464. *The Synthesis of Polyenes with the 1,2-Dimethylprop-1-enyl Group. Isolation of a* cis-*Isomer with Steric Hindrance.*

By D. F. SCHNEIDER and C. F. GARBERS.

POLYENES (III; $n = 0$—3), required for epoxidation studies, have been synthesised by the Wittig reaction.[1] Condensation of the phosphorane (I) with the appropriate all-*trans*-aldehyde (II) gave a mixture of the all-*trans*-polyene (III) and the sterically hindered 4,5-*cis*-isomer (III). Fractionation of the product from the condensation of crotonaldehyde and the phosphorane (I) gave the pure 4,5-*cis*- and all-*trans*-trienes (III; $n = 1$) in an approximate ratio of 1 : 4. No effort was made to isolate the 4,5-*cis*-diene (III; $n = 0$)

$$Me_2C\!:\!CMe\!\cdot\!CH\!:\!PPh_3 + Me\!\cdot\![CH\!:\!CH]_n\!\cdot\!CHO \longrightarrow Me_2C\!:\!CMe\!\cdot\![CH\!:\!CH]_{n+1}\!\cdot\!Me$$
$$\text{(I)} \qquad\qquad \text{(II)} \qquad\qquad \text{(III)}$$
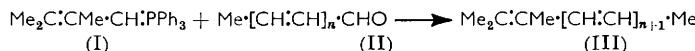
or the 4,5-*cis*-tetraene (III; $n = 2$), but the respective *cis*-isomer, present in the isolated polyenes, was easily isomerised to the corresponding all-*trans*-polyene by addition of traces of iodine. However, the all-*trans*-pentaene (III; $n = 3$) was obtained directly; the higher boiling point of this polyene probably caused the isomerisation of any *cis*-isomer present to the *trans*-isomer, since sterically hindered *cis*-isomers are known to be thermally unstable.

The formation of *cis*- and *trans*-isomers in the Wittig reaction had been observed before.[1,2] If there is much steric hindrance in the *cis*-isomer,[1] or if the phosphorane is stabilised by resonance,[3] the *trans*-isomer is obtained almost exclusively. Furthermore, the stereoselective synthesis of *cis*-olefins from alkylidenetriphenylphosphoranes can be carried out in polar solvents in the presence of Lewis bases.[4] Although the phosphorane (I), from (2,3-dimethylbut-2-enyl)triphenylphosphonium bromide, is partly stabilised by resonance, the formation of some sterically hindered *cis*-isomer in the condensation with the aldehyde (II), in the presence of bromide ion, is therefore to be expected.

The 4,5-*cis*-triene (III; $n = 1$) had an ultraviolet spectrum (Fig. 1) similar to that of other sterically hindered *cis*-isomers.[5] Its infrared spectrum (Fig. 2) markedly differed in the C–H out-of-plane region from that of the all-*trans*-triene (III; $n = 1$). Other sterically hindered *cis*-polyenes exhibit well defined bands at 770—750 cm.$^{-1}$ and no effects in the infrared spectra, attributable to the steric hindrance present, are immediately apparent.[5,6] The infrared spectrum of the 4,5-*cis*-triene (III; $n = 1$) rather resembles those of certain compounds with cyclic disubstituted double bonds.[7] Three strong bands (950, 820, and a narrow triplet at 750, 737, and 725 cm.$^{-1}$) are present for the *cis*- and absent for the all-*trans*-triene (III; $n = 1$). It appears that these three main bands can be related equally well to the sterically hindered olefinic bond.

As an alternative synthesis of the triene (III; $n = 1$), the condensation of iso-propylidenetriphenylphosphorane with but-2-enylideneacetone was attempted. A white precipitate, similar in appearance to the betaine formed in Wittig reactions conducted in ether, was obtained. Heating of this caused no visible change, and treatment with aqueous hydrogen bromide gave isopropyltriphenylphosphonium bromide (83%), which indicated that no new carbon–carbon bond had been formed in the intermediate. The

