphy, *J.*, 1965, 3828.
[3] E. Müller and O. Friedberger, *Ber.*, 1902, **35**, 2652.
[4] J. C. P. Schwarz and M. MacDougall, *J.*, 1956, 3065; A. J. Cleaver, A. B. Foster, E. J. Hedgley, and W. G. Overend, *J.*, 1959, 2578.
[5] G. O. Aspinall and R. J. Ferrier, *Chem. and Ind.*, 1956, 1216.
[6] P. F. Fleury and J. Lange, *J. pharm. Chim.*, 1933, **17**, 107, 196.

Experimental

Buffer solutions used were potassium dihydrogen phosphate (0·065M)–sodium hydroxide (0·035M) for pH 7 and sodium acetate (0·036M)–acetic acid (0·14M) for pH 4.

Methyl 3-Azido-3-deoxy-α-D-glucoside.—Methyl 3-azido-4,6-*O*-benzylidene-3-deoxy-α-D-glucoside [7] (0·4 g.) was boiled under reflux with 50% aqueous acetic acid (20 ml.) for 1 hr. The acetic acid and benzaldehyde were removed by co-distillation with water *in vacuo* and the solution evaporated to give a syrup which crystallised on washing with ether. This solid, after two recrystallisations from ethyl acetate–ethanol–light petroleum gave *methyl 3-azido-3-deoxy-α-D-glucoside* (IV) (42%), m. p. 125—127°, $[\alpha]_D^{25}$ +77° (*c* 0·464 in water) (Found: C, 38·5; H, 6·1; N, 19·1. $C_{17}H_{13}N_3O_5$ requires C, 38·4; H, 6·4; N, 19·2%).

Periodate Oxidations.—(a) *Methyl 2-azido-2-deoxy-α-D-altroside* [7] (I). (i) The compound (0·0205 g.) in buffer (15 ml.; pH 4) was diluted with 0·0303M-sodium periodate solution (10 ml.). At noted intervals, portions (2 ml.) were neutralised (10 ml. saturated sodium hydrogen carbonate) and 0·25 g. of potassium iodide was added. The liberated iodine was estimated after 15 min. (solution stored in the dark) by titration with 0·002N-sodium arsenite solution with BDH starch–iodine indicator. Blank solutions were treated similarly. The results obtained were:

Time (min.)	3	4	6	13·5	26·5
$NaIO_4$ uptake (mol.)	1·90	1·91	1·90	1·93	1·91

(ii) A similar oxidation at pH 7 gave the following results:

Time (min.)	2·5	3·5	5	10	23	105	1200
$NaIO_4$ uptake (mol.)	2·02	2·00	2·03	2·07	2·05	2·09	2·20

(iii) The apparent consumption of periodate was critically dependent on the time for which the products of periodate oxidation were allowed to be in the presence of free iodine. Portions (2 ml.) of the oxidation mixture were removed after 70 min. oxidation and were titrated at various times after the addition of the potassium iodide. The results were:

Time (min.)	5	10	15
Arsenite titre (ml.)	4·78	3·40	2·75

(iv) The compound (0·0663 g.) was oxidised with exactly one mol. of sodium periodate at pH 4 for 16 hr. Portions (2 ml.) of the solution were added to the quenching solution and 0·00224N-iodine solution (20 ml.) was added. Titration against 0·02N-sodium arsenite solution after 15 min. showed that 0·8 mol. of iodine had reacted.

(v) The azido-sugar (0·0185 g.) dissolved in 0·00189M-sodium periodate solution (100 ml.). At noted intervals, portions (10 ml.) were diluted to 250 ml. with water and the optical density at 223 mμ was determined. The following results were obtained:

Time (min.)	10	50	250	1320
$NaIO_4$ uptake (mol.)	0·95	0·98	1·04	1·32

(b) *Methyl 3-amino-2-azido-2,3-dideoxy-α-D-altroside* (II) *hydrochloride.* (i) This compound was oxidised as in (a, ii). The results were:

Time (min.)	1·25	2	5	9·5	16	28	960
$NaIO_4$ uptake (mol.)	1·97	2·07	2·10	2·13	2·14	2·20	2·47

(ii) The compound was oxidised as in (a, v) above. The results were:

Time (min.)	20	60	150	1200
$NaIO_4$ uptake (mol.)	0·92	0·93	0·96	1·08

(c) *Methyl 3-azido-3-deoxy-α-D-glucoside.* This compound was oxidised as in (a, i) and (a, ii). No periodate was reduced during 16 and 48 hr., respectively.

This work was supported in part by the U.S. Department of the Army, through its European office. One of us (C. B. B.) thanks the D.S.I.R. for a maintenance award.

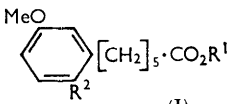
Chemical Laboratory, University of Sussex,
Brighton, Sussex. [*Received, December 4th*, 1964.]

[7] R. D. Guthrie and D. Murphy, *J.*, 1963, 5288.

712. *Ethyl* 6-[2-(4-*Ethoxycarbonylbutyl*)-5-*methoxyphenyl*]-*hexanoate*

By V. Askam and D. Bailey

The compound (I; R^1 = Et, R^2 = $[CH_2]_4 \cdot CO_2Et$) was required as an intermediate in the synthesis of a macrocyclic compound of pharmacological interest. 1-(*m*-Methoxyphenyl)cyclohex-1-ene was prepared by dehydrating the tertiary alcohol formed from the Grignard derivative of *m*-bromoanisole and cyclohexanone. When oxidised with chromic acid, as in the preparation of 5-(*p*-methoxybenzoyl)pentanoic acid,[1] this gave 5-(*m*-methoxybenzoyl)pentanoic acid in 22% yield, together with tarry products. A cleaner product was obtained in 68% yield by ozonolysis.



(I)

5-(*m*-Methoxybenzoyl)pentanoic acid was reduced by the Clemmensen method and the product was esterified with ethanol to give ethyl 6-(*m*-methoxyphenyl)hexanoate (I; R^1 = Et, R^2 = H). This ester reacted with glutaric anhydride and aluminium chloride to give only tarry products. However, in anhydrous hydrogen fluoride a clean product was formed which, after esterification with ethanol and removal of the excess of diethyl glutarate, was separated into two components by chromatography.

The keto-acid obtained by hydrolysis of the main component was 6-(2-glutaroyl-5-methoxyphenyl)hexanoic acid (I; R^1 = H, R^2 = $CO \cdot [CH_2]_3 \cdot CO_2H$) since it was oxidised to 4-methoxyphthalic acid. Substitution in the position *para* to the methoxyl group and *ortho* to the alkyl chain is consistent with the findings of previous workers [2,3] who investigated Friedel–Crafts substitutions of alkoxy-alkyl aromatic compounds. Clemmensen reduction of the above keto-acid, followed by esterification with ethanol, gave the required ethyl 6-[2-(4-ethoxycarbonylbutyl)-5-methoxyphenyl]hexanoate.

Experimental.—M. p.s are corrected. Ultraviolet spectra were determined in spectroscopic ethanol on a Unicam S.P. 700 spectrophotometer, and infrared spectra with potassium bromide discs, unless otherwise indicated, on a Perkin-Elmer Infrared spectrophotometer, model 137.

1-(m-*Methoxyphenyl*)*cyclohexanol.* Cyclohexanone (19·7 g., 0·201 mole) in dry ether (25 ml.) was gradually added (1 hr.) to the Grignard reagent prepared from *m*-bromoanisole [4] (37·5 g., 0·201 mole), magnesium turnings (4·87 g., 0·201 mole), and dry ether (70 ml.). The mixture was refluxed on a water-bath for a further 30 min. and set aside overnight. The yellow solid formed was decomposed with 5N-hydrochloric acid and ice. The resultant yellow liquid was extracted with ether, and the extract washed with sodium hydrogen carbonate solution and water, dried (Na_2SO_4), evaporated, and the residue distilled, to give a colourless *oil* (29·2 g., 71%), b. p. 91—94°/0·9 mm., n_D^{18} 1·5637 (Found: C, 75·7; H, 8·65; OMe, 15·4. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·8; OMe, 14·8%).

1-(m-*Methoxyphenyl*)*cyclohex*-1-*ene.* 1-(*m*-Methoxyphenyl)cyclohexanol (10 g.) was refluxed for 3 hr. with ethanol (100 ml.) saturated with hydrogen chloride, and set aside overnight. Most of the ethanol was distilled off, the residue poured into water, the resulting oil extracted with ether, the dried (Na_2SO_4) extract evaporated, and the residue distilled, to give a colourless oil (8·6 g., 94·2%), b. p. 108—110°/0·5 mm., n_D^{19} 1·5680 (lit.,[5] 90—92°/0·07 mm., n_D^{25} 1·5653), $\nu_{max.}$ 1634 (Ar·C:C) and 730 cm.$^{-1}$ ($\cdot[CH_2]_4\cdot$), $\lambda_{max.}$ 215, 248, and 288 mμ (log ε 4·3, 3·9, and 3·25) (Found: C, 82·8; H, 8·6. Calc. for $C_{13}H_{16}O$: C, 82·9; H, 8·6%).

5-(m-*Methoxybenzoyl*)*pentanoic acid.* Ozone was bubbled through a solution of 1-(*m*-methoxyphenyl)cyclohex-1-ene (9·4 g.) in chloroform (100 ml.) at −30° until no more ozone was absorbed. The chloroform was removed under reduced pressure without heating, water (200

[1] L. F. Fieser and J. Szmuszkovicz, *J. Amer. Chem. Soc.*, 1948, **70**, 3352.
[2] L. F. Fieser and W. C. Lothrop, *J. Amer. Chem. Soc.*, 1936, **58**, 2050.
[3] J. C. Harland and A. Robertson, *J.*, 1939, 937.
[4] M. Silverman and M. T. Bogart, *J. Org. Chem.*, 1946, **11**, 34.
[5] M. T. Davies, D. F. Dobson, D. F. Hayman, G. B. Jackman, M. G. Lester, V. Petrow, O. Stephenson, and A. A. Webb, *Tetrahedron*, 1962, **18**, 751.

ml.) cautiously added, and the mixture made alkaline and extracted with ether which was discarded. The aqueous fraction was made acid and extracted with ether. Distillation of the dried (Na_2SO_4) ethereal extract gave a brown oil which rapidly solidified. Recrystallisation from water gave colourless *needles* (8·0 g., 67·8%). Chromic acid oxidation gave the same product (m. p., mixed m. p., infrared) (21·8%), m. p. 97°, $\nu_{max.}$ 1706 (acid C:O) and 1681 cm.$^{-1}$ (aryl C:O), $\lambda_{max.}$ 217, 249, and 306 mμ (log ε 4·34, 3·9, and 3·4) (Found: C, 66·5; H, 6·4%; Equiv., 238. $C_{13}H_{16}O_4$ requires C, 66·1; H, 6·8%; Equiv., 236). The p-*bromophenacyl ester* (colourless needles from absolute ethanol) had m. p. 82° (Found: C, 57·8; H, 5·0; Br, 18·7; OMe, 7·3. $C_{21}H_{21}BrO_5$ requires C, 58·2; H, 4·9; Br, 18·4; OMe, 7·2%). The *semicarbazone* (colourless needles from absolute ethanol) had m. p. 197·5° (Found: C, 56·9; H, 6·4; N, 14·55; OMe, 10·5. $C_{14}H_{19}N_3O_4$ requires C, 57·3; H, 6·5; N, 14·3; OMe, 10·6%).

6-(m-*Methoxyphenyl*)*hexanoic acid* (I; $R^1 = R^2 = H$). 5-(*m*-Methoxybenzoyl)pentanoic acid (15 g.) was reduced by the Clemmensen method with 3·3N-hydrochloric acid (467 ml.) and an amalgam prepared from zinc wool (31·2 g.) and 5% mercuric chloride solution (61·5 ml.). After 8 hr. the mixture was decanted from the amalgam which was then refluxed with water (3 × 50 ml.) for periods of 5 min. The combined decanted mixtures were extracted with ether and the extract was washed with sodium hydrogen carbonate solution and water, dried (Na_2SO_4), evaporated, and the residue distilled, to give a pale yellow *oil* (11·47 g., 81·3%), b. p. 158—160°/1 mm., n_D^{18} 1·5323, $\nu_{max.}$ 1701 cm.$^{-1}$ (acid C:O) and no aryl C:O absorption, $\lambda_{max.}$ 216 and 275 mμ (log ε 3·8 and 3·2) (Found: C, 70·2; H, 8·2; OMe, 13·8%; Equiv., 222. $C_{13}H_{18}O_3$ requires C, 70·2; H, 8·2; OMe, 13·95%; Equiv., 222). Esterification by refluxing with ethanol saturated with hydrogen chloride gave the *ethyl ester* as a colourless oil (68·4%), b. p. 138—142°/1 mm., n_D^{18} 1·5082, $\nu_{max.}$ 1733 cm.$^{-1}$ (ester C:O) (Found: C, 72·1; H, 8·7. $C_{15}H_{22}O_3$ requires C, 72·0; H, 8·8%).

6-(2-*Glutaroyl*-5-*methoxyphenyl*)*hexanoic acid* (I; $R^1 = H$, $R^2 = CO{\cdot}[CH_2]_3{\cdot}CO_2H$). Ethyl 6-(*m*-methoxyphenyl)hexanoate (5 g., 0·02 mole) and glutaric anhydride (2·5 g., 0·023 mole) were dissolved in anhydrous hydrogen fluoride (*ca.* 50 ml.) in a screw-cap Polythene container. After 5 hr., during which time the container was occasionally gently rotated, the brown solution was allowed to evaporate spontaneously to dryness. The crystalline residue was dissolved in ether and the ether solution thoroughly extracted with ice cold aqueous sodium hydroxide (2%). The alkaline extracts were made acid and extracted with ether. The ethereal extracts were washed and dried (Na_2SO_4), and the ether was distilled off, to leave a yellow oil (6·3 g.) which was esterified with ethanol saturated with hydrochloric acid. The resulting neutral oil was distilled, to give diethyl glutarate (1·92 g.), and a green oil (2·3 g.) with a blue fluorescence in ultraviolet light, b. p. 183—195°/0·15 mm., n_D^{17} 1·5149. Thin-layer chromatography on Kieselgel G (Merck) with benzene–chloroform (1 : 1) as solvent revealed two components (R_F 0·66 and 0·40) detected with ultraviolet light and also by spraying with 2,4-dinitrophenylhydrazine solution.

The oil was dissolved in light petroleum (b. p. 40—60°) and chromatographed in acid-washed alumina. Elution with chloroform–light petroleum (b. p. 40—60°) (1 : 20) yielded two fractions, A and B. Fraction A consisted of a green oil (0·703 g.) having a pale fluorescence; thin-layer chromatography, as above, showed a main component (R_F 0·65) and a subsidiary component (R_F 0·45). Fraction B consisted of a yellow oil (1·507 g.); thin-layer chromatography, as above, showed one fraction (R_F 0·45). Distillation afforded a yellow oil, b. p. 194—197°/0·2 mm., $\lambda_{max.}$ 215, 258, and 308 mμ (log ε 4·13, 3·96, and 3·54), $\nu_{max.}$ 1730 (ester C:O), 1669 (aryl C:O), 1206, 1186, 1121, 1026, and 988 cm.$^{-1}$. Saponification yielded colourless needles of 6-(2-*glutaroyl*-5-*methoxyphenyl*)*hexanoic acid*, m. p. 81° (from benzene), $\nu_{max.}$ (in $CHCl_3$) 1704 (acid C:O) and 1661 cm.$^{-1}$ (aryl C:O) (Found: C, 64·4; H, 7·2. $C_{18}H_{24}O_6$ requires C, 64·2; H, 7·2%).

The Constitution of Fraction B. Fraction B (0·4 g.) was oxidised by refluxing with 11N-nitric acid (5 ml.) for 3 hr.; a further portion of nitric acid was added and the mixture refluxed for a further 1 hr., poured into water, and extracted with ether. The extracts were washed with water, extracted with sodium hydrogen carbonate solution (5%), made acid, and set aside overnight. The precipitated needles were recrystallised from water, to give colourless microneedles (0·04 g.) of 4-methoxyphthalic acid, m. p. and mixed m. p. 164°. Inidividual and mixed infrared spectra were identical.

Ethyl 6-[2-(4-*ethoxycarbonylbutyl*)-5-*methoxyphenyl*]*hexanoate* (I; R^1 = Et, $R^2 = [CH_2]_4{\cdot}CO_2Et$). Ethyl 6-(2-glutaroyl-5-methoxyphenyl)hexanoate (1·39 g.) was reduced

by the Clemmensen method and esterified with ethanol and hydrogen chloride, to give a colourless *oil* (1·305 g., 97·2%), b. p. 184—186°/0·1 mm., n_D^{25} 1·4898, $\lambda_{max.}$ 221 and 275 mμ (log ε 3·91 and 3·39), $\nu_{max.}$ 1730 (ester C:O) cm.$^{-1}$ and no aryl C:O absorption (Found: C, 70·6; H, 9·3. $C_{22}H_{34}O_5$ requires C, 69·8; H, 9·1%). 6-[2-(4-*Carboxybutyl*)-5-*methoxyphenyl*]*hexanoic acid* was obtained by saponification of the above diester, as a colourless oil, b. p. 187—190°/0·1 mm., which slowly solidified and was recrystallised from water to give colourless *needles*, m. p. 69·5°, $\nu_{max.}$ 1704 cm.$^{-1}$ (acid C:O) (Found: C, 66·9; H, 8·2%; Equiv., 322. $C_{18}H_{26}O_5$ requires C, 67·0; H, 8·1%; Equiv., 322).

Microanalyses were carried out by Mr. C. Crouch (School of Pharmacy, University of London). One of us (D. B.) thanks the Pharmaceutical Society of Great Britain for a research scholarship.

WELSH SCHOOL OF PHARMACY, WELSH COLLEGE OF ADVANCED TECHNOLOGY,
CATHAYS PARK, CARDIFF. [*Received, December 7th*, 1964.]

---

713. *The Hydrolysis of Ethyl Acetate in Concentrated Aqueous Sulphuric Acid*

By D. JAQUES

THE hydrolysis of ethyl acetate has been studied in the range 60—100% sulphuric acid, mainly to find whether the rate passes through a maximum as expected for *A*2 reactions.[1] Since the work was completed,[2] the hydrolysis of ethyl acetate has been followed in the range 11—79% sulphuric acid by Lane [3] who interprets his results on the basis of a transition state involving two water molecules:

$$CH_3{\cdot}CO_2Et + H^+ \rightleftharpoons CH_3{\cdot}CO_2EtH^+$$

$$CH_3{\cdot}CO_2EtH^+ + 2H_2O \xrightarrow{\text{slow}} CH_3{\cdot}CO_2H_2^+ + H_2O + EtOH$$

The Table shows first-order rate constants for the hydrolysis of ethyl acetate in sulphuric acid–water mixtures. The three results with 98·4% acid and the three with 75·4% acid give good Arrhenius plots: at 98·4% acid, *A* is 5×10^{15} min.$^{-1}$ and *E* is 24·3 kcal./mole; at 75·4%, *A* is 2×10^{14} min.$^{-1}$ and *E* is 21·9 kcal./mole. As found by Lane,[3] the rate falls from 60 to 85% sulphuric acid; but the present results show a subsequent increase from 85 to 100% acid (see Figure 1).