[1] Trippett, "Advances in Organic Chemistry. Methods and Results," ed. Raphael, Taylor, and Wynberg, Interscience, New York, 1960, Vol. I, p. 83; Schöllkopf, *Angew. Chem.*, 1959, **71**, 260.
[2] Hauser, Brooks, Miles, Raymond, and Butler, *J. Org. Chem.*, 1963, **28**, 372.
[3] House and Rasmusson, *J. Org. Chem.*, 1961, **26**, 4278.
[4] Bergelson and Shemyakin, *Tetrahedron*, 1963, **19**, 149.
[5] *E.g.*, Oroshnik and Mebane, *J. Amer. Chem. Soc.*, 1954, **76**, 5719.
[6] von Planta, Schwieter, Chopard-dit-Jean, Rüegg, Kofler, and Isler, *Helv. Chim. Acta*, 1962, **45**, 548.
[7] Henbest, Meakins, and Wood, *J.*, 1954, 800; Henbest, Meakins, Nicholls, and Wilson, *J.*, 1957, 997.

isopropylidenetriphenylphosphorane probably abstracted a proton from the ketone to give the isopropyltriphenylphosphonium alkoxide (IV).[8] Since the completion of this

$$Ph_3P \cdot CHMe_2^+ \ Me \cdot [CH \vdots CH]_2 \cdot C(O^-) \vdots CH_2 \quad (IV)$$
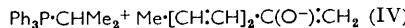
work it has been reported that Wittig reactions between phosphoranes and $\alpha\beta$-unsaturated ketones proceed with difficulty, if at all.[9]
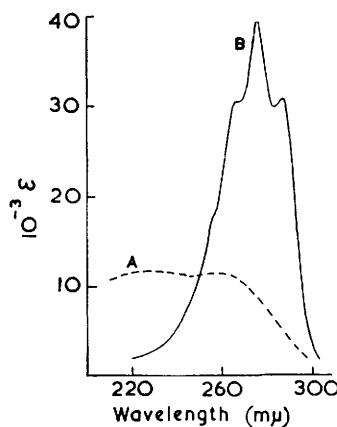

FIG. 1. Ultraviolet spectra of (A) 2,3-dimethyl-4,5-*cis*-octa-2,4,6-triene, and (B) the same solution after isomerisation to all-*trans*-2,3-dimethylocta-2,4,6-triene in cyclohexane.
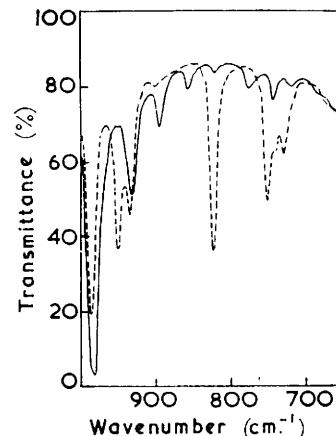
FIG. 2. Infrared spectra of 2,3-dimethyl-4,5-*cis*-octa-2,4,6-triene (broken line) and all-*trans*-2,3-dimethylocta-2,4,6-triene (full line).

Experimental.—Light petroleum had b. p. 40—60°. As far as possible operations were carried out in a nitrogen atmosphere.

(2,3-Dimethylbut-2-enyl)triphenylphosphonium bromide. Quaternisation of triphenylphosphine (140 g.) in ether (500 ml.) with 1-bromo-2,3-dimethylbut-2-ene (80 g.) in ether (100 ml.) gave the *phosphonium salt* (200 g.), m. p. 192° (from benzene–ethanol) (Found: C, 67·7; H, 5·8. $C_{24}H_{24}BrP$ requires C, 67·8; H, 6·1%).

Synthesis of polyenes. (a) *2,3-Dimethylhexa-2,4-diene.* The phosphorane (I), prepared from the phosphonium salt (100 g.) in ether (500 ml.) and ethereal 0·64N-phenyl-lithium (377 ml.), reacted with acetaldehyde (11·5 g.) in ether (20 ml.), to give the intermediate betaine which was decomposed by refluxing the mixture for 20 hr. under pressure (840 mm.). The crude dienes were isolated, dissolved in light petroleum, and filtered through alumina. The eluate was evaporated and the residue distilled, to yield a mixture of the *cis*- and *trans*-dienes (III; $n = 0$) (11·5 g.), b. p. 128—137°, which was dissolved in ether and treated with iodine (1% by weight). The solution was left in diffuse daylight for 2 hr., washed with aqueous sodium thiosulphate and water, dried, and the solvent evaporated. Distillation of the residue gave the all-*trans*-*diene* (III; $n = 0$), b. p. 137—138°, n_D^{25} 1·4752, λ_{max} (in 96% EtOH) 240 mμ (ε 20,700) (Found: C, 86·8; H, 13·1. C_8H_{14} requires C, 87·3; H, 12·7%).