Lane [3] showed that the order of reaction with respect to water is given by the slope of log k/BH^+ against log a_{H_2O},[4] where the concentration of protonated ester is expressed by the equation: $\log_{10} BH^+/B = 0{\cdot}645(-6{\cdot}93 - H_0)$. BH^+ and B are the concentrations of protonated and unprotonated ethyl acetate, respectively. The application of this approach to the present results is shown in Figure 2. The slope, and hence the order with respect to water, is 1·80. Thus, it appears that the trimolecular mechanism is operating up to about 82% sulphuric acid. The slope of the line at higher acid concentrations is −0·16, which suggests that water does not participate in the rate-determining step. This observation is consistent with an *A*1 mechanism, which is supported by other workers.[5]

$$CH_3{\cdot}CO_2Et + H^+ \rightleftharpoons CH_3{\cdot}CO_2EtH^+$$

$$CH_3{\cdot}CO_2EtH^+ \xrightarrow{\text{slow}} CH_3{\cdot}CO_2H + Et^+ \qquad A1$$

---

[1] C. K. Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 786.
[2] D. Jaques, Ph.D. Thesis, Sheffield University, 1959.
[3] C. A. Lane, *J. Amer. Chem. Soc.*, 1964, **86**, 2521.
[4] W. F. Giague, E. W. Hornung, J. E. Kungler, and T. R. Rubin, *J. Amer. Chem. Soc.*, 1960, **82**, 62.
[5] Ref. 1, p. 771; J. A. Leisten, *J.*, 1956, 1572.

The small increase in rate of the unimolecular reaction with acid concentration (see Figure 1) can be qualitatively accounted for by the increase in concentration of protonated ester.

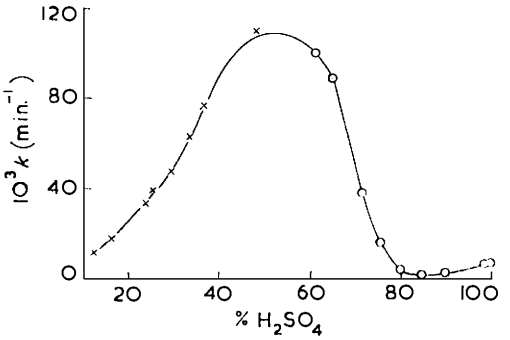


FIGURE 1. The effect of acid concentration on the hydrolysis of ethyl acetate in aqueous sulphuric acid

○, Present work.
×, From R. P. Bell, A. L. Dowding, and J. A. Noble, *J.*, 1955, 3106 (at 25°).

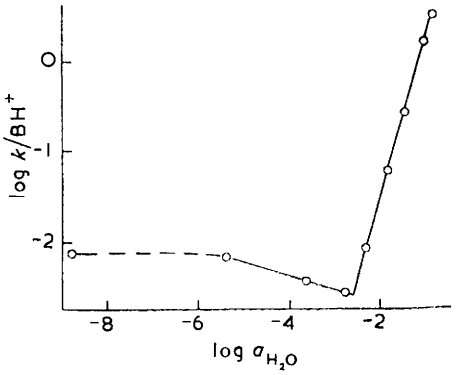


FIGURE 2. Relationship between the rate of hydrolysis of protonated ester and the activity of water

First-order rate constants for the hydrolysis of ethyl acetate (0·2M) in concentrated aqueous sulphuric acid solutions

% H_2SO_4	100·0	98·4	98·4	98·4	90·0	84·4	80·2	75·4	75·4	75·4	71·4	65·0	61·0
Temp.	25·6°	25·6°	29·4°	34·6°	25·6°	25·6°	25·6°	25·6°	29·4°	34·6°	25·6°	25·6°	25·6°
10^3k (min.$^{-1}$)	7·42	6·56	11·2	21·8	3·05	1·88	3·92	16·2	26·5	47·8	37·7	89·1	100

Experimental.—Kinetic measurements. Hydrolysis of ethyl acetate was followed spectrophotometrically by using the ferric chloride complex of the hydroxamic acid:

$$CH_3{\cdot}CO_2Et + NH_2{\cdot}OH \longrightarrow CH_3{\cdot}CO{\cdot}NH{\cdot}OH + EtOH$$

The estimation was based on a method of Peel.[6] Sulphuric acid solvent (50 ml.) and ester (1 ml.) were mixed in the reaction vessel, quickly brought to reaction temperature, and transferred to the thermostat. Samples (5 ml.) were withdrawn at suitable intervals of time and poured on to ice (30 g.). (With solutions containing more than 80% sulphuric acid the ice was further cooled by a carbon dioxide–acetone slurry.) The mixture was rapidly neutralised with 14% and 0·1N-sodium hydroxide. This solution was made up to 500 ml. with water, and 4 ml. were added to 2M-hydroxylamine hydrochloride (2 ml.) and 2·5N-hydrochloric acid (2 ml.). After 10 min., 5·6N-hydrochloric acid (1 ml.) was added, followed by 15% (w/v) ferric chloride (1 ml.) in 0·2N-hydrochloric acid. The optical density was measured at 500 mμ on a Unicam S.P. 500 spectrophotometer. A slight fall in optical density with time was observed, and samples were read within 2 min.

Materials. Ethyl acetate was washed, dried, and fractionally distilled. The concentrations of acids were determined by titration with anhydrous sodium carbonate.

The author thanks Dr. J. A. Leisten for suggesting the topic.

THE UNIVERSITY, SHEFFIELD.
[Present address: CHANCE TECHNICAL COLLEGE, CROCKETTS LANE, SMETHWICK, STAFFORDSHIRE.]
[*Received, November 9th*, 1964.]

[6] J. L. Peel, *Biochem. J.*, 1951, **49**, 62.

714. *Formation of Complex Tin(II) Species in Molten Tin(II) Fluoride*

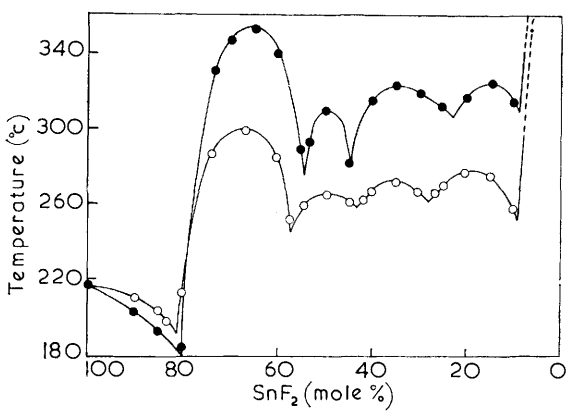
By J. D. Donaldson, J. D. O'Donogue, and (in part) R. Oteng

We have previously studied the systems $MF–SnF_2–H_2O$ (M = Na, K, NH_4) and have reported [1] that two distinct solid phases, $MSnF_3$ and MSn_2F_5 can be obtained from each solution. The presence of the trifluorostannate(II) ion in aqueous solution is already well established [2] and the existence of the pentafluorodistannate(II) ion, $Sn_2F_5^-$, for which we gave preliminary evidence, has recently been confirmed by the determination of the crystal structure [3] of $NaSn_2F_5$.

Tin(II) fluoride melts at 219·5° to give a clear melt, which is stable in the absence of oxygen. We have now studied the reaction between this melt and alkali-metal fluorides, and describe the complex tin(II) species obtained from the systems $MF–SnF_2$ (M = Li, Na, K, Rb, Cs).

The solid phases obtained from the cooled melts of mixtures of tin(II) fluoride and alkali-metal fluoride of varying composition (0—100 mole % of SnF_2) were identified by *X*-ray powder diffraction. The only complex phases identified were SnF_3 and MSn_2F_5 (M = Na, K, Rb, and Cs).

Equilibrium Diagrams for the Systems $NaF–SnF_2$ *and* $KF–SnF_2$.—The equilibrium diagrams for the systems $NaF–SnF_2$ and $KF–SnF_2$ were constructed from cooling-curve



Equilibrium diagrams for the systems ○, $NaF–SnF_2$ and ●, $KF–SnF_2$

values. The cooling curves were obtained in an apparatus similar to that used to determine the solid phases obtained from the molten systems, except that a platinum–rhodium thermocouple was used to obtain accurate temperature measurements. This thermocouple was mounted in a glass sleeve, which could be rotated or moved up and down to allow stirring of the melt and to ensure complete immersion of the hot junction. Powdered mixtures of pure tin(II) and alkali-metal fluoride were melted and the cooling curves obtained by measuring the temperature every 15 seconds. The mixture was then powdered again and the cooling curve checked by repeating the procedure. The *X*-ray powder diffraction data of the products were obtained.

The equilibrium diagrams (see Figure) show features attributable to four congruently melting phases at tin(II) fluoride–alkali-metal fluoride molar ratios of 2 : 1, 1 : 1, 1 : 2, and

[1] J. D. Donaldson and J. D. O'Donoghue, *J.*, 1964, 271.
[2] W. B. Schaap, J. A. Davis, and W. H. Nebergall, *J. Amer. Chem. Soc.*, 1954, **76**, 5226.
[3] R. R. McDonald, A. C. Larson, and D. T. Cromar, *Acta Cryst.*, 1964, **17**, 1104.

1 : 6. The melting points of these phases were 299°, 265°, 273°, and 279° respectively for the $NaF–SnF_2$ system and 354, 310, 323, and 325° for the $KF–SnF_2$ system.

Although four distinct phases are observed on the equilibrium diagrams only two distinct complex phases, MSn_2F_5 and $MSnF_3$ were identified (*X*-ray powder data) in the cooled products.

Discussion.—The complex tin(II) compounds obtained from the molten systems $MF–SnF_2$ are identical with those precipitated from the corresponding aqueous systems. The evidence of this work shows that the predominant species found in aqueous media, *viz.*, SnF_3^- and $Sn_2F_5^-$, are also present in tin(II) fluoride melts. Certainly, the derivatives of these ions are the only new phases identified in the solid products of the melt systems. In view of the equilibrium diagrams, however, the existence of high-temperature phases containing higher proportions of alkali-metal fluoride cannot be ruled out. Similar equilibrium diagrams have been obtained [4] from studies on the systems $MCl–SnCl_2$, but the composition of the products have not been identified by *X*-ray diffraction techniques.

Experimental.—Solid phases obtained from the molten systems $MF–SnF_2$. Mixtures of tin(II) fluoride and alkali-metal fluoride of various compositions (0—100 mole % of SnF_2) were prepared by grinding the pure components to a fine powder in a dry-box. The powder was transferred to a platinum crucible in a vacuum apparatus and all traces of oxygen in the system were removed by passing dry oxygen-free nitrogen through the system before evacuating it. The temperature of the mixture was then raised until a clear melt was obtained, and was kept constant for about 15 min., the system was cooled and the products in the resulting solid identified by *X*-ray powder diffraction photography. No new phases were obtained in the system $LiF–SnF_2$, but derivatives of complex tin(II) species were obtained from each of the other systems. The solid phases identified in solids obtained from melts of various compositions were:

Composition of the melt (mole % SnF_2)	Products identified
>68	SnF_2, MSn_2F_5
67	MSn_2F_5
66—51	MSn_2F_5, $MSnF_3$
50	$MSnF_3$
<49	$MSnF_3$, MF

All the lines on the powder photographs could be attributed to one of the phases listed in the Table, and there was no evidence for the existence of any other phases in the solid products. The results of *X*-ray powder diffraction measurements on the sodium and potassium derivatives of the trifluorostannate(II) and pentafluorodistannate(II) have been given by us in a previous paper,[1] but the values for the rubidium and cæsium derivatives are new.

Preparation and properties of rubidium and cæsium derivatives of complex tin(II) *species.* The rubidium and cæsium derivatives of the trifluorostannate(II) and pentafluorodistannate(II) ions in aqueous solution were prepared on a small scale by the usual methods.[1] We determined stannous and total tin [5] and fluoride [1] by methods described previously, and rubidium and cæsium gravimetrically as their tetraphenylboronates,[6] the average results for the analyses of the four rubidium and cæsium complex tin(II) fluorides are tabulated; these are in agreement with the percentages calculated for the formulae given.

Suggested compounds	$RbSnF_3$	$RbSn_2F_5$	$CsSnF_3$	$CsSn_2F_5$
Sn(II) (%)	45·3	57·1	38·8	50·7
Total Sn (%)	44·9	56·6	38·4	50·3
RbCs (%)	32·1	20·4	42·6	28·7
F (%)	22·2	23·0	19·1	21·2

The properties of these materials are similar to those of the other fluorostannate(II) complexes; they are not hygroscopic and are fairly resistant to hydrolysis and to atmospheric

[4] Li Ch'Ih-Fa and I. S. Morozov, *Zhur. neorg. Khim.*, 1963, **8**, 708.
[5] J. D. Donaldson and W. Moser, *Analyst*, 1959, **84**, 10.
[6] K. Sporek and A. F. Williams, *Analyst*, 1955, **80**, 347.

oxidation. We have found that recrystallisation of the pure rubidium and cæsium trifluorostannates(II), in the absence of an excess of alkali fluoride, gave, like the sodium and potassium materials, the corresponding pentafluorodistannate(II).

Crystallography. (i) Rubidium trifluorostannate(II) consists of colourless acicular crystals with straight extinction and positive elongation; $n = 1{\cdot}56$. Crystal data; $RbSnF_3$, $M = 261{\cdot}2$, orthorhombic, $a = 14{\cdot}80 \pm 0{\cdot}03$, $b = 13{\cdot}29 \pm 0{\cdot}03$, $c = 8{\cdot}25 \pm 0{\cdot}02$ Å, $U = 1623$ Å^3, $D_m = 4{\cdot}30$ (by displacement of organic solvents), $Z = 16$, $D_c = 4{\cdot}27$. Filtered Cu K_α-radiation; single crystal rotation and Weissenberg photographs about *c*.

(ii) Rubidium pentafluorodistannate(II) consists of colourless six-sided plates which are

X-Ray powder-diffraction values for complex tin(II) fluorides

(s, m, w, etc., denote relative intensities); dif. = diffuses.

Rubidium trifluorostannate(II)

d (Å)	Index of refln.	Calc. *d* spacings	*d* (Å)	*d* (Å)
4·90w	300, 220	4·93	1·948w	1·424mw
4·65w	310	4·62	1·930mw	1·390mw
4·34w	030	4·43	1·909mw	1·368vw
3·66w	400	3·70	1·876mw	1·355w
3·39vs	122	3·40	1·846m	1·279vvw
3·32vs	040	3·32	1·819vvw	1·249vvw
3·24vs	140, 420	3·23	1·792vvw	1·237vvw
3·04w	331	3·06	1·750vvw	
2·91w, 2·89w dif.	510	2·91	1·728vvw	
			1·697vvw	
2·53vvw	141	2·55	1·673vvw	
2·47vw	600	2·45	1·654vvw	
2·39s	251	2·40	1·637vvw	
2·25m	522	2·26	1·625m	
2·22vw	233	2·22	1·567vvw	
2·12vvw	260, 700	2·10	1·515mw	
			1·515mw	
2·03vvw	104, 243	2·03	1·494mw	
2·00vvw	114	2·00	1·444mw	

Rubidium pentafluorodistannate(II)

5·08m	020	4·96	1·816w	1·345vw
3·48vs	012	3·45	1·801m	1·321vw
3·38ms	311	3·40	1·768w	1·226vw
3·21vw	320	3·19	1·737mw	1·155vvw
2·99ms	410	2·98	1·683w	
2·45vw	003	2·45	1·536w	
2·13ms	340	2·13	1·385mw	
2·08m	600	2·08	1·361vvw	

Cæsium trifluorostannate(II)

d (Å)	Index of refln.	Calc. *d* spacings	*d* (Å)	*d* (Å)
7·18vvw	200	7·20	1·993mw	
5·96vvw	120	5·85	1·947m	
4·83vvw	300	4·80	1·913ms	
3·76w	111	3·77	1·789mw	
3·58s	400	3·60	1·722mw	
3·44vs	211	3·42	1·702mw	
3·41vs	301	3·42	1·639vvw	
3·27s	020	3·27	1·626vvw	
3·18mw	120	3·19	1·586vw	
2·67vw	121	2·67	1·543w	
2·62w	510	2·63	1·530w	
2·48vw	501	2·48	1·520vvw	
2·42s	420	2·42	1·485w	
2·15vvw	601	2·15	1·454vvw	
2·05ms	611	2·05	1·431vvw	
2·02ms	402	2·02	1·420vvw	
			1·358vvw	
			1·341vvw	

Cæsium pentafluorodistannate(II)

4·80vvw	400	4·80	1·901s	1·271w
4·35vvw	002	4·27	1·815s	1·228vw
3·72vvw	212	3·72	1·800s	1·173vvw
3·52vs	022	3·52	1·760s	1·154vvw
3·20s	600	3·20	1·665vw	1·146vvw
3·00s	601	3·00	1·596w	
2·97s	032	2·97	1·540vw	
2·52vvw	432, 720	2·53	1·500w	
2·46vw	403	2·45	1·481w	
2·29vw	503	2·29	1·409m	
2·18s	632	2·18	1·371m	
2·11s	433	2·11	1·363vw	
2·05vw	243	2·05	1·349vvw	
2·00w	533	2·01	1·329vvw	

pseudohexagonal with $n = 1{\cdot}62$. Crystal data: $RbSn_2F_5$, $M = 417{\cdot}9$, orthorhombic, $a = 12{\cdot}48 \pm 0{\cdot}03$, $b = 9{\cdot}92 \pm 0{\cdot}02$, $c = 7{\cdot}35 \pm 0{\cdot}02$ Å, $U = 910$ Å^3, $D_m = 4{\cdot}65$ (by displacement of organic solvents) $Z = 6$, $D_c = 4{\cdot}57$. Filtered Cu K_α-radiation; single-crystal rotation and Weissenberg photographs about *c*.

(iii) Cæsium trifluorostannate(II) consists of colourless acicular crystals with straight extinction and positive elongation and $n = 1{\cdot}58$. Crystal data: $CsSnF_3$, $M = 308{\cdot}6$, orthorhombic $a = 14{\cdot}41 \pm 0{\cdot}03$, $b = 6{\cdot}59 \pm 0{\cdot}02$, $c = 4{\cdot}82 \pm 0{\cdot}01$ Å, $U = 458$ Å^3, $D_m = 4{\cdot}44$ (by displacement of organic solvents). $Z = 4$, $D_c = 4{\cdot}48$ c. Filtered Cu K_α-radiation; single-crystal rotation and Weissenberg photographs about *c*.

(iv) Cæsium pentafluorodistannate(II) consists of colourless six-sided plates which are pseudohexagonal, with $n = 1{\cdot}64$. Crystal data: $CsSn_2F_5$, $M = 465{\cdot}3$, orthorhombic $a = 19{\cdot}20$

± 0·04, b = 12·44 ± 0·03, c = 8·54 ± 0·02 Å, U = 2040 Å^3, D_m = 4·58 (by displacement of organic solvents), Z = 12, D_c = 4·54. Filtered Cu K_α-radiation: single-crystal rotation and Weissenberg photographs about c.

Annexed Table contains the X-ray powder diffraction values for all four complexes, obtained by using an 11·64 cm. camera with Cu K_α-radiation. The d spacings longer than 2·00 Å have been indexed.

One of us (J. D. O'D.) is grateful to the International Tin Research Institute for a maintenance grant.

(J. D. D., J. D. O'D.) Department of Chemistry, (R. O.) Department of Physics,
Chelsea College of Science and Technology,
Manresa Road, London S.W.3. [*Received, December 11th*, 1964.]

---

715. *The Proton Magnetic Resonance Spectra of Some Complex Platinum Hydrides*

By J. Powell and B. L. Shaw

A series of platinum hydrides of the type *trans*-[PtHX(MR_3)$_2$] (X = anionic ligand; M = P, As; R = alkyl or aryl) has been previously described.[1] The chemical shifts and phosphorus–hydrogen coupling constants for hydrogen attached to platinum were reported for complexes of type *trans*-[PtHX(PEt_3)$_2$] with X = NO_3, Cl, Br, I, NO_2, SCN, and CN, but only with X = Cl was the platinum–hydrogen coupling constant observed and

Chemical shifts (τ), phosphorous–hydrogen, and platinum–hydrogen coupling constants (c./sec.) of complex platinum hydrides of the type *trans*-[PtHXL_2] (X = anionic ligand, L = PEt_3, $AsEt_3$), measured at 60 Mc/sec. in benzene at 33·5°

X	L	τ	J(PH)	J(PtH)	Comments
NO_3	P	33·6	15·6	1322	
–O–N=O	P	29·4	16·7	1003	
–N=C=O *	P	27·7	Unresolved	1080	Peaks broadened
–N=C=S †	P	27·6	14	1086	Peaks broadened
–O–C≡N *	P	27·0	14·5	‡	
Cl	P	26·8	14·5	1275	
Br	P	25·55	13·8	1346	
–S–C≡N †	P	22·95	14·5	1233	
I	P	22·65	13·3	1369	
–C≡N	P	17·6	15·6	778	
–N=C=S †	As	29·9	—	‡	Peak broadened; width at ½ height *ca.* 10 c./sec.
Cl	As	29·3	—	1117	
Br	As	27·75	—	1185	
–SCN †	As	24·75	—	1046	
I	As	24·6	—	1220	

* In a mixture of cyanato- and isocyanato-complexes. † In a mixture of thiocyanato- and isothiocyanato-complexes. ‡ Too weak to be observed.

measured. We have redetermined the proton magnetic resonance spectra of these complexes and also that of the complex with X = OCN, and those of some similar complexes with triethylarsine as the neutral ligand. Complete data are given in the Table. Agreement with the previously reported τ and J(PH) values is good except that for the complex *trans*-[PtHBr(PEt_3)$_2$] we find J(PH) = 13·8 rather than 15 c./sec. Platinum–hydrogen coupling constants J(PtH) are very large but show little correlation with

[1] J. Chatt and B. L. Shaw, *J.*, 1962, 5075.

J(PH) or τ values. Except for the cyanato- and thiocyanato-complexes all spectra showed (1) a central absorption of relative intensity ~4 due to molecules containing platinum isotopes without a nuclear spin of one half and (2) two symmetrically spaced absorptions of intensity ~1 due to the platinum-195 isotope (spin $\frac{1}{2}$, 33% natural abundance). The absorptions with the triethylphosphine complexes were 1 : 2 : 1 triplets due to splitting by the phosphorus nuclei (phosphorus-31, spin $\frac{1}{2}$, 100% natural abundance) but sharp singlets with the triethylarsine complexes (arsenic has an electric quadruple moment and probably a very short relaxation time so that its magnetic effect is averaged to zero).

Previously,[1] the complex *trans*-[PtH(NO_2)(PEt_3)$_2$] was formulated as a nitro- rather than a nitrito-complex on the basis of its infrared absorption spectrum in a Nujol mull. If this were the structure in benzene solution one would expect some splitting and/or broadening of the hydrogen resonance by the nitrogen bonded in the *trans*-position (nitrogen-14, spin 1 usually causes splitting and broadening of hydrogen resonances; see below). Since the 1 : 2 : 1 triplets are very sharp we suggest that this compound is present mainly in the nitrito-form *trans*-[PtH(ONO)(PEt_3)$_2$] (platinum bonded to oxygen) in benzene solution. Infrared spectra in benzene solution are an unreliable guide to structure because of strong absorption by the benzene.

The " thiocyanato "-complex *trans*-[PtH(SCN)(PEt_3)$_2$] showed two sets of resonance patterns which we attribute to the presence of both the thiocyanato-complex (platinum bonded to sulphur) and the isothiocyanato-complex (platinum bonded to nitrogen). The 1 : 2 : 1 triplet at τ 22·95 was very sharp and we assign this to the thiocyanato-complex but the 1 : 2 : 1 triplet at τ 27·6 had broad peaks due to coupling with the nitrogen of the isothiocyanato-group. The ratio of thiocyanato-complex : isothiocyanato-complex was *ca.* 1 : 3. The triethylarsine complex [PtH(SCN)($AsEt_3$)$_2$] similarly showed sharp peaks due to the thiocyanato-complex and a broad peak due to the isothiocyanato-complex, the ratio thiocyanato-complex : isothiocyanato-complex was *ca.* 1 : 2. Previously, the complex *trans*-[PtH(SCN)(PEt_3)$_2$] was formulated as the isothiocyanato(–N=C=S)-complex on the basis of its infrared absorption spectrum in Nujol. Because of the very high *trans* labilising effect of the hydride ligand,[2] on dissolving this isothiocyanato-complex in benzene equilibrium with the thiocyanato-complex could be established rapidly. Similarly for the nitro- and nitrito-complexes.

The complex *trans*-[PtH(OCN)(PEt_3)$_2$] showed three broad absorptions due to the isocyanato-complex (platinum bonded to nitrogen) and a weak but very sharp 1 : 2 : 1 triplet which we attribute to the cyanato-complex, the ratio of cyanato-complex to isocyanato-complex was *ca.* 1 : 9. As one would expect the τ values for the isocyanato- and isothiocyanato-complexes are practically identical.

Previously, it has been shown that there is a good correlation between decreasing platinum–hydrogen stretching frequency (*i.e.*, bond strength) and increasing *trans*-effect of the ligand in the *trans*-position.[3,4] It has also been pointed out that there is some agreement between decreasing chemical shift and increasing *trans*-effect of the ligand in the *trans*-position to the hydrogen.[1] The order of increasing trans-effects is $NO_3^- < Cl^- < Br^- < I^- \sim NO_2^- \sim SCN^- < CN^-$. Re-formulation of the " nitro "-hydride complex as a " nitrito "-complex gives a better fit between its chemical shift value and this series since, although the position of the nitrito-group in the *trans*-effect series is not known, one would expect it to be low like other ligands single-bonded through oxygen. Perhaps an important factor in the decreasing chemical shift in going from the nitrato-complex to the cyanide complex is an increasing platinum–hydrogen distance with decreasing electron density round the proton.

[2] F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J.*, 1961, 2207.
[3] J. Chatt and B. L. Shaw, Proceedings of the XVIIth Internat. Congress Co-ord. Chem., 1959, Butterworths Scientific Publications, London, 1961, p. 147.
[4] J. Chatt, *Proc. Chem. Soc.*, 1962, 318.

Another factor could be increasing back donation from the non-bonding *d*-orbitals of the platinum to the ligands. This would probably increase in the order $NO_3 < Cl < Br < I \sim NO_2 \sim SCN < CN$,[5,6] and progressively lower the *d*-electron density around the hydride ligand giving rise to the observed sequence of τ values.

THE SCHOOL OF CHEMISTRY, THE UNIVERSITY, LEEDS 2. [*Received, December 14th*, 1964.]

[5] L. E. Orgel, *J. Inorg. Nuclear Chem.*, 1956, **2**, 137.
[6] J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J.*, 1955, 4456.

---

716. *The Use of Formic Acid in the Beckmann Rearrangement*

By T. VAN ES

MANY reagents have been used in the Beckmann rearrangement of ketoximes;[1] the use of formic acid has been reported[2,3] for the rearrangement of certain *o*-hydroxy-ketoximes. It is now found that, by refluxing a solution of the ketoxime in formic aid, the amide is obtained in good yield. The Table shows the ketoximes used, yields, and times of reflux.

Oxime of	Time of reflux (hr.)	Yield of amide (%)
Acetophenone	6	90 (Acetanilide)
p-Methylacetophenone	6	85 (*N*-Acetyl-*p*-toluidine)
Propiophenone	6	80 (Propionanilide)
Benzophenone	1	93
p,p'-Dimethylbenzophenone	6	95
p,p'-Dimethylaminobenzophenone	3	60
o-Carboxybenzophenone	6	85 (Phthalanilide)
Cyclohexanone	3	42

With benzophenone oxime acetate, the same result is obtained as with benzophenone, but benzophenone oxime methyl ether is unchanged. α-Benzoin oxime is cleaved to benzaldehyde (60%) and benzonitrile when refluxed for 6 hr.; likewise, α-benzil monoxime gives benzoic acid (75%) and benzonitrile. Isatin monoxime, 9,10-phenanthraquinone and 1-nitrosoethyl benzoylacetate are unchanged, even on prolonged refluxing with formic acid.

Experimental.—The appropriate oxime (1·0 g.) and formic acid (15 c.c.; 98—100%) were refluxed for the periods indicated. The products were isolated in the usual manner after removing the formic acid and diluting the solution with water.

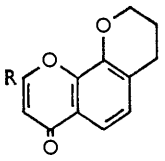
DEPARTMENT OF CHEMISTRY, UNIVERSITY OF THE WITWATERSRAND,
JOHANNESBURG, SOUTH AFRICA. [*Received, December 14th*, 1964.]

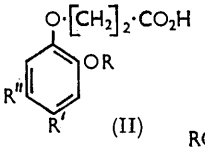
[1] L. G. Donaruma and W. Z. Heldt, *Org. Reactions*, 1960, **11**, 1.
[2] J. Meisenheimer, W. Theilacker, and O. Beiszwenger, *Annalen*, 1932, **495**, 249.
[3] K. von Auwers and O. Jordan, *Ber.*, 1925, **58**, 26.

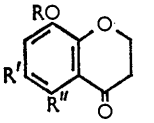
717. *The Acetylation of 8-Hydroxychroman and a New Series of Dihydropyranochromones*

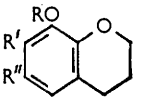
By P. S. Bramwell and A. O. Fitton

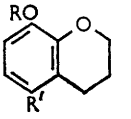
Syntheses of dihydropyranochromones derived from resorcinol and quinol have recently been described,[1,2] and an essentially similar series of reactions has now led to new 2-substituted dihydropyranochromones (I). Thus, a suitable *o*-substituted phenoxypropionic acid, *e.g.*, (II; R = Ac, R′ = R″ = H), was cyclised and the resulting chroman-4-one (III; R = Ac, R′ = R″ = H) on Clemmensen reduction yielded 8-hydroxychroman (IV; R = R′ = R″ = H).


(I)


(II)


(III)


(IV)


(V)

Acetylation of 8-hydroxychroman using the complex of boron trifluoride and acetic acid, however, yielded a mixture of 7-acetyl-8-hydroxychroman (IV; R = R″ = H, R′ = Ac) and 6-acetyl-8-hydroxychroman (IV; R = R′ = H, R″ = Ac).

The identity of the major product as the 7-acetyl isomer was confirmed by its infrared carbonyl absorption, which was typical of that in an *o*-hydroxyacyl system.[3]

That the second product from the acetylation was 6-acetyl-8-hydroxychroman, and not the alternative 5-isomer, was established by methylation and reduction. The resulting ethylmethoxychroman possessed an infrared spectrum identical with that of 6-ethyl-8-methoxychroman (IV; R = Me, R′ = H, R″ = Et) which was unambiguously synthesised, as was the alternative 5-ethyl-8-methoxychroman (V; R = Me, R′ = Et). The unambiguous syntheses were closely related. Thus, 4-ethylguaiacol [4] was condensed with β-chloropropionic acid and the resulting β-(4-ethyl-2-methoxyphenoxy)propionic acid cyclised in polyphosphoric acid yielding 6-ethyl-8-methoxychroman-4-one (III; R = Me, R′ = Et, R″ = H) from which 6-ethyl-8-methoxychroman was obtained by Clemmensen reduction. 5-Ethyl-8-methoxychroman resulted from a similar series of reactions starting with 5-ethylguaiacol.[5]

Acetylation of 8-methoxychroman (IV; R = Me, R′ = R″ = H) yielded only 6-acetyl-8-methoxychroman (IV; R = Me, R′ = H, R″ = Ac) which was also obtained by methylation of the known 6-acetyl-8-hydroxychroman.

The dihydropyranochromones were obtained from Claisen condensation of 7-acetyl-8-hydroxychroman with various esters, followed by cyclisation of the resulting diketones, as in the method of Schmutz *et al.*[6] (see Table).

[1] P. Naylor and G. R. Ramage, *J.*, 1960, 1956.
[2] A. O. Fitton and G. R. Ramage, *J.*, 1963, 5426.
[3] N. M. Cullinane, R. A. Woolhouse, and V. V. Bailey-Wood, *Rec. Trav. chim.*, 1961, **80**, 116.
[4] Boots Pure Drug Co. Ltd., and J. Marshall, B.P. 317,194.
[5] R. Schwarz and K. Capok, *Monatsh.*, 1952, **83**, 883.
[6] J. Schmutz, R. Hirt, F. Kunzle, E. Eichenberger, and H. Lauener, *Helv. Chim. Acta*, 1953, **36**, 620.

2-Substituted derivatives of 8,9-dihydro-7*H*-pyrano[2,3-*h*]chromone (I)

(Prepared from 7-acetyl-8-hydroxychroman by the method of Schmutz *et al.*[6])

R in (I)	Yield (%)	M. p.	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
Me	35	176°	72·6	5·9	—	$C_{13}H_{12}O_3$	72·3	5·6	—
Ph	30	205	77·6	5·4	—	$C_{18}H_{14}O_3$	77·7	5·1	—
2-Pyridyl...	40	181	72·8	4·9	5·2	$C_{17}H_{13}NO_3$	73·1	4·7	5·0
3-Pyridyl...	34	245	73·1	4·7	5·0				
4-Pyridyl...	45	224	72·7	5·0	4·8				
CO_2Et	45	176	65·7	5·2	—	$C_{15}H_{14}O_5$	65·7	5·1	—
CO_2H	86 *	282	62·9	4·4	—	$C_{13}H_{10}O_5$	63·4	4·0	—
H	55 †	185	70·9	4·9	—	$C_{12}H_{10}O_3$	71·3	5·0	—

* From acid hydrolysis of (I; R = CO_2Et). † From decarboxylation of (I; R = CO_2H).

Experimental.—8-*Acetoxychroman*-4-*one* (III; R = Ac, R′ = R″ = H). A mixture of β-*o*-acetoxyphenoxypropionic acid (50 g.) (prepared from *O*-acetylation of β-*o*-hydroxyphenoxypropionic acid [7]), and polyphosphoric acid (500 g.) was stirred at >45° for 2 hr. then added to water (1 l.). The mixture was extracted with chloroform, and the extract washed with aqueous sodium hydrogen carbonate and water. Evaporation of the dried ($MgSO_4$) extract yielded a residue (37 g.), which on crystallisation from water (charcoal) gave 8-*acetoxychroman*-4-*one* as needles, m. p. 95° (Found: C, 64·2; H, 4·9. $C_{11}H_{10}O_4$ requires C, 64·1; H, 4·9%).

8-*Hydroxychroman* (IV; R = R′ = R″ = H). A mixture of 8-acetoxychroman-4-one (9·85 g.), zinc amalgam (40 g.), and 5N-hydrochloric acid (50 ml.) was heated under reflux for 1 hr. The liquid was decanted from the excess of zinc and extracted with ether. The extract was washed with water, dried ($MgSO_4$), and evaporated. Fractionation of the residue gave 8-*hydroxychroman* (3·58 g.), b. p. 94—97°/1·2 mm. (Found: C, 71·5; H, 6·9. $C_9H_{10}O_2$ requires C, 71·9; H, 6·7%).

7-*Acetyl*-8-*hydroxychroman* (IV; R = R″ = H, R′ = Ac). A mixture of 8-hydroxychroman (10 g.) and boron trifluoride–acetic acid complex (40% w/w; 50 ml.) was heated at 165° under a dry nitrogen atmosphere during 15 min., then added to water (200 ml.). The mixture was extracted with chloroform and evaporation of the extract yielded a product which was repeatedly extracted with light petroleum (b. p. 100—120°). Fractionation of the residue obtained after evaporation of the solvent gave 7-*acetyl*-8-*hydroxychroman* (5·3 g.), b. p. 168—170°/0·2 mm., which solidified and crystallised from aqueous ethanol as needles, m. p. 86—87° (Found: C, 68·7; H, 6·3. $C_{11}H_{12}O_3$ requires C, 68·7; H, 6·3%).

6-*Acetyl*-8-*hydroxychroman* (IV; R = R′ = H, R″ = Ac). A further fraction from the residue described in the above preparation gave 6-*acetyl*-8-*hydroxychroman*, b. p. 185—190°/0·2 mm., which solidified and crystallised from light petroleum (b. p. 100—120°) as prisms, m. p. 114—116° (Found: C, 68·8; H, 6·5. $C_{11}H_{12}O_3$ requires C, 68·7; H, 6·3%).

8-*Methoxychroman* (IV); R = Me, R′ = R″ = H). A method similar to that mentioned above for the preparation of 8-hydroxychroman, but starting from 8-methoxychroman-4-one [8] (5 g.), gave 8-*methoxychroman* (2·2 g.), b. p. 92—94°/1·2 mm. (Found: C, 73·3; H, 7·2. $C_{10}H_{12}O_2$ requires C, 73·1; H, 7·4%).

8-Methoxychroman formed a *dinitro-derivative* (formed with concentrated nitric acid in glacial acetic acid) as needles, m. p. 178—179° (Found: C, 47·3; H, 3·8; N, 10·6. $C_{10}H_{10}N_2O_6$ requires C, 47·3; H, 4·0; N, 11·0%).