(b) *4,5-cis- and all-trans-2,3-dimethylocta-2,4,6-triene* (III; $n = 1$). The betaine, prepared as in (a) from the phosphonium salt (50 g.) and crotonaldehyde (8·7 g.), was heated at 60° for 5 hr., and the mixture worked up as in (a). The residue after chromatography on alumina was fractionated, to yield: (i) *4,5-cis-triene* (III; $n = 1$) (1·3 g.), b. p. 59—61°/15 mm., λ_{max} (in cyclohexane) 225—232, 254—257 mμ (ε 11,600, 11,400) (Found: C, 88·4; H, 11·75. $C_{10}H_{16}$ requires C, 88·2; H, 11·8%); (ii) intermediate fraction (2 g.), b. p. 62—83°/15 mm.; and (iii) all-*trans*-*triene* (III; $n = 1$) (4·6 g.), b. p. 83°/15 mm., n_D^{25} 1·5450, λ_{max} (in cyclohexane) 276, 287 mμ (ε 42,600, 32,900), ν_{max} (film) 984 cm.$^{-1}$ (Found: C, 87·6; H, 11·7%).

The 4,5-*cis*-triene (III; $n = 1$) (3·79 mg.), in cyclohexane, was treated with iodine (0·04 mg.),

[8] Ansell and Thomas, *J.*, 1961, 539.
[9] *E.g.*, Trippett and Walker, *J.*, 1961, 1266; Pommer, *Angew. Chem.*, 1960, **72**, 811.

and after 4 hr. in diffuse daylight the solution showed an absorption spectrum similar to that of the all-*trans*-triene, λ_{max}. 276, 287 mμ (ε 39,300, 30,700).

(c) *2,3-Dimethyldeca-2,4,6,8-tetraene.* The condensation of the phosphorane (I) and hexa-2,4-dienal (II; $n = 2$) was carried out as in (a), and, after refluxing of the mixture on a water-bath for 4 hr., the *cis*- and *trans*-iomers (III; $n = 2$) (74%), b. p. 61—74°/0·01 mm., were isolated and isomerised as in (a), to yield the *all*-trans-*tetraene* (III; $n = 2$), b. p. 71—72°/0·03 mm., λ_{max}. (in 96% EtOH) 295, 307, 322 mμ (ε 37,000, 53,700, 46,800) (Found: C, 89·0; H, 11·0. $C_{12}H_{18}$ requires C, 88·9; H, 11·1%).

(d) *2,3-Dimethyldodeca-2,4,6,8,10-pentaene.* Octa-2,4,6-trienal (II; $n = 3$), prepared according to the procedure of Pippen and Nonaka in 71% yield,[10] b. p. 65—67°/0·5 mm., m. p. 57° (from light petroleum) (Found: C, 78·5; H, 8·3. Calc. for $C_8H_{10}O$: C, 78·7; H, 8·2%), was condensed with the phosphorane (I), to give a betaine which was decomposed by stirring for 1 hr. at room temperature. The reaction mixture was worked up as in (a), and, after chromatography, the pentaene was isolated as a solid (91%). Distillation gave the *all*-trans-*pentaene* (III; $n = 3$), b. p. 114—116°/0·6 mm., λ_{max}. (in cyclohexane) 321, 337, 355 mμ (ε 44,700, 70,500, 67,900) (Found: C, 89·5; H, 10·7. $C_{14}H_{20}$ requires C, 89·4; H, 10·6%).

Reaction of isopropylidenetriphenylphosphorane with but-2-enylideneacetone. But-2-enylideneacetone (17·2 g.) in ether (20 ml.) was added to isopropylidenetriphenylphosphorane, prepared from isopropyltriphenylphosphonium bromide (60 g.) and ethereal 0·722N-phenyl-lithium (216 ml.). In an exothermic reaction a thick white precipitate formed, which was heated at 60° for 5 hr. No apparent change took place, and solids were filtered off, boiled with ether, and collected at the pump. The solid was treated with an excess of aqueous hydrogen bromide and the reaction mixture extracted with chloroform. The extract was dried, filtered, evaporated *in vacuo*, and the residue recrystallised repeatedly from ethanol–benzene, to yield isopropyltriphenylphosphonium bromide (49·8 g., 83%), m. p. and mixed m. p. 239°.

The ether-soluble material gave a distillate (1·6 g.), b. p. 80—85°/22 mm., shown by gas chromatography to consist of four components; also, a residue from which triphenylphosphine (3 g.), m. p. (from EtOH) and mixed m. p. 79°, was isolated.

UNIVERSITY OF STELLENBOSCH, STELLENBOSCH,
    REPUBLIC OF SOUTH AFRICA.

[10] Pippen and Nonaka, *J. Org. Chem.,* 1958, **23**, 1580.

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465. *Potassium Trisoxalatoruthenium*(III): *Magnetic Susceptibility, Absorption Spectrum, and Ligand-exchange Experiments.*

By R. W. OLLIFF and A. L. ODELL.

As part of a more extensive investigation [1] of oxalato-complexes, spectroscopic, magnetic, and exchange data on the trisoxalatoruthenium(III) complex have been obtained. Unlike its ferric analogue,[2] the ruthenium complex has a low magnetic moment [3-5] and shows no ligand exchange.

Experimental.—Potassium trisoxalatoruthenium(III) was prepared by the methods of Charonnat,[3,4] and by dissolving ruthenium(III) hydroxide in boiling oxalic acid solution (Found: Ru, 18·6; C_2O_4, 46·8. Calc. for $K_3RuOx_3,4\frac{1}{2}H_2O$: Ru, 18·0; C_2O_4, 46·8%).

Solutions of the complex gave no precipitate with barium chloride until acidified, and no test for higher oxidation states of ruthenium when tested by the method of Crowell and Yost.[6]

[1] Odell and Olliff, *J.,* 1964, 2417.
[2] Weinland and Holtmeier, *Z. anorg. Chem.,* 1928, **173**, 49; Clark, Curtis, and Odell, *J.,* 1954, 63.
[3] Charonnat, *Compt. rend.,* 1924, **178**, 1279.
[4] Charonnat, *Ann. Chim. (France),* 1931, (x), **16**, 123.
[5] Dwyer and Sargeson, *J. Phys. Chem.,* 1956, **60**, 1331.
[6] Crowell and Yost, *J. Amer. Chem. Soc.,* 1928, **50**, 374.

Magnetic measurements were performed with the Gouy balance described previously.[2]

Ultraviolet absorption spectra were obtained on a Shimadzu Spectrophotometer, mode QR 50.

Ligand-exchange experiments were carried out by using carbon-14-labelled sodium oxalate, prepared [2] from sodium [^{14}C]formate (obtained from the Radiochemical Centre, Amersham, England). Solutions of the complex were mixed with solutions of the labelled ligand, and aliquot portions removed after various time intervals. The free ligand was precipitated as barium oxalate and counted as infinitely thick solid samples with an end-window geiger counter. Acidification of the filtrate and addition of further barium ions caused decomposition of the complex and precipitation of barium oxalate. The sample of " complexed " oxalate was always slightly contaminated with " free " ligand.

Results and Discussion.—(a) *Magnetic susceptibility.* The magnetic susceptibility data for the solid complex were as follows.

$$90°\text{K}: \chi_g = 7\cdot91 \times 10^{-6}\text{c.g.s.u.}; \quad \chi_m = 4460 \times 10^{-6}\text{c.g.s.u.}; \quad \mu_{\text{eff.}} = 1\cdot80 \text{ B.M.}$$

$$198°\text{K}: \chi_g = 4\cdot25 \times 10^{-6}\text{c.g.s.u.}; \quad \chi_m = 2400 \times 10^{-6}\text{c.g.s.u.}; \quad \mu_{\text{eff.}} = 1\cdot95 \text{ B.M.}$$

$$298°\text{K}: \chi_g = 3\cdot00 \times 10^{-6}\text{c.g.s.u.}; \quad \chi_m = 1690 \times 10^{-6}\text{c.g.s.u.}; \quad \mu_{\text{eff.}} = 2\cdot04 \text{ B.M.}$$

The value at room temperature is in good agreement with that of Dwyer and Sargeson ($\mu_{\text{eff.}} = 2\cdot01$ B.M.).[5] Measurements on aqueous solutions at $298°\text{K}$ gave $\chi_g = 3\cdot09 \times 10^{-6}$ c.g.s.u., in substantial agreement with the value obtained for the solid.