6-*Acetyl*-8-*methoxychroman* (IV; R = Me, R′ = H, R″ = Ac). (*a*) A solution of 8-methoxychroman (1 g.) in boron trifluoride–acetic acid complex (40% w/w; 5 ml.) was heated under a dry nitrogen atmosphere for 1 hr. at 50—60°, then added to water (30 ml.). The mixture was extracted with ether and the extract was washed with aqueous sodium hydrogen carbonate. Evaporation of the dried ($MgSO_4$) extract yielded a residue (0·5 g.) which, on crystallisation from light petroleum (b. p. 100—120°), gave 6-*acetyl*-8-*methoxychroman* as prims, m. p. 96—97° (Found: C, 69·9; H, 6·8. $C_{12}H_{14}O_3$ requires C, 69·8; H, 6·8%).

[7] P. F. Wiley, *J. Amer. Chem. Soc.*, 1951, **73**, 4205.
[8] J. Cologne and A. Guyot, *Bull. Soc. chim. France*, 1958, 325.

(*b*) 6-Acetyl-8-hydroxychroman (0·5 g.) and dimethyl sulphate (0·4 g.) were stirred and heated under reflux with anhydrous potassium carbonate (0·4 g.) and dry acetone (17 ml.) during 8 hr. The mixture was cooled and filtered and the filtrate evaporated. The residue was dissolved in ether and washed with aqueous sodium hydroxide. Evaporation of the dried ($MgSO_4$) ethereal solution gave a residue (0·3 g.) which crystallised as prisms, m. p. 96—97°, identical with the above material.

β-(4-*Ethyl*-2-*methoxyphenoxy*)*propionic acid* (II; R = Me, R′ = Et, R″ = H). A solution of β-chloropropionic acid (8·6 g.) and potassium carbonate (5·6 g.) in water (100 ml.) was added to a solution of 4-ethylguaiacol (14 g.) and potassium hydroxide (5·4 g.) in water (150 ml.), and the mixture heated on a steam-bath for 2 hr. After being cooled, the mixture was acidified with concentrated hydrochloric acid and extracted with ether. The product was removed from the ethereal extract by washing with aqueous sodium hydrogen carbonate followed by acidification of the latter and filtration. Crystallisation of the residue (2·2 g.) from water (charcoal) gave β-(4-*ethyl*-2-*methoxyphenoxy*)*propionic acid* as needles, m. p. 104° (Found: C, 64·1; H, 7·2. $C_{12}H_{16}O_4$ requires C, 64·2; H, 7·2%).

A similar preparation from 5-ethylguaiacol (14 g.) gave β-(5-*ethyl*-2-*methoxyphenoxy*)*propionic acid* (II; R = Me, R′ = H, R″ = Et) (2 g.) which crystallised from water (charcoal) as needles, m. p. 124—126° (Found: C, 64·1; H, 7·2. $C_{12}H_{16}O_4$ requires C, 64·2; H, 7·2%).

6-*Ethyl*-8-*methoxychroman*-4-*one* (III; R = Me, R′ = Et, R″ = H). A mixture of β-(4-ethyl-2-methoxyphenoxy)propionic acid (5 g.) and polyphosphoric acid (50 g.) was stirred at 50° for 2 hr. then added to water (200 ml.). The mixture was extracted with ether and the extract washed with aqueous sodium hydrogen carbonate. Fractionation of the residue obtained after evaporation of the extract gave 6-*ethyl*-8-*methoxychroman*-4-*one* (3·5 g.), b. p. 136—138°/0·7 mm. (Found: C, 70·1; H, 6·5; $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%).

A similar preparation from β-(5-ethyl-2-methoxyphenoxy)propionic acid (3 g.) gave 5-*ethyl*-8-*methoxychroman*-4-*one* (III; R = Me, R′ = H, R″ = Et) (2·1 g.), b. p. 140—142°/1·25 mm., which solidified and crystallised from light petroleum (b. p. 40—60°) as prisms, m. p. 46—48° (Found: C, 69·8; H, 6·9. $C_{12}H_{14}O_3$ requires C, 69·8; H, 6·8%).

6-*Ethyl*-8-*methoxychroman* (IV; R = Me, R′ = H, R″ = Et). A mixture of 6-ethyl-8-methoxychroman-4-one (3·3 g.), zinc amalgam (10 g.), and 5N-hydrochloric acid (20 ml.) was heated under reflux for 2 hr. then cooled. The liquid was decanted from the excess of zinc and extracted with ether. Fractionation of the residue obtained after evaporation of the dried ($MgSO_4$) extract yielded 6-*ethyl*-8-*methoxychroman* (1·8 g.), b. p. 108—110°/0·7 mm. (Found: C, 75·2; H, 8·5. $C_{12}H_{16}O_2$ requires C, 74·9; H, 8·4%).

A similar preparation from 5-ethyl-8-methoxychroman-4-one (1·8 g.) gave 5-*ethyl*-8-*methoxychroman* (V; R = Me, R′ = Et) (1 g.), b. p. 106—108°/0·5 mm. (Found: C, 74·4; H, 8·5. $C_{12}H_{16}O_2$ requires C, 74·9; H, 8·5%).

The authors are indebted to Benger Laboratories Ltd., Holmes Chapel, Cheshire, for the award of the Benger Research Studentship (to P. S. B.).

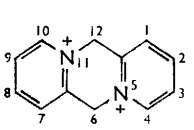
THE ROYAL COLLEGE OF ADVANCED TECHNOLOGY,
SALFORD, LANCS.

[*Received, December 16th,* 1964.]

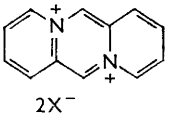
718. *Cyclic Quaternary Ammonium Salts. Part II.*[1] *Dipyrido*[1,2-a:1′,2′-d]*pyrazidi-inium Salts*

By E. E. Glover and G. H. Morris

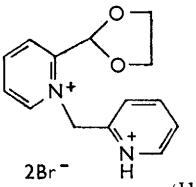
Recently [1] we reported attempts to obtain the aromatic diquaternary system (II) by the dehydrogenation of the diquaternary-dihydro salts (I). We now record the direct synthesis of these aromatic diquaternary salts.



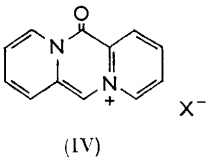
(I)



(II)



(III)



(IV)

Attempted quaternisation of pyridine-2-aldoxime with 2-pyridylmethyl bromide hydrobromide [2] in tetramethylene sulphone was unsuccessful, the only products isolated being the diquaternary salt (I; X = Br) and pyridine-2-aldoxime hydrobromide. However, by using 2-(1,3-dioxalan-2-yl)pyridine and 2-pyridylmethyl bromide hydrobromide a red oil was obtained [presumably (III)] and characterised as the dipicrate. The salt was cyclised by boiling 48% hydrobromic acid giving the aromatic diquaternary salt (II; X = Br) in good overall yield (43%).

Hydrogenation of (II; X = Br) gave the dihydrobromide salt [2-4] of the corresponding perhydro-base.

The aromatic diquaternary salts (II) are easily oxidised and the dipicrate salt (II; X = picrate), when heated in alcohol or nitromethane, was converted to the monopicrate (IV; X = picrate).[1] Further, the dibromide salt (II; X = Br) was oxidised by selenium dioxide to the monobromide (IV; X = Br).[1] The previously reported [1] mechanistically obscure conversion of the diquaternary dihydro-salts (I) into the monosalts (IV) under dehydrogenation conditions is thus rationalised. It seems probable that initial dehydrogenation of the dihydro-system (I) to the aromatic system (II) occurs with subsequent oxidation by picric acid or nitromethane to the monosalt (IV).

It is noteworthy that although no diquaternary salt of simple pyrazines has been reported, diquaternary salts of phenazine [5] are known as well as dipyrido[1,2-*a*:2′1′-*c*]-[6] and dipyrido[1,2-*a*:1′,2′-*d*]-pyrazidi-inium salts.

Experimental.—Melting points were determined on a Kofler hot-stage apparatus except where otherwise stated.

1-(2-*Pyridylmethyl*)-2-(1,3-*dioxalan*-2-*yl*)*pyridinium bromide hydrobromide* (III). 2-Pyridylmethyl bromide hydrobromide [2] (0·253 g.), 2-(1,3-dioxalan-2-yl)pyridine (0·3 g.), and tetramethylene sulphone (4 ml.) were warmed on a water-bath until the solids had dissolved. After 7 days, the solution was filtered, giving the diquaternary dihydrosalt (I; X = Br) [1,2] (0·025 g.,

[1] E. E. Glover and G. H. Morris, *J.*, 1964, 3366.
[2] F. Sörm and L. Šedivý, *Coll. Czech. Chem. Comm.*, 1948, **13**, 289.
[3] C. K. Bradsher and J. C. Parham, *J. Org. Chem.*, 1963, **28**, 83.
[4] K. Winterfeld and H. Rath, *Arch. Pharm.*, 1960, **293**, 141.
[5] H. Hillemann, *Ber.*, 1938, **71***B*, 34.
[6] D. H. Corr and E. E. Glover, *Chem. and Ind.*, in the press.

14·5%). Addition of ethyl acetate and ether to the filtrate gave a red oil [probably (III)] which was separated and washed with ether. Addition of alcoholic picric acid gave the *dipicrate* which crystallised from alcohol as yellow prisms, m. p. 135° (0·287 g., 41%) (Found: C, 44·6; H, 2·8; N, 16·0. $C_{20}H_{17}N_5O_9,C_6H_3N_3O_7$ requires C, 44·6; H, 2·9; N, 16·0%).

Dipyrido[1,2-a:1′,2-d]*pyrazidi-inium bromide* (II; X = Br). The oil (III; from 0·253 g. of 2-pyridylmethyl bromide hydrobromide) was boiled under reflux in 48% hydrobromide acid (15 ml.) for 40 min. Concentration of the solution under reduced pressure followed by the addition of alcohol gave the *dibromide* which crystallised from methanol–di-isopropyl ether as the monohydrate, m. p. 246—248° (decomp.; capillary) (0·147 g., 43%) (Found: C, 40·2, 40·25; H, 3·6, 3·4; N, 8·2, 7·5. $C_{12}H_{10}Br_2N_2,H_2O$ requires C, 40·0; H, 3·4; N, 7·8%); $\lambda_{max.}$ in water 1990, 2620, and 4480° Å ($\log_{10}\varepsilon$ 4·03, 3·94, and 2·97). The *perchlorate* crystallised from methanol–di-isopropyl ether as pale yellow needles, m. p. 275—277° (decomp.) (Found: C, 37·8; H, 2·8; N, 7·6. $C_{12}H_{10}Cl_2N_2O_8$ requires C, 37·8; H, 2·6; N, 7·4%).

12-*Oxo*-12H-*dipyrido*[1,2-a:1′,2′-d]*pyrazin-5-ium picrate* (IV; X = *picrate*). Addition of alcoholic picric acid to the dibromide (II; X = Br) gave the dipicrate (II; X = picrate) as yellow prisms, m. p. 162—164°. Attempted crystallisation of this dipicrate (0·1 g.) from nitromethane gave the monopicrate (IV; X = picrate) [1] as golden needles, m. p. 221—223° (0·07 g., 88%). It was found that crystallisation of the dipicrate (II; X = picrate) from any solvent in which it was soluble resulted in its slow conversion into the monopicrate (IV; X = picrate).

12-*Oxo*-12H-*dipyrido*[1,2-a:1′,2′-d]*pyrazin-5-ium Bromide* (IV; X = Br). Resublimed selenium dioxide (0·09 g.) was added to a solution of the bromide (II; X = Br) (0·2 g.) in glacial acetic acid (15 ml.) and water (2 ml.). The solution was boiled under reflux for 5 min. and cooled. Acetone (2·5 ml.) was added and the solution boiled for a further 5 min. The solution was cooled and selenium filtered off. Evaporation of the filtrate under reduced pressure gave the bromide (IV; X = Br) [1] as a brown residue which crystallised from methanol as orange prisms (0·06 g., 37%), m. p. >350°. The infrared spectrum of this sample was identical with that of the sample obtained by the oxidation of the dihydro-compound (I; X = Br).[1]

trans,trans-*Perhydrodipyrido*[1,2-a:1′,2-d]*pyrazine Dihydrobromide* (*V, as dihydrobromide*). The dibromide (II; X = Br) as the monohydrate (0·248 g.) in glacial acetic acid (15 ml.) and 48% hydrobromic acid (1 ml.) was hydrogenated completely at atmospheric pressure; the uptake was 112 ml. (7 double bonds require 108 ml.). The catalyst was filtered off and the filtrate evaporated. The residue (0·248 g.) crystallised from alcohol as prisms, m. p. 383—384° (decomp.; capillary) (lit.,[4] m. p. 360—361°) (Found: C, 36·75; H, 7·1; N, 7·6. Calc. for $C_{12}H_{24}N_2Br_2,2H_2O$: C, 36·75; H, 7·2; N, 7·15%). The m. p. and infrared spectrum were identical with those of the dihydrobromide of the perhydro-base (V).[1] The dipicrate crystallised from water as yellow prisms m. p. 289—293° (decomp., capillary) (lit.,[4] m. p. 289—293°). The sample was identical with the dipicrate of the perhydro-base (Found: C, 44·05; H, 4·5. Calc. for $C_{12}H_{22}N_2,2C_6H_3N_3O_7$: C, 44·2; H, 4·3%).

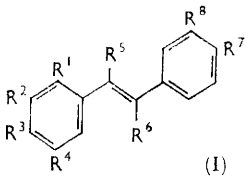
Department of Chemistry, Constantine College of Technology,
Middlesbrough, Yorks. [*Received, December 17th*, 1964.]

719. *The Preparation of Some Substituted Stilbenes*

By E. N. Morgan, P. J. Palmer, (Miss) L. Kruszynska, and W. R. N. Williamson

A number of αα′-substituted stilbenes (I; a—h) were prepared, in order to investigate the effect upon their pharmacological activity of variation of type of substitution, both in the aromatic rings and the alkyl side-chains. The spacial analogy [1] between αα′-dialkylstilbenes and steroids was kept in mind; and a guide to the choice of alkyl substitution was the effect of its variation on steroids.[2]

(I):	a	b	c	d	e	f	g	h
R_1	Me	Me	Me	Me	H	H	H	H
R_2	H	H	H	H	H	Me	Me	H
R_3	H	H	OMe	OMe	Me	OH	OH	H
R_4	MeO	OH	H	H	H	H	H	H
R_5	Et	Et	Et	Et	Et	Et	Et	H
R_6	Pr^n	Pr^n	Et	Pr^n	Et	Et	Pr^n	Et
R_7	H	H	NH_2	NH_2	NH_2	H	OH	NH_2
R_8	H	H	H	H	H	H	Me	H



(I)

The general scheme of synthesis of the stilbenes which was best adapted to variation of substitution was that of Dodds *et al.*,[3] involving preparation of a 2-arylacetophenone, alkylation at the 2-position, reaction with an alkyl Grignard reagent and dehydration of the resulting alcohol. In cases where the final stilbene contained an amino-group the synthesis began with a nitro-substituted acid chloride for the preparation of the acetophenone and the nitro-group was reduced at the stage before the Grignard reaction. The *trans*-orientation of the stilbenes was assumed from the methods of preparation and their spectral properties, but a rigorous assignment is difficult when only one stereoisomer is available. The preparation of a number of functional derivatives of the known *trans*-4-stilbeneamine is described below. None of the stilbenes tested pharmacologically showed anti-inflammatory activity; but some of them inhibited cholesterol synthesis and were œstrogenic.

Experimental.—*2-Arylacetophenones.* These were prepared by a Friedel–Crafts reaction between the appropriate arylacetic acid chloride and substituted benzene (see Table). Orientation of these compounds was checked by reference to their infrared spectra.

2-Arylacetophenone	Found (%)	Required (%)	Physical constants	Yield (%)
2-Phenyl-2′-methoxy-5-methyl	C, 79·5; H, 7·0	$C_{16}H_{16}O_2$: C, 80·0; H, 6·7	B. p. 132·5°/0·05 mm.	26
2-(*p*-Nitrophenyl)-2′-methyl-4′-methoxy	C, 66·9; H, 5·4; N, 5·2	$C_{16}H_{15}NO_4$: C, 67·4; H, 5·3; N, 4·9	M. p. 108—109°	33
2-(*p*-Nitrophenyl)-4′-methyl	C, 70·7; H, 5·4; N, 5·4	Calc. for $C_{15}H_{13}NO_3$: C, 70·6; H, 5·1; N, 5·5	M. p. 113—113·5°	80·5
* 2-Phenyl-3′-methyl-4′-methoxy	C, 80·1; H, 6·9	$C_{16}H_{16}O_2$: C, 79·9; H, 6·7	M. p. 63—65°	29
† 2-(3-Methyl-4-methoxy)-3′-methyl-4′-methoxy	C, 75·1; H, 7·3	$C_{18}H_{20}O_3$: C, 76·0; H, 7·1	M. p. 67—72°	59

* Also prepared in 25% yield (m. p. 69—70°) by saturing a solution of phenylacetic acid in *o*-methylanisole with boron trifluoride. † Prepared by saturating a solution of 3-methyl-4-methoxyphenylacetic acid in *o*-methylanisole with boron trichloride.

[1] J. Grundy, *Chem. Rev.*, 1957, **57**, 302.
[2] V. A. Drill and B. Riegel in *Recent Progr. Hormone Res.*, ed. G. Pincus, 1958, **XIV**, 29.
[3] E. C. Dodds, L. Golberg, W. Lawson, and R. Robinson, *Proc. Roy. Soc.*, 1939, *B*, **127**, 140.

2-*Alkyl ketones*. The above acetophenones were alkylated at the 2-position using published [4] procedures to give the following compounds: 2-*Phenyl*-2′-*methoxy*-5′-*methylvalerophenone* (69%), b. p. 143—147°/0·25 mm., n_D^{20} 1·5637 (Found: C, 80·6; H, 8·1. $C_{19}H_{22}O_2$ requires C, 80·8; H, 7·85%); 2-(p-*nitrophenyl*-2′-*methyl*-4′-*methoxybutyrophenone* (69·8%), b. p. 219—220°/0·6 mm., n_D^{20} 1·599 (Found: C, 69·4; H, 6·1; N, 4·5. $C_{18}H_{19}NO_4$ requires C, 69·0; H, 6·1; N, 4·5%); 2-(p-*nitrophenyl*)-2′-*methyl*-4′-*methoxyvalerophenone* (42%), b. p. 226—230°/0·4 mm., n_D^{20} 1·596 (Found: C, 70·9; H, 7·1; N, 4·15. $C_{19}H_{21}NO_4$ requires C, 69·7; H, 6·5; N, 4·3%); 2-(p-*nitrophenyl*)-4′-*methylbutyrophenone* (37·6%), yellow rhombs from light petroleum (b. p. 80—100°)–benzene, m. p. 53—54·5° (Found: C, 72·7; H, 5·8; N, 5·2. $C_{17}H_{17}NO_3$ requires C, 72·1; H, 6·05; N, 4·9%); 2-*phenyl*-3′-*methyl*-4′-*methoxybutyrophenone* (65%), b. p. 161°/0·3 mm., n_D^{25} 1·5846 (Found: C, 81·0; H, 7·9. $C_{18}H_{20}O_2$ requires C, 80·6; H, 7·5%); 2-(3-*methyl*-4-*methoxyphenyl*)-3′-*methyl*-4′-*methoxyvalerophenone* (75%), b. p. 201—202°/0·3 mm. (Found: C, 76·7; H, 7·85. $C_{21}H_{26}O_3$ requires C, 77·3; H, 8·0%).