The variation of $\mu_{\text{eff.}}$ with temperature has been considered by Kotani.[7] For low-spin d^5 complexes with considerable spin–orbit coupling, Kotani's formula is $\mu_{\text{eff.}} = (3 + 8kT/\lambda)^{\frac{1}{2}}$, where λ is the spin–orbit coupling constant. The above data lead to $\lambda = -1440$ cm.$^{-1}$ for $K_3RuOx_3,4\frac{1}{2}H_2O$. This can be compared with λ-values for other Ru(III) compounds, derived from magnetic susceptibility values in the literature.[8-11] These λ-values range from -820 to -2280 cm.$^{-1}$, with a mean value of -1270 cm.$^{-1}$.

The best method for obtaining spin–orbit coupling data is that of paramagnetic resonance absorption. However only one Ru(III) complex has been investigated in any detail, $Ru(NH_3)_6Cl_3$,[12] and this study is complicated by the presence of three crystallographically distinct types of ruthenium. The data are not inconsistent with a λ-value of about -1500 cm.$^{-1}$. Griffiths [13] suggests a value of $\lambda = -1490$ cm.$^{-1}$. Figgis [14] has suggested that a slight distortion along one of the octahedral axes would lead to a similar splitting of the d_ϵ level when combined with the spin–orbit coupling effect. Such a distortion could be expected to arise from the Jahn-Teller effect, but as Orgel [15] has pointed out this would be expected to be small in low-spin d^5 complexes unless there was a high degree of π-bonding. Fitting our results to the tables given by Figgis [14] leads to: spin–orbit coupling, $\lambda = -1330$ cm.$^{-1}$; trigonal splitting, $\Delta' = 1330$ cm.$^{-1}$; electron delocalisation constant, $k = 0\cdot9$. The positive value of Δ' indicates elongation of the bonds along one axis, but the actual lengthening is probably quite small.

It has been pointed out by Howard,[16] and by Bleaney and O'Brien,[17] that a complete interpretation of low-spin paramagnetic resonance results requires a consideration of electron delocalisation, in agreement with the value of k found above.

[7] Kotani, *J. Phys. Soc. Japan*, 1949, **4**, 293.

[8] Asmussen, " Magnetochemistry of Complexes," Jul, Gjellerups Forlag, Copenhagen, 1944, p. 160.

[9] Hartmann and Buschbeck, *Z. phys. Chem. (Frankfurt)*, 1957, **11**, 120.

[10] Lewis and Mabbs, quoted in Lewis and Wilkins, " Modern Inorganic Chemistry," Interscience, New York, 1960, p. 448.

[11] Gleu and Rehm, *Z. anorg. Chem.*, 1936, **227**, 237.

[12] Griffiths, Owen, and Ward, *Proc. Roy. Soc.*, 1953, *A*, **219**, 526.

[13] Griffiths, " The Theory of Transition Metal Ions," Cambridge University Press, Cambridge, 1961, p. 438.

[14] Figgis, *Trans. Faraday Soc.*, 1961, **57**, 198.

[15] Orgel, " Transition Metal Chemistry," Methuen, London, 1960, p. 62.

[16] Howard, *J. Chem. Phys.*, 1935, **3**, 207.

[17] Bleaney and O'Brien, *Proc. Phys. Soc.*, 1956, *B*, **69**, 1216.

(b) *Absorption spectrum.* The spectrum consists of four absorption bands (at 15,850, 20,400, 26,600, and 34,700 cm.$^{-1}$) superimposed on what appears to be a charge-transfer band at about 200 mμ. On the assumption that this large band has a guassian shape, it is possible to obtain corrected molar extinction coefficients for the ligand-field bands. The values of $\varepsilon_{corr.}$ for the above bands are 11, 28, 350, and 320, respectively.

The spectrum was the same when measured on solutions of the complex in water and on solutions obtained by dissolving ruthenium(III) hydroxide in oxalic acid.

The strong-field electrostatic matrices of Tanabe and Sugano [18] predict eight transitions from the ground state, d_{ϵ}^5, to the doublet states of the configuration $d_{\epsilon}^4 d_{\gamma}^1$, and two transitions from the ground state to quartet states of $d_{\epsilon}^4 d_{\gamma}^1$.

If the two low-intensity bands (15,850 and 20,400 cm.$^{-1}$) are assigned to the two spin-forbidden transitions, they should be separated by $8B$, whence $B = 560$ cm.$^{-1}$. If we assume that $C/B = 4$, we obtain $10Dq = 28,700$ cm.$^{-1}$

Using these values of Dq and B, the eight doublet–doublet transitions are predicted to be in the range 250—400 mμ. By including non-diagonal elements in the Tanabe–Sugano matrices, it can be seen that they fall into two groups, each of four transitions of similar energy. Graphical superimposition of gaussian curves of $\varepsilon = 100$ at the predicted positions shows that only two clear maxima will be observed, with ε of 350—400. From the observed peaks, $10Dq$ and B can be estimated to be 28,000 and 500 cm.$^{-1}$, respectively.

(c) *Reactivity.* No ligand exchange was observed before decomposition became serious (20 min.); this result is in accord with the general unreactivity of low-spin complexes.

[18] Tanabe and Sugano, *J. Phys. Soc. Japan*, 1954, **9**, 753, 766.

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466. *Differences in Amine Substitution Reactions of some Fluoroperhalogenomethylphosphines.*

By JOHN F. NIXON.

THE literature does not contain reports of the reaction between alkyl- or aryl-fluorophosphines and amines, although studies of the reaction between $Ni(PF_3)_4$ [1] and PF_3,BH_3 [2] with ammonia indicate that complete ammonolysis of the P–F bonds occurs in each case. Stable fluorophosphines of the type RPF_2 and R_2PF have been synthesised only in cases where R is an electron-withdrawing group.[3-6] This Note is concerned with the amine substitution reactions of two such fluorophosphines, where the electron-withdrawing groups are trichloromethyl and trifluoromethyl, and illustrates the factors affecting the mechanism of the reaction.

When difluorotrichloromethylphosphine [6] is treated with dimethylamine, no salt formation occurs, but the phosphorus–carbon bond breaks, producing chloroform and dimethyl-aminodifluorophosphine:

$$CCl_3 \cdot PF_2 + Me_2NH \longrightarrow CCl_3H + F_2P \cdot NMe_2$$

[1] Seel, Ballreich, and Schmutzler, *Chem. Ber.*, 1961, **94**, 1173.
[2] Kodama and Parry, *J. Inorg. Nuclear Chem.*, 1961, **17**, 125.
[3] Kulakova, Zinovev, and Soborovskii, *J. Gen. Chem. (U.S.S.R.)*, 1959, **29**, 3916.
[4] Schmutzler, *Chem. and Ind.*, 1962, 1868.
[5] Burg and Brendel, *J. Amer. Chem. Soc.*, 1958, **80**, 3198.
[6] Nixon, *Chem. and Ind.*, 1963, 1555.

The latter product has been prepared by fluorination of the corresponding chloro-compound,[7] and by the direct reaction of dimethylamine with phosphorus trifluoride.[8]

Fluorobistrifluoromethylphosphine, $(CF_3)_2PF$,[5] on the other hand, splits out hydrogen fluoride to give dimethylaminobistrifluoromethylphosphine, $(CF_3)_2P \cdot NMe_2$.[9] Preliminary studies also indicate that difluorotrifluoromethylphosphine, $CF_3 \cdot PF_2$, is cleaved at the phosphorus–fluorine bond.[10]

The reaction between difluorotrichloromethylphosphine and dimethylamine is the first report of phosphorus–carbon cleavage with the phosphorus–halogen bonds remaining intact, since previous reports show that cleavage of the perfluoroalkyl group attached to phosphorus (*e.g.*, the alkaline hydrolysis of halogenoperfluoroalkylphosphines [11,12]) always led to simultaneous fission of the phosphorus–halogen bonds.

The difference in behaviour of these systems arises from the greater ease of carbanion formation of the trichloromethyl group compared with fluorine or trifluoromethyl. The perhalogenomethyl groups can act as pseudo-halogens, and have been assigned the following values on the Pauling electronegativity scale: CF_3, 3·3;[13] CCl_3, 2·76.[14] If bond-energy considerations were the most important in these reactions, both trifluoro- and trichloromethylfluorophosphines would be expected to be cleaved at the phosphorus–carbon bond, owing to the great strength of the P–F bond.

Studies with haloforms [15] indicate that the effects of polarisability and *d*-orbital resonance are important in determining the ease of carbanion formation. The high energy required to expand the outer electronic octet of fluorine would thus explain why fluorine is the poorest of the halogens at facilitating carbanion formation, despite its greater electronegativity.