2-(p-*Aminophenyl*)-2′-*methyl*-4′-*methoxybutyrophenone*. 2-(*p*-Nitrophenyl)-2′-methyl-4′-methoxybutyrophenone (31·3 g.) in 96% ethanol (200 ml.) with granulated tin (47·6 g.) was reduced by gradual addition of concentrated hydrochloric acid (130 ml.) with subsequent refluxing for 1 hr. to give the *amine* (95%) as a brown viscous oil (Found: C, 76·5; H, 7·2; N, 5·0. $C_{18}H_{21}NO_2$ requires C, 76·3; H, 7·5; N, 4·9%). Attempted distillation of a 109 g. sample gave only 20 g. of the amine, b. p. 210—215°/0·3—0·5 mm. (Found: C, 76·5; H, 7·5; N, 5·0%).

2-(p-*Aminophenyl*)-4′-*methylbutyrophenone*. Hydrogenation of the corresponding nitro-compound in ethanol over platinum gave the *amino-compound* (86%) as light yellow rhombs, m. p. 78—80° (Found: C, 81·0; H, 7·5; N, 5·8. $C_{17}H_{19}NO$ requires C, 80·6; H, 7·6; N, 5·5%).

trans-α-*Ethyl*-2-*methoxy*-5-*methyl*-α′-*n*-*propyl*-2-*stilbene* (Ia). 2-Phenyl-2′-methoxy-5′-methylvalerophenone (22·71 g.) in ether (75 ml.) was added slowly to a stirred cooled solution of ethylmagnesium bromide [from ethyl bromide (23 g.) and magnesium (5 g.) in ether (125 ml.)]. The mixture was stirred and refluxed for 1 hr. After pouring into ice and ammonium chloride, the ether was separated, the aqueous phase extracted with ether, and the combined ether solutions washed with 2N-sulphuric acid, sodium hydrogen carbonate solution, and water, and dried ($MgSO_4$) and evaporated. The residual oil was distilled to give 2-(α-*ethyl*-α-*hydroxy*-β-*n*-*propylphenethyl*)-4-*methylanisole* (17·7 g.), b. p. 140°/0·2 mm., n_D^{20} 1·5559 (Found: C, 81·0; H, 8·9. $C_{21}H_{28}O_2$ requires C, 80·7; H, 9·0%), $\nu_{max.}$ 3504 cm.$^{-1}$ (OH). On attempted dehydration of the above alcohol (12·3 g.) by refluxing (8 hr.) with acetyl chloride the product boiled over a range and contained acetoxyl (infrared). Deacetoxylation failed to occur in boiling pyridine, but on standing overnight in the presence of powdered iodine the product, after removal of iodine (thiosulphate), yielded the required *stilbene* (4·3 g.), b. p. 129—131°/0·4 mm., n_D^{23} 1·5612 (Found: C, 85·9; H, 8·55. $C_{21}H_{26}O$ requires C, 85·7; H, 8·9%), $\nu_{max.}$ 1674(w), 1599, 1493, 1243, 1034, 864, 752, 694 cm.$^{-1}$, $\lambda_{max.}$ 211 (ε 25,550), 281 (ε 4880), 321 mμ (ε 1908) (cf. Braude, for ultraviolet spectra of *trans*-stilbenes [5]). When the above Grignard reaction was repeated on 59·1 g. of the valerophenone the product dehydrated on distillation to give the stilbene (55·18 g.) (Found: C, 85·25; H, 8·7%), which remained spectrally unaltered (infrared and ultraviolet) on treatment with iodine (presumptive evidence for *trans* orientation of double bond [1]).

trans-α-*Ethyl*-5-*methyl*-α′-*n*-*propyl*-2-*stilbenol* (Ib). The above methoxystilbene was not demethylated when heated with pyridine hydrochloride at 230° for 6 hr., but when 34·17 g. were heated at 170° for 3·5 hr. with methylmagnesium iodide from Mg (11·14 g.) and methyl iodide (26·8 ml.) and processed in the usual way the *stilbenol* (29·92 g.) was obtained as an oil, b. p. 131—133°/0·25 mm., n_D^{20} 1·5664 (Found: C, 85·9; H, 8·55; OMe, nil. $C_{20}H_{24}O$ requires C, 85·7; H, 8·6; OMe, nil %), $\nu_{max.}$ 3535 (OH), 1636 cm.$^{-1}$ (C=C); $\lambda_{max.}$ 208 (ε 30,580), 283·5 (ε 3,960). Hydrogenation of the stilbenol (13·4 g.) over platinum in acetic acid required 40·5 hr. for theoretical hydrogen uptake and gave 2-(α-*ethyl*-β-*n*-*propylphenethyl*)-p-*cresol* (11·8 g.) as a light yellow oil, b. p. 152—154°/1·3—1 mm. (Found: C, 84·2; H, 9·5. $C_{20}H_{26}O$ requires C, 85·1; H, 9·5%), $\nu_{max.}$ 3474, 3424 (OH), 1252 cm.$^{-1}$ (C–O); $\lambda_{max.}$ 284 (ε 2520).

trans-αα′-*Diethyl*-2′-*methyl*-4′-*methoxy*-4-*stilbenamine* (Ic). 2-(*p*-Aminophenyl)-2′-methyl-4′-methoxybutyrophenone (33·5 g.) was refluxed with ethylmagnesium bromide [from Mg (8·52 g.)

[4] R. Neher and K. Miescher, *Helv. Chim. Acta*, 1946, **29**, 449; M. Rubin and H. Wishinsky, *J. Amer. Chem. Soc.*, 1944, **66**, 1948.

[5] E. A. Braude, *J.*, 1949, 1902.

and ethyl bromide (38·65 g.)] in ether (750 ml.). The product, after hydrolysis and extraction, was heated at 200°/20 mm. for 1 hr. and distilled to yield the *stilbeneamine* (24 g.) as a pale yellow glass, b. p. 184°/0·2 mm., n_D^{20} 1·5938 (Found: C, 81·2; H, 8·5; N, 4·9. $C_{20}H_{25}NO$ requires C, 81·3; H, 8·5; N, 4·7%), $\nu_{max.}$ 3448, 3378 (NH_2), 1615 (C=C?), 1605, 1564, 1507 (Ar) cm.$^{-1}$; $\lambda_{max.}$ 236 (ε 16,650), 278 mμ (6400).

trans-α-*n-Propyl*-α′-*ethyl*-2′-*methyl*-4′-*methoxystilbeneamine* (Id). The crude product (46 g.) from a Grignard reaction between ethylmagnesium bromide [from Mg (10·02 g.) and ethyl bromide (45·4 g.)] and 2-(*p*-aminophenyl)-2′-methyl-4′-methoxyvalerophenone (41·3 g., obtained crude by reduction of the corresponding nitro-compound) was heated at 180—190°/20 mm. for 1·25 hr. and distilled to give the *stilbeneamine* (20 g.) as a pale yellow oil, b. p. 192—194°/0·2 mm. (Found: N, 4·6. $C_{21}H_{27}NO$ requires C, 4·5%), $\nu_{max.}$ 3474, 3378 (NH_2), 1664 (C=C?), 1608, 1567, 1510 (Ar) cm.$^{-1}$.

trans-αα′-*Diethyl*-4′-*methylstilbeneamine hydrochloride* (Ie). The product of the Grignard reaction between ethylmagnesium iodide [from Mg (5·4 g.) and ethyl iodide (35 g.)] and 2-(*p*-aminophenyl)-4′-methylbutyrophenone (20·25 g.) in ether (300 ml.) was heated at 200°/20 mm. for 1 hr. and distilled, b. p. 184—190°/0·9 mm. (16·09 g.). This was treated in ethanol (20 ml.) with concentrated hydrochloric acid (40 ml.) to give a solid (15·07 g.) which was triturated with ether and twice crystallised from ethanol–0·5N-hydrochloric acid (1 : 4) to give the *stilbeneamine hydrochloride* (8·9 g.) as buff needles, m. p. 164—166° (decomp.) (Found: C, 74·9; H, 7·8; N, 4·8. $C_{19}H_{24}ClN$ requires C, 75·6; H, 7·9; N, 4·6%), $\nu_{max.}$ 2640 (NH_3^+), 1612 (C=C?), 1567, 1560, 1507 cm.$^{-1}$ (Ar).

trans-αα′-*Diethyl*-3-*methyl*-4-*stilbenol* (If). Impure *trans*-αα′-diethyl-3-methyl-4-methoxystilbene (18·1 g.), b. p. 144—151°/0·6 mm. was prepared by reaction of 2-phenyl-3′-methyl-4′-methoxybutyrophenone (21 g.) with ethylmagnesium bromide and the product was demethylated by heating at 170—180° for 1·25 hr. with methylmagnesium iodide [from methyl iodide (14·2 ml.) and magnesium (5·9 g.)]. After decomposition with ice and 2N-hydrochloric acid (200 ml.), followed by extraction with ether, the *stilbenol* (15·4 g.) was obtained as a pale yellow oil, b. p. 150—154°/0·5 mm., n_D^{27} 1·5818 (Found: C, 86·0; H, 8·4. $C_{19}H_{22}O$ requires C, 85·5; H, 8·7%).

trans-α-*Ethyl*-α′-*n-propyl*-3,3′-*dimethyl*-4,4′-*stilbenediol* (Ig). trans-α-Ethyl-α′-n-propyl-3,3′-dimethyl-4,4′-dimethoxystilbene (38·66 g.), plates, m. p. 186—188° [from benzene–light petroleum (b. p. 60—80°)] (Found: C, 81·2; H, 7·2. $C_{23}H_{30}O_2$ requires C, 81·6; H, 8·9%) was prepared from 2-(3-methyl-4-methoxyphenyl)-3′-methyl-4′-methoxyvalerophenone (45 g.) by reaction, as before, with ethylmagnesium bromide. The methoxy-stilbene was demethylated at 170—175° with methylmagnesium iodide to give the *stilbenediol* (11·87 g.), b. p. 187—190°/0·3 mm. (Found: C, 81·0; H, 8·4. $C_{21}H_{26}O_2$ requires C, 81·25; H, 8·4%).

trans(?)-α-*Ethyl*-4-*stilbeneamine hydrochloride hemihydrate* (Ih). 2-(*p*-Aminophenyl)butyrophenone [6] (13·5 g.) reduced with lithium aluminium hydride (2 g.) in ether gave 1-*phenyl*-2-(*p-aminophenyl*)*butan*-1-*ol* (9·48 g.) as a pale yellow solid, m. p. 99—100°, from light petroleum (b. p. 100—120°) (Found: C, 78·7; H, 8·0; N, 5·6. $C_{16}H_{19}NO$ requires C, 79·6; H, 7·9; N, 5·8%). This alcohol (6 g.) was kept at room temperature in acetic acid (33 ml.) saturated with hydrogen chloride for 72 hr. Concentrated hydrochloric acid (30 ml.) was added and the mixture stored for three days. A pale yellow solid was filtered off and recrystallised from ethanol–2N-hydrochloric acid to give the *stilbeneamine hydrochloride hemihydrate* (5·25 g.) as fine needles, m. p. 192° (decomp.) (Found: C, 71·5; H, 6·7; N, 4·8. $C_{16}H_{18}ClN,0{\cdot}5H_2O$ requires C, 71·5; H, 7·1; N, 5·2%).

Derivatives of trans-4-*stilbeneamine*. 4-(N-*Ethylamino*)*stilbene*. trans-*N*-Acetyl-4-stilbeneamine [7] (60·2 g.) was refluxed for 1 hr. with lithium aluminium hydride (15 g.) in benzene–ether (1 l.). Processing in the usual manner gave the *N*-ethylstilbeneamine (43 g.) as needles, m. p. 127—128°, from methylated spirits (Found: C, 86·3; H, 7·7; N, 6·6. $C_{16}H_{17}N$ requires C, 86·05; H, 7·7; N, 6·3%).

trans-4-(*Acetoxyacetyl*-N-*ethylamino*)*stilbene*. The above *N*-ethyl compound (43 g.) in pyridine (75 ml.) was treated at 50° with acetoxyacetyl chloride (29 g.) for 30 min., poured into water, and the product recrystallised from ethanol to give *acetoxyacetyl derivative* (54·8 g.) as white needles, m. p. 104—105° (Found: C, 74·9; H, 6·45; N, 4·3. $C_{20}H_{21}NO_3$ requires C, 74·3; H, 6·55; N, 4·3%).

[6] G. Brownlee, F. C. Copp, W. M. Duffin, and I. M. Tonkin, *Biochem. J.*, 1943, **37**, 572.
[7] P. Pfeiffer and S. Sergiewskaju, *Ber.*, 1911, **44**, 1107.

2-(N-*Ethyl*-p-trans-*styrylanilino*)*ethanol*. The above amide was reduced in benzene–ether with lithium aluminium hydride (12 g.) to give the *ethanol* (44·3 g.) as pale yellow feathery needles, m. p. 85—87°, from aqueous ethanol (Found: C, 81·2; H, 8·0; N, 5·2. $C_{18}H_{21}NO$ requires C, 80·9; H, 7·2; N, 5·2%), $\nu_{max.}$ 3272 (OH), 970 (trans C=C) cm.$^{-1}$.

2-(N-*Ethyl*-p-*phenylanilino*)*ethanol*. The above alcohol (10 g.) was hydrogenated in ethanol (400 ml.) over 10% palladium on charcoal. Removal of solvent and catalyst gave 2-(N-*ethyl*-p-*phenylanilino*)*ethanol* (6 g.) as a colourless solid, b. p. 192—194°/0·65 mm., m. p. 27—28° (Found: C, 79·5; H, 9·0; N, 5·45. $C_{18}H_{23}NO$ requires C, 80·25; H, 8·6; N, 5·2). Refluxing this compound (6 g.) with excess of methyl iodide for 9 hr. gave *ethyl*(2-*hydroxyethyl*)*methyl*-(p-*phenethylphenyl*)*ammonium iodide* (7·29 g.) as pale cream needles, m. p. 154° (decomp.) from ethanol–ether (Found: N, 3·5. $C_{19}H_{26}INO$ requires N, 3·4%).

trans-4′-*Styrylformanilide*. 4-Aminostilbene [from the hydrochloride (6·5 g.)] was refluxed for 10 min. with 98% formic acid (50 ml.) and the product gave the *formyl derivative* (4·49 g.), m. p. 220—221°, upon recrystallisation from aqueous pyridine (Found: C, 79·8; H, 5·9; N, 6·7. $C_{15}H_{13}NO$ requires C, 80·7; H, 5·9; N, 6·3%), $\nu_{max.}$ 3270 (NH), 1653 (NHCO), 970 (trans C=C) cm.$^{-1}$.

Trimethyl-(trans-p-*styrylphenyl*)*ammonium iodide*. Refluxing *p*-dimethylaminostilbene (4 g.) [8] for 8 hr. with methyl iodide (20 ml.) and ethanol (50 ml.) gave the *iodide* (3·7 g.) as pale yellow plates, m. p. 212° (decomp.) from methylated spirits–water (Found: C, 55·2; H, 6·0; N, 3·55. $C_{16}H_{17}NI,C_2H_5OH$ requires C, 54·5; H, 5·8; N, 3·5%).

We thank Dr. R. E. Bowman for discussions, Miss E. M. Tanner for determination and interpretation of spectra, Mr. F. H. Oliver for microanalyses, and Miss J. A. Richards for technical assistance with some compounds.

PARKE, DAVIS AND CO., HOUNSLOW, MIDDLESEX. [*Received, December 17th*, 1964.]

[8] B. B. Dey and K. K. Row, *J. Indian Chem. Soc.*, 1925, **1**, 277.

---

720. *The Reduction of Bistriphenylphosphine Tricarbonyl Cobalt*(I) *Salts*

By J. A. MCCLEVERTY, A. DAVISON, and G. WILKINSON

TRIPHENYLPHOSPHINE reacts with dicobalt octacarbonyl in polar and non-polar organic solvents to form $(Ph_3P)_2Co(CO)_3^+ Co(CO)_4^-$ (I) in moderate yields.[1] If solutions containing the salt (I) are heated under nitrogen at 40—60°, there is vigorous evolution of carbon monoxide and nearly quantitative conversion into the dimeric species $[Ph_3PCo(CO)_3]_2$ (II) which precipitates as a red-brown powder.

The dimer (II) can also be prepared by reduction in ethereal suspension of the salt (I) with sodium borohydride. It is likely that a reaction intermediate is the hydride, $Ph_3PCo(CO)_3H$, and in an effort to demonstrate this, a suspension of the salt and sodium borohydride in a cold ether or polyether was extracted with degassed diethyl ether and water. The yellow diethyl ether fraction was found to contain the borine Ph_3PBH_3 but no traces of the expected hydride. The other products of the reaction were the dimer (II), which was precipitated when the reaction began, and sodium tetracarbonylcobaltate, which was identified by precipitation of the tris-*o*-phenanthrolinenickel(II) salt. The reaction mechanism thus seems to be as follows:

(1) $(Ph_3P)_2Co(CO)_3^+Co(CO)_4^- + NaBH_4 + R_2O \longrightarrow Ph_3PCo(CO)_3H + Na^+Co(CO)_4^- + Ph_3P + R_2O{\cdot}BH_3$

(2) $R_2O{\cdot}BH_3 + Ph_3P \longrightarrow Ph_3P{\cdot}BH_3 + R_2O$

(3) $2Ph_3PCo(CO)_3H \longrightarrow [Ph_3PCo(CO)_3]_2 + H_2$

---

[1] R. F. Heck, *J. Amer. Chem. Soc.*, 1963, **85**, 657; W. Hieber and E. Lindner, *Z. Naturforsch.*, 1961, **16***b*, 137.