From the above observations, and from the fact that dichlorotrichloromethylphosphine undergoes P–Cl fission rather than P–C fission when treated with dimethylamine,[10] it appears that the order of ease of carbanion formation in these substitution reactions at phosphorus is $Cl > CCl_3 > F > CF_3$.

EXPERIMENTAL

Experimental.—The compounds were extremely sensitive to air and moisture, and were handled in a high-vacuum manifold. Stopcocks were lubricated with Halocarbon grease, and molecular-weight and vapour-tension measurements were obtained using an immersible tensimeter in conjunction with mercury manometers.

Preparation of fluorophosphines. The preparation of difluorotrichloromethylphosphine was described previously.[6] Vapour-tension measurements on the liquid in the range 16—40° lead to the equation $\log_{10} p$ (mm.) $= 7 \cdot 777 - 1699/T$, b. p. 73·1°, and a Trouton constant of 22·4 cal./deg. mole. Similarly, measurements on the solid in the range —9 to 10° lead to the equation $\log_{10} p$ (mm.) $= 8 \cdot 543 - 1920/T$. From the two equations the m. p. is calculated to be 15·2°, in good agreement with that observed (15·8—16·4°). The infrared spectrum, measured on a Perkin–Elmer model 21 double-beam spectrometer, using a 10 cm. gas cell with sodium chloride windows, consists of a very strong absorption at 844 cm.$^{-1}$ and a shoulder at 860 cm.$^{-1}$ (P–F stretching), and a medium peak at 777 cm.$^{-1}$ and a shoulder at 765 cm.$^{-1}$ (C–Cl stretching). A weak absorption at 812 cm.$^{-1}$ was not assigned. The ^{19}F and ^{31}P nuclear magnetic resonance spectra have been described.[6]

Fluorobistrifluoromethyl- and difluorotrifluoromethyl-phosphine were prepared by known methods,[3,5] and their purity was confirmed by molecular weight, vapour tension, infrared and ^{19}F nuclear magnetic resonance measurements. A point of interest emerging from the infrared

[7] Noth and Vetter, *Chem. Ber.*, 1963, **96**, 1298.
[8] Cavell, unpublished results.
[9] Harris, *J.*, 1958, 512.
[10] Nixon, unpublished results.
[11] Bennett, Emeléus, and Haszeldine, *J.*, 1953, 1565.
[12] Emeléus and Smith, *J.*, 1959, 375.
[13] Lagowski, *Quart. Rev.*, 1959, **13**, 233.
[14] Kangarise, *J. Amer. Chem. Soc.*, 1955, **77**, 1377.
[15] Hine, Burske, Hine, and Langford, *J. Amer. Chem. Soc.*, 1957, **79**, 1406.

spectra is the steady increase in the P–F stretching frequency in the series $(CF_3)_2PF$, $CF_3 \cdot PF_2$, PF_3 (855, 870, 892 cm.$^{-1}$) [16] as the trifluoromethyl group is replaced by the more electronegative fluorine.

In a typical experiment, difluorotrichloromethylphosphine (2·056 mmoles) and dimethylamine (1·965 mmoles) reacted on warming the mixture slowly from $-196°$ to room temperature, with total consumption of the amine. No salt formation occurred and subsequent vacuum fractionation gave a colourless liquid at $-78°$ which was shown to be a mixture of chloroform and dimethylaminodifluorophosphine by molecular weight determination (Found: 115·0; CCl_3H, 119·3. Calc. for $F_2P \cdot NMe_2$, 113·0). The infrared spectrum showed the two components clearly, whilst the proton nuclear magnetic resonance spectrum showed only a pair of triplets identical with those of a genuine sample of the phosphine,[8] and a single low-field line (τ 2·75) which was attributed to chloroform.

Complete separation of the components could not be achieved by further fractionation, presumably because of hydrogen-bonding effects enhanced by the low bath-temperatures. Hydrogen chloride was added to the mixture, to give immediately dimethylamine hydrochloride (1·827 mmoles), and the chlorodifluorophosphine so formed was easily separated from the much less volatile chloroform (1·980 mmoles). Sometimes the products contained small amounts ($<5\%$) of trisdimethylaminophosphine [17] formed by a competing reaction of dimethylaminodifluorophosphine with the amine.