The isolation of the borine is an indication of its relatively high stability in comparison with borine etherates or the borine adduct, $BH_3Co(CO)_4^-$, of the tetracarbonylcobaltate anion. The latter has been shown to be weak and to dissociate very readily.[2]

The salt, $(Ph_3P)_2Co(CO)_3^+PF_6^-$ (III) may also be reduced by either hydrazine in boiling ethanol or by borohydride. With hydrazine, the major product is the dimer (II) and the ether extracts of the reaction mixture, after treatment with degassed water, are yellow and, under nitrogen, slowly deposit small amounts of (II) suggesting the presence of a hydride intermediate. However, the concentrations of the hydride, if present, must be very low as it could not be detected by proton magnetic resonance spectroscopy. With sodium borohydride, the salt (III) affords the dimer (II) and small amounts of $Ph_3P{\cdot}BH_3$.

Experimental.—Microanalyses were by the Microanalytical Laboratory of Imperial College. Infrared spectra were recorded by using a Grubb–Parsons grating spectrophotometer.

Reduction of $(Ph_3P)_2Co(CO)_3^+Co(CO)_4^-$. $(Ph_3P)_2Co(CO)_3^+Co(CO)_4^-$ (3 g.) was dissolved in degassed dimethoxyethane (50 ml.), and sodium borohydride (0·2 g.) was added to the solution. The red-brown *dimer* $[Ph_3PCo(CO)_3]_2$ was precipitated immediately and was collected by filtration. The yield, after washing with ether and petroleum (b. p. 30—40°), was 1·43 g. (98% based on the salt). The pale yellow filtrate was treated with water (100 ml.), and the mixture extracted with ether (100 ml.). The yellow aqueous extract gave a precipitate of $[Ni(o\text{-phen})_3]^{2+}\{[Co(CO)_4]^-\}_2$ when treated with an aqueous solution of $(o\text{-phen})_3NiCl_2$. The ethereal layer was washed repeatedly with water and, after being dried ($MgSO_4$), was evaporated to low bulk; white crystals of *triphenylphosphine–borine* [m. p. 187·5—189° (sealed tube)] formed on cooling. The product (0·38 g., 40%) obtained pure by sublimation at 100°/0·1 mm. (m. p. 188—189°, lit.,[3] 188°) (Found: C, 77·4; H, 6·5%; *M*, 298. Calc. for $C_{18}H_{18}PB$: C, 78·3; H, 6·5%; *M*, 276).

Reduction of $(Ph_3P)_2Co(CO)_3^+PF_6^-$. The salt was prepared by adding tetra-n-butylammonium hexafluorophosphate to a dioxan solution of $(Ph_3P)_2Co(CO)_3^+Co(CO)_4^-$. The solution was filtered and evaporated affording the hexafluorophosphate $(Ph_3P)_2Co(CO)_3^+PF_6^-$. The latter (1 g.) was treated with hydrazine (25 ml.; 10% solution in ethanol) in boiling ethanol (100 ml.) and the mixture worked up as before, the yield of $[Ph_3PCo(CO)_3]_2$ being 0·47 g. (94% based on the salt). The yellow ether extract slowly gave small amounts of the dimer under nitrogen.

Thermal decomposition of $(Ph_3P)_2Co(CO)_3^+Co(CO)_4^-$. The salt (1 g.) was suspended in benzene (100 ml.) under nitrogen and boiled for 10 min. The red-brown solid was filtered off and washed with ether and petroleum (b. p. 30—40°). The yield was 0·95 g. (98·5% based on the salt).

Infrared spectra. The carbonyl complexes also were characterised by their spectra in the carbonyl region.[4]

Ph_3PBH_3 (in methylene chlorine solution): 2380m (terminal B–H stretching frequency).

The authors thank the D.S.I.R. for supporting funds (A. D.) and the Carnegie Trust for the Universities of Scotland for a scholarship (J. A. McC.).

Inorganic Chemistry Research Laboratories,
Imperial College of Science and Technology, London S.W.7.

[Present addresses: (A. D.) Room 6—428B, Department of Chemistry,
Massachusetts Institute of Technology, Massachusetts, U.S.A.
(J. A. McC.) Department of Chemistry, University of Sheffield,
Sheffield 10.]

[*Received, December* 21*st*, 1964.]

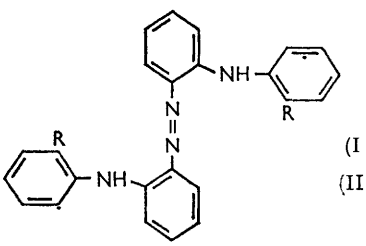
[2] G. W. Parshall, *J. Amer. Chem. Soc.*, 1964, **86**, 361.
[3] H. G. Heal, *J. Inorg. Nuclear Chem.*, 1961, **16**, 209.
[4] O. Vohler, *Chem. Ber.*, 1958, **91**, 1235.

721. 2,2′-*Dianilinoazobenzene*

By L. T. Allan and G. A. Swan

Irradiation of *o*-bromoaniline with ^{60}Co γ-rays afforded a purple compound (B), $C_{24}H_{18}Br_2N_4$, which has not been identified.[1] As azobenzene has now been detected among the γ-radiolysis products of a mixture of aniline and bromobenzene,[2] it seemed possible that compound (B) might be 2,2′-bis-(2-bromoanilino)azobenzene (I), so we attempted the synthesis of the latter.

Oxidation of primary aromatic amines to azo-compounds by phenyl iodosoacetate,[3] manganese dioxide,[4] or oxygen in the presence of pyridine and cuprous chloride [5] has been reported. With 2-aminodiphenylamine, however, all these oxidising agents yielded 2-amino-3,5-dihydro-5-phenyl-3-phenyliminophenazine. It is of interest that the latter compound is a minor product, accompanied by much more of the isomeric 2-anilino-3,5-dihydro-3-imino-5-phenylphenazine, when the amine hydrochloride is oxidised by ferric chloride; oxidation of the hydrochloride by *p*-benzoquinone yields approximately equal amounts of the two isomers.[6] Oxidation of 2-aminodiphenylamine by ammonium peroxydisulphate, lead dioxide, or dilute nitric acid yielded black, infusible products.



(I : R = Br)
(II : R = H)

Reduction of 2-nitrodiphenylamine with zinc and sodium hydroxide solution yielded 2,2′-dianilinoazobenzene (II), but similar reduction of 2-bromo-2′-nitrodiphenylamine yielded a number of products, none of which appeared to be the required compound (I). Other reducing agents either yielded 2-aminodiphenylamine or left the nitro-compound unattacked.

Oxidation of 2-amino-*N*-acetyldiphenylamine or 2-amino-2′-bromo-*N*-acetyldiphenylamine by phenyl iodosoacetate or oxygen in the presence of pyridine and cuprous chloride failed to yield azo-compounds.

Experimental.—*2-Aminodiphenylamine.* 2-Nitrodiphenylamine [7] (0·80 g.) was dissolved in methanol (50 ml.) at room temperature. Hydrazine hydrate (100%, 7 ml.) was added. Small amounts of Raney nickel were then added at intervals with continuous shaking and cooling (ice-bath). When the colour of the solution had almost disappeared, more catalyst was added to decompose the excess of hydrazine, and the solution was kept at room temperature overnight, filtered, and diluted with twice its own volume of water. Recrystallisation of the resulting precipitate from aqueous methanol gave the amine (0·44 g.), m. p. 76—77° (lit., 79—80°) (Found: C, 78·1; H, 6·45; N, 15·25. Calc. for $C_{12}H_{12}N_2$: C, 78·25; H, 6·5; N, 15·25%).

Oxidation of 2-Aminodiphenylamine. (*a*) 2-Aminodiphenylamine (0·46 g.) in dry benzene

[1] J. D. Parrack, G. A. Swan, and P. S. Timmons, *J.*, 1962, 924.
[2] J. M. Fayadh and G. A. Swan, unpublished work.
[3] K. H. Pausacker, *J.*, 1953, 1989; G. B. Barlin, K. H. Pausacker, and N. V. Riggs, *J.*, 1954, 3122.
[4] O. H. Wheeler and D. Gonzalez, *Tetrahedron*, 1964, **20**, 189.
[5] A. P. Terent'ev and Ya. D. Mogilyanskii, *Doklady Akad. Nauk S.S.S.R.*, 1955, **103**, 91.
[6] V. C. Barry, J. G. Belton, J. F. O'Sullivan, and D. Twomey, *J.*, 1956, 888.
[7] F. Kehrmann and E. Havas, *Ber.*, 1913, **46**, 341.

(5 ml.) was refluxed with manganese dioxide [8] (1·1 g.) for 6 hr. using a Dean and Stark separator. The dioxide was filtered and washed with benzene. The filtrate was concentrated to a small volume and chromatographed on alumina. Benzene–chloroform (19 : 1) eluted a solid (0·3 g.) which crystallised from benzene as a solid, m. p. 254—256°, identical with an authentic sample of 2-amino-3,5-dihydro-5-phenyl-3-phenyliminophenazine, kindly supplied by Dr. V. C. Barry (Found: C, 80·75; H, 5·4; N, 14·05. Calc. for $C_{24}H_{18}N_4,\frac{1}{2}C_6H_6$: C, 81·0; H, 5·2; N, 14·0%).

(*b*) 2-Aminodiphenylamine (0·44 g.) in benzene (5 ml.) was added to a solution of phenyl iodosoacetate [9] (1·55 g.) in benzene. The mixture was kept at room temperature for 40 hr., and yielded 2-amino-3,5-dihydro-5-phenyl-3-phenyliminophenazine (0·10 g.).

(*c*) 2-Aminodiphenylamine (0·51 g.) was dissolved in pyridine (10 ml.). A little crystalline cuprous chloride was added. A stream of oxygen was bubbled through the solution for 12 hr., then the solution was filtered and evaporated to dryness under reduced pressure. The residue when chromatographed yielded 2-amino-3,5-dihydro-5-phenyl-3-phenyliminophenazine (0·19 g.).

2,2′-Dianilinoazobenzene. A solution of sodium hydroxide (6 g.) in water (20 ml.) was added to a suspension of 2-nitrodiphenylamine (3·02 g.) in ethanol (10 ml.). Zinc dust (4·5 g.) was added in small portions to the vigorously stirred mixture over 30 min. More ethanol (30 ml.) and sodium hydroxide (3 g.) were added and the mixture was refluxed with stirring for 6 hr. The residual zinc was filtered off and the filtrate was allowed to cool overnight. The resulting precipitate was collected (0·63 g.), dissolved in a small volume of benzene, and chromatographed on alumina, from which benzene–chloroform (19 : 1) eluted a red solid. Recrystallisation from methanol yielded the *product* (0·55 g.) as crystals, m. p. 160—162° (Found: C, 79·45; H, 5·7; N, 14·9. $C_{24}H_{20}N_4$ requires C, 79·10; H, 5·55; N, 15·35%); $\lambda_{max.}$ (EtOH) 245, 295, and 512 mμ (log ε 4·51, 4·53, and 4·21), $\lambda_{min.}$ 254 and 378 mμ.

N-Acetyl-2-aminodiphenylamine. A solution of 2-nitro-*N*-acetyldiphenylamine [10] (0·08 g.) in ethanol (15 ml.) was shaken with hydrogen and Adams catalyst (0·05 g.) at room temperature and atmospheric pressure. The hydrogen consumption was 95% of the theoretical after 15 min., when the hydrogenation was stopped. The catalyst was filtered off and the filtrate was evaporated to dryness under reduced pressure. Recrystallisation of the residue from ethanol afforded the *product* as crystals, m. p. 116—117° (Found: C, 74·25; H, 6·2; N, 12·5. $C_{14}H_{14}N_2O$ requires C, 74·3; H, 6·25; N, 12·4%).

N-Acetyl-2-bromo-2′-nitrodiphenylamine. 2-Bromo-2′-nitrodiphenylamine [11] (0·31 g.) was refluxed with acetic anhydride (2 ml.) in the presence of zinc chloride. The hot solution was poured on to crushed ice (20 g.) to yield a dark yellow oil which solidified after stirring. The solid was collected and recrystallised from methanol to give the *product* (0·33 g.) as crystals, m. p. 158—160° (Found: C, 49·8; H, 3·45; N, 7·75. $C_{14}H_{11}BrN_2O_3$ requires C, 50·15; H, 3·3; N, 8·35%).

N-Acetyl-2-amino-2′-bromodiphenylamine. *N*-Acetyl-2-bromo-2′-nitrodiphenylamine (0·06 g.) was hydrogenated as described for *N*-acetyl-2-nitrodiphenylamine and gave the *product* which separated from methanol as crystals (0·05 g.), m. p. 142—143° (Found: C, 55·2; H, 4·3; N, 9·05. $C_{14}H_{13}BrN_2O$ requires C, 55·1; H, 4·3; N, 9·2%).

This work was sponsored by Air Force Materials Laboratory, Research and Technology Division, A.F.S.C., through the European Office of Aerospace Research, United States Air Force.

Department of Organic Chemistry, The University of Newcastle upon Tyne, Newcastle upon Tyne 1. [*Received, December 21st*, 1964.]

[8] J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J.*, 1952, 1094.
[9] J. Böeseken and G. C. C. C. Schneider, *J. prakt. Chem.*, 1931, [ii], **131**, 285.
[10] F. Kehrmann and E. Baumgartner, *Helv. Chim. Acta*, 1926, **9**, 673.
[11] D. L. Vivian and J. L. Hartwell, *J. Org. Chem.*, 1953, **18**, 1065.

722. *Some Magnetic and Spectral Properties of Copper(II) Benzoate Complexes*

By J. Lewis and F. Mabbs

Salts of copper(II) monocarboxylates have been shown to exist as dimeric molecules, in which appreciable metal–metal interaction occurs, *e.g.*, copper acetate, or polynuclear aggregates in which metal–metal interaction is much smaller. It has recently been postulated that the structure of the copper(II) complexes formed by aryl carboxylic acids can in part be correlated with the pK_a of the acid,[1] the dimeric structure being favoured for acids with high pK_a values. As may be expected, the change in structure does not occur sharply at any particular value of pK_a, and it is of interest to examine the salts of acids in this critical region p$K_a \sim 4{\cdot}2$. With benzoic acid (p$K_a = 4{\cdot}18$), by varying the method of preparation, we have been able to isolate a series of anhydrous compounds which differ appreciably in their magnetic properties. Table 1 summarises the magnetic data for these

Table 1

Magnetic data

Compound	μ at 300°K (B.M.)	Parameters obtained from curve fitting g	J (cm.$^{-1}$)	$N(\alpha) \times 10^6$
Cu(benzoate)$_2$. Prep. 1	1·78	Do not behave magnetically as binuclear complexes		
,, ,, 2	1·53			
,, ,, 3	1·56			
,, ,, 4	1·45			
,, ,, 5	1·40	2·18	340	100
Cu(benzoate)$_2$–ethyl alcohol	1·43	2·20	340	100
Cu(benzoate)$_2$–benzoic acid	1·42	2·18	310	60 *
		2·18	320	100 *
Cu(benzoate)$_2$–pyridine	1·42	2·18	300—320 ‡	
Cu(benzoate)$_2$–(4,4′-bipyridyl)$_{\frac{1}{2}}$	1·48	2·20	~300 †	100

* Either of these sets of values is a reasonable fit for experimental data. † Probably decreasing slightly with temperature. ‡ Appears to vary as temperature decreases.

compounds. For preparations 1 and 4, the temperature variation of the magnetic susceptibility (see Experimental section) indicates the presence of a small percentage of a form with a higher susceptibility. Preparations 1, 3, and 5, however, appear to give distinct and different forms of the anhydrous copper benzoate. Samples 3 and 4 were prepared by a method similar to that subsequently used by Inoue and his co-workers.[2] Inoue *et al.* reported room-temperature moments which are in reasonable agreement with the values obtained in this work. For the susceptibility–temperature data, it has been only possible to fit the data from one preparation (5) to the formula given by Figgis and Martin [3] for the variation of the magnetic properties of a binuclear copper complex. The parameters obtained from a curve-fitting procedure for preparation 5 and some of the adducts, on the basis of such a binuclear interaction, are given in Table 1. The values are comparable to those observed in the copper acetate systems.

As with other carboxylates of copper, copper benzoate formed adducts readily with a variety of ligands. The magnetic moments at 300°K for the ethyl alcohol and benzoic acid adducts are in good agreement with those reported previously.[2,4] However, our

[1] J. Lewis and R. C. Thompson, *Nature*, 1963, **200**, 468; J. Lewis, *Pure Appl. Chem.*, 1965, **10**, 11.
[2] M. Inoue, M. Kishita, and M. Kubo, *Inorg. Chem.*, 1964, **3**, 239.
[3] B. N. Figgis and R. L. Martin, *J.*, 1956, 3837.
[4] R. D. Gillard, D. M. Harris, and G. Wilkinson, *J.*, 1964, 2838.

value (1·40 B.M.) for the monopyridine adduct is considerably higher than the previous[4] value (1·30 B.M.); the reason for this is not known, but it seems unlikely that it is due to traces of the most probable impurity, *i.e.*, the bispyridine adduct, as there would have to be about 10% of this material present to account for the difference at room temperature Since the bispyridine adduct has been reported[4] to have $\mu_{eff} = 1{\cdot}9$ B.M. at room temperature and presumably behaves in a normal manner expected for copper(II) complexes, the contribution to the susceptibility at 80°K would be of the order of $400—500 \times 10^{-6}$ c.g.s. units. This would certainly lead to an increase in the susceptibility at low temperature which we have not observed.

The effect of the terminal ligands on the strength of the exchange interaction does not seem to be very marked for the examples studied. The small differences in the value of J quoted in Table 1 are only just significant. So far the only ligands reported to have any marked effect on the strength of the exchange interaction, in complexes which already adopt the binuclear configuration, are aniline and *p*- and *m*-toluidine,[5] where the value o J is markedly decreased.

Copper benzoate trihydrate has been shown to have a polymeric structure consisting of chains of copper atoms bridged by benzoate groups and water molecules,[6] with the Cu–Cu distance 3·15 Å in the chain. The measurement of the susceptibility over a temperature range, however, indicates that there is no appreciable exchange interaction between the copper atoms since the behaviour approximates well to a Curie–Weiss law with $\theta = 15°$.

TABLE 2

Diffuse-reflectance spectra

Compound	Band I (cm.$^{-1}$)	Band II: Approx. position (cm.$^{-1}$)	Band II: Comments
$Cu(benzoate)_2,3H_2O$	14,250	—	—
$Cu(benzoate)_2$ (1)	15,300	24,000—27,000	A not very pronounced shoulder
,, (3)	14,900	,,	
,, (5)	15,200	,,	
$Cu(benzoate)_2$–pyridine	13,750	24,000—30,000	Pronounced shoulder
$Cu(benzoate)_2$–(4,4′-bipyridyl)$_{\frac{1}{2}}$ ...	13,550	,,	Less pronounced shoulder than for pyridine adduct
$Cu(benzoate)_2$–benzoic acid	14,800	,,	
$Cu(benzoate)_2$–ethyl alcohol	14,450	,,	

The measurements of the diffuse-reflectance spectra of the complexes over the range 1000—350 mμ are summarised in Table 2. Of most interest is the shoulder in the region 24,000—30,000 cm.$^{-1}$, present in the complexes which show significant magnetic exchange interactions. This shoulder is unlikely to be a property of the benzoate group itself, since it is absent in copper benzoate trihydrate. These observations are similar to previous findings on other binuclear copper compounds,[1,5,7,8] but its origin has not been explained.

Experimental.—Copper(II) *benzoate trihydrate.* This was prepared by adding a dilute solution of sodium benzoate to a solution of copper sulphate, filtering off the pale blue product, washing with water, and drying in air (Found: C, 46·8; H, 4·5; Cu, 17·7. Calc. for $C_{14}H_{16}CuO_7$: C, 46·7; H, 4·5; Cu, 17·7%).

Anhydrous copper(II) *benzoate.* (1) Copper benzoate trihydrate was dehydrated in a vacuum at 100° for 2 hr. (Found: C, 54·3; H, 3·4; Cu, 20·8%). (2) Copper benzoate trihydrate was dehydrated in air at 110° for 1 hr. (Found: C, 54·5; H, 3·4; Cu, 20·8%). (3) According to the method of Inoue *et al.*,[2] the copper benzoate–ethyl alcohol adduct was heated in air at 90° for 1 hr. (Found: C, 54·7; H, 3·3; Cu, 21·0%). (4) Using the method employed by Inoue *et al.*,[2] the ethyl alcohol adduct of copper benzoate was refluxed with carbon tetrachloride for 1 hr.

[5] E. Kokot and R. L. Martin, *Inorg. Chem.*, 1964, **3**, 1306.
[6] H. Koizumi, K. Osaki, and T. Watanabe, *J. Phys. Soc. Japan.*, 1963, **18**, 117.
[7] R. L. Martin and H. Wateman, *J.*, 1957, 2545.
[8] M. L. Tonnet, S. Yamada, and I. G. Ross, *Trans. Faraday Soc.*, 1964, **60**, 840.

The product was washed with a little carbon tetrachloride and dried in air (Found: C, 54·0; H, 3·7; Cu, 20·9%). (5) Anhydrous copper benzoate from (2) was dissolved in methyl alcohol and the solution allowed to crystallise. An unstable methyl alcohol adduct was isolated, and heated in a vacuum at the temperature of boiling carbon tetrachloride for 3 hr. (Found: C, 55·5; H, 3·4; Cu, 20·8. Calc. for $C_{14}H_{10}CuO_4$: C, 55·0; H, 3·3; Cu, 20·8%).

Copper benzoate–benzoic acid. A solution of sodium benzoate (2·8 g.) in 0·1N-aqueous benzoic acid (100 ml.) at 60° was added to a cold solution of copper(II) sulphate pentahydrate (2 g.) in water (50 ml.). The turquoise precipitate which formed immediately was filtered off, washed with a little cold water, and dried in air (Found: C, 58·6; H, 3·9; Cu, 14·7. Calc. for $C_{21}H_{16}CuO_6$: C, 58·9; H, 3·8; Cu, 14·9%).

Copper benzoate–ethyl alcohol. This was prepared by the method of Inoue *et al.*[2] (Found: C, 53·9; H, 4·5; Cu, 18·2. Calc. for $C_{16}H_{16}CuO_5$: C, 54·6; H, 4·6; Cu, 18·1%).

Copper benzoate–pyridine. Anhydrous copper(II) benzoate was dissolved in freshly distilled

$Cu(benzoate)_2,3H_2O$

Temp. (°K)	295·4	281·4	262·8	238·5	217·9	200·0	178·7	163·8	146·6	126·8	113·4	99·2	91·3	78·2
$\chi_{Cu} \times 10^6$	1552	1617	1735	1859	2067	2224	2518	2778	3098	3516	3894	4357	4631	5389

$Cu(benzoate)_2$ (1)

Temp. (°K)	308·0	283·9	264·2	244·6	223·7	176·8	159·1	140·6	114·3	95·9
$\chi_{Cu} \times 10^6$	1303	1352	1419	1453	1549	1733	1856	1944	2141	2175

$Cu(benzoate)_2$ (2)

Temp. (°K)	306·3	302·6	296·0	292·5	276·9	260·8	249·6	228·9	216·9	195·7
$\chi_{Cu} \times 10^6$	970	972	987	989	987	987	994	999	982	979
Temp. (°K)	191·2	172·0	163·8	151·6	139·2	127·0	112·0	103·0	93·4	91·6
$\chi_{Cu} \times 10^6$	955	932	898	876	853	821	794	784	802	811

$Cu(benzoate)_2$ (3)

Temp. (°K)	300·5	280·4	260·4	238·9	217·9	199·7	180·8	159·1	140·0	121·4	109·1	98·2	88·5	78·0
$\chi_{Cu} \times 10^6$	1008	1023	1037	1045	1061	1045	1045	1008	942	893	848	791	734	698

$Cu(benzoate)_2$ (4)

Temp. (°K)	310·4	305·0	293·5	287·1	263·8	249·1	229·5	209·8	190·2
$\chi_{Cu} \times 10^6$	879	881	868	868	855	866	842	827	782
Temp. (°K)	176·8	158·3	146·0	126·7	114·3	104·7	91·8	87·4	80·0
$\chi_{Cu} \times 10^6$	749	686	626	576	533	513	479	496	544

$Cu(benzoate)_2$ (5)

Temp. (°K)	312·0	297·4	276·4	262·4	242·0	223·2	206·2
$\chi_{Cu} \times 10^6$	802	810	800	784	763	741	727
Temp. (°K)	189·6	173·7	156·0	134·1	11·44	98·7	78·0
$\chi_{Cu} \times 10^6$	683	630	544	429	314	232	152

$Cu(benzoate)_2$–Ethyl alcohol

Temp. (°K)	300·1	283·8	266·1	248·6	230·3	209·4	189·6	169·6	148·2	127·0	112·8	95·2	78·2
$\chi_{Cu} \times 10^6$	857	857	839	825	803	758	706	632	526	407	324	224	166

$Cu(benzoate)_2$–Benzoic acid

Temp. (°K)	306·0	290·5	275·0	258·7	239·8	221·8	199·3	183·0
$\chi_{Cu} \times 10^6$	840	840	842	836	804	801	756	707
Temp. (°K)	164·8	146·3	128·0	112·3	100·1	93·6	87·8	79·8
$\chi_{Cu} \times 10^6$	647	570	454	352	259	195	175	124

$Cu(benzoate)_2$–pyridine

Temp. (°K)	308·0	299·9	281·2	260·4	238·7	218·8	202·8
$\chi_{Cu} \times 10^6$	837	837	841	818	801	785	746
Temp. (°K)	182·9	160·8	140·6	123·3	106·8	94·3	79·2
$\chi_{Cu} \times 10^6$	716	648	543	435	350	275	200

$Cu(benzoate)_2$–(4,4′-Bipyridyl)$_1$

Temp. (°K)	307·7	304·0	290·2	275·8	258·0	247·0	238·5	218·3
$\chi_{Cu} \times 10^6$	926	922	924	930	947	934	926	905
Temp. (°K)	197·5	187·6	165·0	146·2	125·8	110·0	94·2	78·0
$\chi_{Cu} \times 10^6$	884	854	772	684	564	462	373	285

pyridine and the solution concentrated under reduced pressure over conc. sulphuric acid to give initially the royal blue bispyridine adduct which lost pyridine to give the light green monopyridine adduct (Found: C, 59·3; H, 3·8; Cu, 16·4. Calc. for $C_{19}H_{15}CuNO_4$: C, 59·4; H, 4·0; Cu, 16·5%).

Copper benzoate hemi-(4,4'-bipyridyl). A solution of 4,4'-bipyridyl (0·5 g.) in acetone (15 ml.) was added to a solution of copper(II) benzoate (2·2 g.) in acetone (150 ml.). The pale green *precipitate* which formed after a few minutes was filtered off, washed with acetone, and dried in air (Found: C, 59·2; H, 3·9; Cu, 16·6; N, 3·8. $C_{19}H_{14}CuNO_4$ requires C, 59·4; H, 3·7; Cu, 16·5; N, 3·7%).

Magnetic Measurements. The absolute magnetic susceptibilities of the compounds were measured at room temperature by the Gouy method, with equipment calibrated by means of nickel chloride solution.[9] The relative susceptibilities were measured over a temperature range using an apparatus based on a design described previously.[10]

Diffuse-reflectance spectra. These (Table 2) were measured over the range 1000—300 mμ with a Beckman DK2A ratio recording spectrometer.

One of the authors (F. M.) thanks N.A.T.O. for a scholarship during the tenure of which this work was performed.

DEPARTMENT OF CHEMISTRY, THE UNIVERSITY,
MANCHESTER 13. [*Received, December 23rd*, 1964.]

[9] H. R. Nettleton and S. Sugden, *Proc. Roy. Soc.*, 1941, *A*, **173**, 313.
[10] B. N. Figgis and R. S. Nyholm, *J.*, 1959, 331.

---

723. *Acylimidazoles in the Synthesis of Protected Amino-acid p-Nitrophenyl Esters*

By H. D. LAW

PROTECTED amino-acid *p*-nitrophenyl esters,[1] which have proved extremely valuable as carboxyl-activated components in peptide synthesis,[2] are usually prepared from the protected amino-acid and *p*-nitrophenol in the presence of *NN'*-dicyclohexylcarbodiimide.[3,4] Other condensing agents have been employed [5,6] and syntheses have also been reported which involve acid chlorides,[7] mixed anhydrides,[7] and aryl phosphites,[8] sulphites,[8] and carbonates.[9] This Paper describes the preparation of these esters *via* acylimidazole intermediates.

NN'-Carbonyldi-imidazole was first employed in peptide synthesis by Paul and Anderson.[10] The reagent was reacted with a protected amino-acid to form the protected aminoacylimidazole derivative. Subsequently, addition of the amino-component resulted

[1] M. Bodanszky, *Nature*, 1955, **175**, 685.
[2] H. D. Law, review in "Progress in Medicinal Chemistry," eds. G. P. Ellis and G. B. West, Butterworths, London, vol. 4, in the press.
[3] D. F. Elliott and D. W. Russell, *Biochem. J.*, 1957, **66**, 49P.
[4] M. Rothe and F. W. Kunitz, *Annalen*, 1957, **609**, 88.
[5] M. Bodanszky and C. A. Birkhimer, *Chem. and Ind.*, 1962, 1620.
[6] D. T. Elmore and J. Smyth, *Proc. Chem. Soc.*, 1963, 18.
[7] M. Bodanszky, *Acta Chim. Acad. Sci. Hung.*, 1957, **10**, 335.
[8] B. Iselin, W. Rittel, P. Sieber, and R. Schwyzer, *Helv. Chim. Acta*, 1957, **40**, 373.
[9] T. Wieland, B. Heinke, K. Vogeller, and H. Morimoto, *Annalen*, 1962, **655**, 189.
[10] R. Paul and G. W. Anderson, *J. Amer. Chem. Soc.*, 1960, **82**, 4596.

in the formation of the peptide in good yield and, under the best conditions, with very little racemisation. Staab [11] has shown that *NN'*-carbonyldi-imidazole may be employed successfully in the synthesis of a variety of alkyl and aryl esters. Its use in the synthesis of the desired *p*-nitrophenyl esters was therefore investigated.

To determine the optimum conditions, the formation of *p*-nitrophenyl *N*-benzyloxycarbonylglycinate was first studied (see Table). The best yield of ester (54%) was

Effect of variations in technique on the preparation of *p*-nitrophenyl *N*-benzyloxycarbonylglycinate by the use of *NN'*-carbonyldi-imidazole

N-Benzyloxycarbonylglycine (moles)	*NN'*-Carbonyldi-imidazole (moles)	*p*-Nitrophenol (moles)	Yield (%)	Reaction conditions
1	1	3	50—54	Standard procedure
1	1	1	30	Standard procedure
1	1	3	19	Hot *
1	1	3	48	+ Sodium *p*-nitrophenate †
1	1	1	8	+ Trifluoroacetic acid ‡

* Reaction mixture heated under reflux for 20 hr. † Sodium *p*-nitrophenate (5 mg.) added to final reaction mixture. ‡ Trifluoroacetic acid (2 moles) added to final reaction mixture.

obtained when 3 moles of *p*-nitrophenol were used for each mole of protected amino-acid. Because of the difficulty of separating the product from the large amount of *p*-nitrophenol which was present, it is likely that the amount of ester formed was considerably in excess of that which could be isolated. However, when less *p*-nitrophenol was taken, the yield of ester was reduced.

The formation of simple alkyl and aryl esters by the acylimidazole route is reported to proceed in better yields at elevated temperatures; [11] at room temperature the yield is increased dramatically by the addition of a small amount of alkoxide.[12] Neither of these factors influences favourably the formation of *p*-nitrophenyl *N*-benzyloxycarbonylglycinate.

Anhydrides of carboxylic acids can be formed with the aid of *NN'*-carbonyldi-imidazole, but the reaction is only of preparative value when the equilibrium of the reaction can be displaced in favour of the formation of the anhydride.[13] This can be achieved if the imidazole is removed from the reaction mixture in the form of an insoluble salt, for example, as its trifluoroacetate. In the preparation of *p*-nitrophenyl benzyloxycarbonylglycinate, the addition of trifluoroacetic acid to the final reaction mixture, in an amount equivalent to the total amount of imidazole present, greatly reduced the yield of ester.

Under the optimum conditions thus determined, the yields of other *N*-benzyloxycarbonylamino-acid *p*-nitrophenyl esters were not good. Thus the following yields of the *p*-nitrophenyl esters were obtained: *N*-benzyloxycarbonyl-L-phenylalanine (30%); tris-benzyloxycarbonyl-L-arginine (52%); *N*-benzyloxycarbonyl-*O*-methyl-L-tyrosine (40%).

N-(Trifluoroacetyl)imidazole may be used in place of *NN'*-carbonyldi-imidazole to produce anhydrides of carboxylic acids [13] and the same substitution may be made advantageously in the synthesis of *p*-nitrophenyl esters. Under the optimum conditions, *p*-nitrophenyl *N*-benzyloxycarbonylglycinate was obtained in 64% yield by the use of this reagent. In this case, *N*-benzyloxycarbonylglycine and *p*-nitrophenol could be taken in equivalent amounts. The yield of ester was not affected by the order of addition of the *p*-nitrophenol and *N*-(trifluoroacetyl)imidazole. An equivalent amount of *N*-(trifluoroacetyl)imidazole was sufficient to obtain a maximum yield of the ester, but excess was

[11] H. A. Staab, *Angew. Chem.*, 1959, **71**, 194.
[12] H. A. Staab, W. Rohr, and A. Mannschreck, *Angew. Chem.*, 1961, **73**, 143.
[13] H. A. Staab, G. Walther, and W. Rohr, *Chem. Ber.*, 1962, **95**, 2073.

usually taken since the reagent is subject to decomposition in the presence of traces of water. Most of the amino-acids studied gave good yields of *p*-nitrophenyl esters by this procedure. Thus the following yields of the *p*-nitrophenyl esters were obtained: *N*-benzyloxycarbonyl-L-phenylalanine (72%); *N*-benzyloxycarbonyl-β-benzyl-L-aspartic acid (66%); trisbenzyloxycarbonyl-L-arginine (80%); *N*-benzyloxycarbonyl-L-proline (78·5%); *N*-benzyloxycarbonyl-L-glutamine (40—65%); *N*-benzyloxycarbonyl-L-asparagine (13%).

In general, the method seems less satisfactory than available alternatives, but may be useful in some specific instances in which other methods give low yields of ester, for example, in the preparation of *p*-nitrophenyl *N*-benzyloxycarbonyl-β-benzyl-L-aspartate. However, the poor yield of *p*-nitrophenyl *N*-benzyloxycarbonyl-L-asparaginate is disappointing.

Experimental—*NN′-Carbonyldi-imidazole procedure.* *NN′*-Carbonyldi-imidazole (20 mmoles) * was added to a stirred solution of the *N*-benzyloxycarbonylamino-acid (20 mmoles) in dry tetrahydrofuran (10—20 ml.) at −10°. The mixture was stirred at −10° to −5° for 1 hr. after which time the *NN′*-carbonyldi-imidazole had generally dissolved. *p*-Nitrophenol (60 mmoles) was added to the mixture at −10° and stirring was continued at this temperature for a further hour. The reaction mixture was finally allowed to warm to room temperature and was stirred for 4 hr. (or overnight). Evaporation of the tetrahydrofuran under reduced pressure left an oil which was taken up in ethyl acetate (150 ml.) and extracted with 20% acetic acid (3 × 30 ml.), saturated sodium hydrogen carbonate solution (5 × 30 ml., until washings alkaline), and saturated brine (2 × 20 ml.). The dried (Na_2SO_4) ethyl acetate solution was evaporated under reduced pressure to yield a crystalline residue.

Examples. *p*-Nitrophenyl *N*-benzyloxycarbonylglycinate (50—54%), recrystallised from absolute ethanol, had m. p. 124—126° [lit.,[8] di-*p*-nitrophenyl sulphite method, 95%, m. p. 124—125°].

p-Nitrophenyl *N*-benzyloxycarbonyl-L-phenylalaninate (30%), recrystallised from absolute ethanol, had m. p. 123—124·5°, $[\alpha]_D^{19}$ −21·0° (*c* 1·8 in DMF) {lit.,[14] tri-*p*-nitrophenyl phosphite method, 75%, m. p. 126·5—127·5°, $[\alpha]_D^{25}$ −8·9° (*c* 2·2 in $CHCl_3$); lit.,[15] *NN′*-dicyclohexylcarbodi-imide method, 75%, m. p. 126—126·5°, $[\alpha]_D^{20}$ −24·7° (*c* 2 in DMF)}.

p-Nitrophenyl trisbenzyloxycarbonyl-L-argininate (52%), recrystallised from absolute ethanol, had m. p. 123°, $[\alpha]_D^{20}$ −13·9° (*c* 3 in DMF) (lit.,[16] m. p. 126—127°).

p-Nitrophenyl *N*-benzyloxycarbonyl-*O*-methyl-L-tyrosinate (40%), recrystallised from absolute ethanol, had m. p. 118°, $[\alpha]_D^{18\cdot5}$ −9·0° (*c* 2·25 in AcOEt) {lit.,[17] *NN′*-dicyclohexylcarbodi-imide method, 75%, m. p. 121—122°, $[\alpha]_D^{18\cdot5}$ −9·0° (*c* 1·6 in AcOEt)}.

N-(*Trifluoroacetyl*)*imidazole procedure.* Freshly distilled *N*-(trifluoroacetyl)imidazole [18] (20—40 mmoles) in solution in dry tetrahydrofuran (6—10 ml.) was added in one batch to a solution of the *N*-benzyloxycarbonylamino-acid (20 mmoles) and *p*-nitrophenol (21 mmoles) in dry tetrahydrofuran at 0°. A precipitate of imidazole trifluoroacetate generally started to appear immediately. After a further hour at 0°, the reaction mixture was stirred at room temperature for 4 hr. At this stage the addition of water (20 ml.), followed by evaporation of the tetrahydrofuran under reduced pressure, sometimes gave a crystalline product which could be removed by filtration, dried, and recrystallised (method A). Alternatively, no water was added and the imidazole trifluoroacetate was removed by filtration. Evaporation of the tetrahydrofuran solution gave a semi-crystalline residue which was taken up in ethyl acetate and washed as in the *NN′*-carbonyldi-imidazole procedure (method B).

* When the reagent assayed <95% *N,N′*-carbonyldi-imidazole, it was assumed that the inert impurity was imidazole. Extra quantities of the reagent and of *p*-nitrophenol were taken accordingly.

[14] M. Goodman and K. C. Steuben, *J. Amer. Chem. Soc.*, 1959, **81**, 3980.
[15] M. Bodanszky and V. Du Vigneaud, *J. Amer. Chem. Soc.*, 1959, **81**, 6072.
[16] E. D. Nicolaides, H. A. DeWald, P. G. Shorley, and H. O. J. Collier, *Nature*, 1960, **187**, 773.
[17] H. D. Law and V. Du Vigneaud, unpublished work.
[18] H. A. Staab and G. Walther, *Chem. Ber.*, 1962, **95**, 2070.

In a preliminary series of experiments, *N*-(trifluoroacetyl)imidazole was treated with the *N*-benzyloxycarbonylamino-acid prior to the addition of the *p*-nitrophenol. Yields were identical with those obtained by the above procedure.

Examples

p-Nitrophenyl *N*-benzyloxycarbonylglycinate (Methods A and B) was recrystallised from absolute ethanol, 64%, m. p. 125·5—127·5°.

p-Nitrophenyl *N*-benzyloxycarbonyl-L-phenylalaninate (Method B) was recrystallised from absolute ethanol, 72%, m. p. 125°, $[\alpha]_D^{18}$ −25° (*c* 1·49 in DMF).

p-Nitrophenyl *N*-benzyloxycarbonyl-β-benzyl-L-aspartate (Method B) was recrystallised from ethyl acetate–light petroleum, 66%, m. p. 75—77°, $[\alpha]_D^{18}$ −26·8° (*c* 2·5 in DMF), $[\alpha]_D^{17}$ −20·8° (*c* 2·6 in MeOH) {lit.,[19] tri-*p*-nitrophenyl phosphite method, 51%, m. p. 76°, $[\alpha]_D^{22}$ −16·6° ± 0·5° (*c* 1 in DMF); −30·0° ± 0·5° (*c* 1 in MeOH). A sample prepared in these laboratories (tri-*p*-nitrophenyl phosphite method) by Dr. R. W. Hanson had m. p. 76°, $[\alpha]_D^{19}$ −30·6° (*c* 5·5 in DMF), $[\alpha]_D^{19\cdot5}$ −22·0° (*c* 3·67 in MeOH)}.

p-Nitrophenyl trisbenzyloxycarbonyl-L-arginate (Method B) was purified by trituration in boiling ethanol, 80%, m. p. 129—130°, $[\alpha]_D^{20}$ −17·9° (*c* 2·7 in DMF).

p-Nitrophenyl *N*-benzyloxycarbonyl-L-prolinate was recrystallised from absolute ethanol, 78·5%, m. p. 92—95°, $[\alpha]_D^{19}$ −66·5° (*c* 3·56 in DMF) {lit.,[20] 89%, m. p. 94—96°, $[\alpha]_D^{20}$ −68° (*c* 2 in DMF)}.

p-Nitrophenyl *N*-benzyloxycarbonyl-L-glutaminate. Because of its insolubility in tetrahydrofuran, *N*-benzyloxycarbonyl-L-glutamine was mainly in suspension during the reaction with *N*-(trifluoroacetyl)imidazole. Nonetheless, reaction was usually rapid and the reaction mixture became solid. After 12 hr., the solvent was removed under reduced pressure and dilute acetic acid added to the solid residue. The insoluble matter was filtered off and washed thoroughly with dilute acetic acid, aqueous sodium hydrogen carbonate, and water. After drying in air, the crude product was obtained in high yield (−70%, m. p. 136—139°, infrared spectrum identical with that of an authentic sample prepared by the *NN'*-dicyclohexylcarbodi-imide method), but during recrystallisation from *NN*-dimethylformamide–water, considerable losses usually occurred. The ester was finally obtained pure in 40—65% yield, m. p. 154—156°, $[\alpha]_D^{19}$ −20° (*c* 2·1 in DMF) {lit.,[20] *NN'*-dicyclohexylcarbodi-imide method, 59%, m. p. 155—156°, $[\alpha]_D^{20}$ −24° (*c* 2 in DMF)}.

p-Nitrophenyl *N*-benzyloxycarbonyl-L-asparaginate. *N*-Benzyloxycarbonyl-L-asparagine was reacted in suspension in tetrahydrofuran with *N*-(trifluoroacetyl)imidazole in the usual manner. An orange colour generally developed in the reaction mixture. The product was difficult to isolate by either method A or B and yields were variable. The product was recrystallised from *NN*-dimethylformamide–water, −13%, m. p. 158—161° {lit.,[20] *NN'*-dicyclohexylcarbodi-imide method, 43%, m. p. 165—166°, $[\alpha]_D^{20}$ −31·5° (*c* 2 in DMF)}.

I am indebted to Mr. W. F. Hurst for skilful technical assistance during the course of this work.

[19] S. Guttman, *Helv. Chim. Acta*, 1961, **44**, 721.
[20] M. Bodanszky and V. Du Vigneaud, *J. Amer. Chem. Soc.*, 1959, **81**, 5688.

MILES-AMES RESEARCH LABORATORIES,
STOKE COURT, STOKE POGES, BUCKINGHAMSHIRE. [*Received, December 30th*, 1964.]

724. *Free-radical Addition of Phosphine to Allene*

By H. Goldwhite

Phosphine undergoes free-radical addition to a wide variety of unsaturated compounds,[1] but its addition to allene has not yet been reported. This reaction has now been examined as part of a programme of synthetic approaches to phosphetan.

Initiation of the addition by azobisisobutyronitrile [2] was not successful. When an allene–phosphine mixture (1 : 2 molar), containing 10 mole-% of the initiator, was heated at 53 atmospheres (initial) at 77° for 11 hr., some of the starting materials were recovered, and much polymeric material was produced. Initiation by ultraviolet light, however, produced in addition to polymeric material, a small yield of a 1 : 1 adduct, which was characterised as isopropenylphosphine, $CH_2{:}CHMe{\cdot}PH_2$ rather than the isomeric allylphosphine, on the basis of the following spectral characteristics.

The unsaturated nature of the compound and the presence of a PH grouping were shown by intense infrared absorption at 1640 and 2300 cm.$^{-1}$. The presence of a methyl group is suggested by medium-to-strong absorption at 1370—1390 and 1450 cm.$^{-1}$, attributable to deformation modes of a CH_3–C group.[3] The proton magnetic resonance spectrum of the undiluted compound at 60 Mc./sec. confirms the presence of the methyl group and is in agreement with the suggested structure. The spectrum is simple consisting, under low resolution, of only two bands, at $\delta = 1{\cdot}68$ p.p.m. (downfield relative to external $Me_4Si = 0$) of intensity corresponding to 3 hydrogen atoms (Me), and at $\delta = 4{\cdot}24$ p.p.m. corresponding to 2 hydrogen atoms ($CH_2{:}C$). At high resolution each band shows multiplet structure, presumably due to small couplings to phosphorus and to the other hydrogen atoms present. An unusual feature of the spectrum is the absence of any discernible resonance absorption assignable to hydrogen atoms attached to phosphorus. This phenomenon has been noted in this laboratory in the n.m.r. spectra of other primary phosphines,[4] and may be due to a fast exchange reaction of this type of hydrogen atom.

In an attempt to confirm the structure of isopropenylphosphine its reaction with chlorine was studied. The reaction was complex and did not result in the simple conversion of the phosphine to a phosphonous dichloride.[5] Only 1·2 moles of hydrogen chloride per mole of phosphine was liberated, and the presence of a non-volatile residue indicated that condensation was occurring.

The formation of isopropenylphosphine by free-radical addition of phosphine to allene is analogous to the formation of 2-bromopropene in the addition of hydrogen bromide to allene under free-radical conditions.[6] The low yield of volatile product in the phosphine addition, plus the substantial conversion of starting materials into polymeric products, prevent the drawing of any conclusions about the selectivity of addition of the PH_2 radical to allene.

Experimental.—Phosphine was prepared by heating dry phosphorous acid, and was purified by fractional condensation *in vacuo*. Allene was a commercial sample containing about 1·5% of propene, but no detectable propyne. Materials were handled in a conventional vacuum system and mixtures were separated by fractional condensation therein. Molecular weights were determined by Regnault's method.

[1] F. W. Stacey and J. F. Harris, "Organic Reactions," vol. 13, ed. R. Adams *et al.*, John Wiley and Sons, New York, 1963, p. 218.
[2] M. M. Rauhut, H. A. Currier, A. M. Semsel, and V. P. Wystrach, *J. Org. Chem.*, 1961, **26**, 5138.
[3] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co., London, 1958, p. 13.
[4] J. Bissey, B. Fontal, and H. Goldwhite, unpublished observations.
[5] G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J.*, 1963, 1083.
[6] K. Griesbaum, A. A. Oswald, and D. N. Hall, *J. Org. Chem.*, 1964, **29**, 2404.

Ultraviolet irradiation of a mixture of phosphine and allene. In each of three transparent 250 ml. silica tubes was placed phosphine (0·805 g., 0·0237 mole) and allene (1·068 g., 0·0267 mole). The tubes were placed 9 inches from a Hanovia UVS 250-w lamp and were irradiated for 11 hr.; a heavy brown deposit forming in each tube. The volatile contents of the tubes were combined and distilled *in vacuo* to give a mixture of allene and phosphine (0·0968 mole) plus *isopropenylphosphine* (0·0166 g., 0·00224 mole, 3% based on phosphine) (Found: P, 41·5%; *M*, 73·5. C_3H_7P requires P, 41·9%; *M*, 74·0). The vapour pressure of the phosphine over the range 0—25° followed the equation $\log_{10} P$ (mm.) = 6·80 − (1185/*T*), giving an extrapolated b. p. of 29°.

This investigation was supported by a Public Health Service Research Grant from the National Cancer Institute.

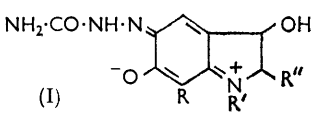
Department of Chemistry, California State College at Los Angeles,
Los Angeles, California 90032. [*Received, January 1st*, 1965.]

---

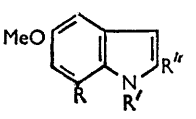
725. *The Chemistry of the Aminochromes. Part VII.* The Preparation of 6-Hydroxyindole Derivatives by the Alkaline Degradation of Aminochrome Semicarbazones*

By R. A. Heacock and O. Hutzinger

The removal of the semicarbazide residue from adrenochrome monosemicarbazone (I; R = R″ = H, R′ = Me) by a multistage process, which involved the reduction of the semicarbazone, and pyrolysis of the methyl ether of the product have been described by Iwao.[1] In this manner, 6-methoxy-*N*-methylindole (II; R = R″ = H, R′ = Me) was obtained in relatively low overall yield from (I; R = R″ = H, R′ = Me).



(I)



(II)

It was reported at the end of the last century that *p*-benzoquinone monosemicarbazone could be converted to phenol, in virtually quantitative yield, on treatment with hot aqueous alkali.[2] The present investigation has shown that this simple procedure can be applied satisfactorily to the degradation of the aminochrome semicarbazones; the corresponding 6-hydroxyindole derivatives can be obtained, as their methyl ethers, from the products of the reaction in satisfactory yields.

6-Methoxy-*N*-methylindole (II; R = R″ = H, R′ = Me) was obtained from adrenochrome monosemicarbazone (I; R = R″ = H, R′ = Me) in 46% yield by this procedure. Four 6-methoxyindoles, namely: 6-methoxy-7,*N*-dimethylindole (II; R = R′ = Me, R″ = H); 6-methoxy-*N*-isopropylindole (II; R = R″ = H, R′ = Pr^i); 6-methoxy-2-methylindole (II; R = R′ = H, R″ = Me), and 6-methoxy-2,*N*-dimethylindole (II;

* Part VI, G. L. Mattok and R. A. Heacock, *Canad. J. Chem.*, 1965, **43**, 119.

[1] J. Iwao, *Pharm. Bull.* (*Japan*), 1956, **4**, 244.
[2] J. Thiele and W. Barlow, *Annalen*, 1898, **302**, 311.

R = H, R′ = R″ = Me) were obtained in a similar manner, in satisfactory yields, from the corresponding aminochrome monosemicarbazones.

Experimental.—Aminochrome semicarbazones. Adrenochrome monosemicarbazone was available commercially (Koch-Light Laboratories). 7-Methyladrenochrome monosemicarbazone,[3] *N*-isopropylnoradrenochrome monosemicarbazone,[4] and 2-methylnoradrenochrome monosemicarbazone [4] were prepared by the methods described in the literature.

2-Methyladrenochrome monosemicarbazone. A solution of 3,4-dihydroxyephedrine hydrochloride (m. p. 190—192°; lit.,[5] 190—191°) (5 g., prepared from α-bromo-3,4-dimethoxypropiophenone by a procedure similar to that described for the preparation of the analogous homoephedrine derivative [6]) in water (50 ml.) was oxidised with a solution of potassium ferricyanide (30 g.) and sodium hydrogen carbonate (10 g.) in water (100 ml.). A solution of semicarbazide hydrochloride (8 g.) and sodium acetate (8 g.) in water (50 ml.) was added to the above deep red solution. After the mixture had been stirred at room temperature for 10 min. and allowed to stand at 5° for 5 hr., an orange solid separated out, which on recrystallisation from aqueous pyridine afforded *2-methyladrenochrome monosemicarbazone* (3·2 g.) as orange needles (totally decomposed, without melting, by 222°) (Found: C, 52·8; H, 5·7; N, 22·2. $C_{11}H_{14}N_4O_3$ requires C, 52·8; H, 5·6; N, 22·4%).

Degradation of semicarbazones. Solid potassium hydroxide (2 g.) was added, with stirring, in a nitrogen atmosphere, to a suspension of the aminochrome monosemicarbazone (0·5 g.) in water (20 ml.) at 90°; the resulting deep red-brown solution was boiled (in an atmosphere of nitrogen) until effervescence had ceased (*ca.* 2—5 min.). The temperature of the solution was reduced to *ca.* 50° by the addition of crushed ice; dimethyl sulphate (2·5 ml.) was added dropwise and the mixture was cautiously heated to 80°, and maintained at this temperature for 5 min. The resulting solution was cooled to room temperature and extracted several times

The degradation of some aminochrome monosemicarbazones to some 6-methoxyindole derivatives

Semicarbazone	6-Methoxyindole	Yield (mg.)[a] (%)	M. p.	Ultraviolet absorption maxima (mμ) of product[b]	Found (%) C	H	N	Reqd. (%) C	H	N
Adrenochrome	*N*-Methyl[c]	160 (46)	30°[d]	222, 274, 291, 299sh[e,f]						
7-Methyladrenochrome	7,N-Dimethyl[g]	190 (54)	93°	224, 275, 292sh, 302sh	75·6	7·3	8·0	75·4	7·5	8·0
N-Isopropylnoradrenochrome	N-Isopropyl[h]	90 (25)	Oil[i]	227, 275, 294, 302sh	76·2	8·0	7·2	76·2	8·0	7·4
2-Methylnoradrenochrome	2-Methyl[j]	140 (41)	103°[k]	224, 267, 297	74·5	7·0	8·9	74·5	6·9	8·7
2-Methyladrenochrome	2,N-Dimethyl	130 (38)	78—79°	227, 275, 295, 306sh	75·4	7·6	8·1	75·4	7·5	8·0

[a] The yield of product obtained from 0·5 g. of the semicarbazone. [b] The spectra of the 6-methoxyindole derivatives were recorded in solution in ethanol on a Unicam S.P. 800 recording spectrophotometer. [c] Purified *via* the picrate. The picrate was obtained as red-brown needles from ethanol, m. p. 123° (lit.,[1] 123°). [d] Lit.,[1] m. p. 30—32°. [e] Lit.[1] values 224, 275, 292 mμ. [f] sh = shoulder. [g] Purified by recrystallisation from light petroleum (b. p. 80—100°) or heptane. [h] Purified by high-vacuum distillation or *via* the picrate. The picrate of 6-methoxy-*N*-isopropylindole was obtained as red-brown needles from aqueous ethanol, m. p. 96° (Found: C, 51·9; H, 4·5; N, 13·2. $C_{18}H_{18}N_4O_8$ requires C, 51·7; H, 4·3; N, 13·4%). [i] B. p. 70° (bath)/0·2 mm. [j] Purified by recrystallisation from light petroleum (b. p. 80—100°) or heptane. [k] Lit.,[7,8] m. p. 102—103°. [l] Purified *via* the picrate. The picrate of 6-methoxy-2,*N*-dimethylindole was obtained as red-brown needles from aqueous ethanol, m. p. 125—126° (Found: C, 50·6; H, 4·1; N, 14·0. $C_{17}H_{16}N_4O_8$ requires C, 50·5; H, 4·0; N, 13·9%).

[3] R. A. Heacock and O. Hutzinger, *Canad. J. Chem.*, submitted for publication.
[4] J. D. Bu'Lock and J. Harley-Mason, *J.*, 1951, 712.
[5] M. Brockmühl, G. Ehrhart, and L. Stein, U.S.P. 1,877,756/1932 (*Chem. Abs.*, 1933, **27**, 1095).
[6] A. Lespagnol and E. Cuinguet, *Ann. pharm. franç.*, 1960, **18**, 445.
[7] E. Späth and O. Brunner, *Ber.*, 1925, **58**, 518.
[8] Th. Wieland and K. Rühl, *Chem. Ber.*, 1963, **96**, 260.

with peroxide-free ether. The combined extracts were washed with N-potassium hydroxide solution, dried (Na_2SO_4), and evaporated to dryness. When possible, the crude product was purified by recrystallisation from a suitable solvent, light petroleum (b. p. 80—100°), or heptane, or by distillation *in vacuo*. In some cases, however, it was necessary to isolate the 6-methoxyindole derivative as its picrate, and to regenerate the product by decomposing the complex on an alumina column. The relevant data for the compounds prepared are given in the Table.

This investigation was supported by grants from the Department of National Health and Welfare (Ottawa) and the Saskatchewan Department of Public Health.

THE PSYCHIATRIC RESEARCH UNIT, UNIVERSITY HOSPITAL,
SASKATOON, SASKATCHEWAN, CANADA. [*Received, January 11th*, 1965.]