Fluorobistrifluoromethylphosphine reacted immediately with dimethylamine on warming to room temperature, with formation of a white solid. The major product was dimethylaminobistrifluoromethylphosphine, $(CF_3)_2P \cdot NMe_2$ (74%), identified by its molecular weight (Found: 215·5. Calc. 213), vapour tension, and infrared spectrum.[9] The identity was absolutely confirmed by the proton nuclear magnetic resonance spectrum which consisted of a doublet of septets.[18] A small amount ($<10\%$) of more volatile material was identified as fluoroform by its infrared spectrum.

Difluorotrifluoromethylphosphine employed in one experiment caused salt formation; this work will be described in a later Paper.

[16] Wilson and Polo, *J. Chem. Phys.*, 1952, **20**, 1716.
[17] Burg and Slota, *J. Amer. Chem. Soc.*, 1958, **80**, 1107.
[18] Packer, *J.*, 1963, 960.

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467. *The Preparation and Properties of Trichloromethyl-phosphonous Acid.*

By John F. Nixon.

Whereas the trichloromethyl group in trichlorotrichloromethylsilane is readily cleaved by cold water,[1] the corresponding trifluoromethyl compound [2] can be hydrolysed to a trifluoromethylpolysiloxane. Likewise, trifluoromethylphosphonous acid solutions have been prepared by aqueous hydrolysis of the phosphonous dihalides at room temperature,[3] and trichloromethylphosphonous dichloride is decomposed by boiling water [4] to chloroform and phosphorous acid. We now report the very slow (2 days at room temperature) hydrolysis of trichloromethylphosphonous dichloride to trichloromethylphosphonous acid, $CCl_3P(OH)_2$. The acid is a colourless, involatile, cystalline solid, melting at 34° with decomposition, and is trimeric, thus differing from the dimeric trifluoromethyl analogue.[5]

[1] Di Giorgio, Sommer, and Whitmore, *J. Amer. Chem. Soc.*, 1948, **70**, 3512.
[2] Haszeldine and Marklow, *J.*, 1956, 962.
[3] Bennett, Eméleus, and Haszeldine, *J.*, 1954, 3896.
[4] Ginsburg and Yakubovich, *J. Gen. Chem. (U.S.S.R.)*, 1958, **28**, 710.
[5] Burg and Griffiths, *J. Amer. Chem. Soc.*, 1961, **83**, 4333.

The equivalent weight indicates that the acid is monobasic, and is therefore more accurately formulated as the phosphinic acid trimer $(CCl_3HPO\cdot OH)_3$.

The infrared spectrum provides further evidence for this structure, showing medium-weak, but sharp, absorption at 2380 cm.$^{-1}$, attributed to P–H-stretching, and a strong band at 978 cm.$^{-1}$, probably due to the bending of the P–H bond.[6] The P=O stretching mode is seen clearly in the sodium or potassium salt, but in the acid the strong band at 1228 cm.$^{-1}$ is partly obscured by a very strong broad ($\sim$150 cm.$^{-1}$) band centred at 1060 cm.$^{-1}$, indicative of strong intermolecular hydrogen bonding within the trimer network since it disappears on salt formation. This assignment is supported by the absence of a band in the 3600 cm.$^{-1}$ region (free O–H stretching).

Three broad bands centred at 2900m, 2260w, and 1720m cm.$^{-1}$, which also disappear on salt formation, can be assigned, by analogy with recent work,[7] to vibrations of the O–H group under conditions of very strong hydrogen bonding. A strong band at 765 cm.$^{-1}$ is undoubtedly due to C–Cl stretching, whilst the remaining band of medium intensity at 784 cm.$^{-1}$ is in the region attributed to P–C stretching vibrations.[8,9] The nuclear magnetic resonance spectrum of an aqueous solution of the acid shows only a doublet for the hydrogen directly attached to phosphorus ($J_{P,H}$ = 605 c./sec.; τ = 3·15).

The P=O stretching frequency is lower than that of the corresponding trifluoromethyl compound,[5] and is in good agreement with the value predicted from the empirical formula of Bell *et al.*,[10] using a value of 2·76 [11] for the trichloromethyl group on the electronegativity scale.

Trichloromethylphosphonous acid is not decomposed to the corresponding phosphine in the normal way. Instead, cleavage of the phosphorus–carbon bond occurs, and chloroform is formed. This type of behaviour is known also for the perfluoroalkylphosphonous acids,[12,13] and *o*-hydroxy- and *p*-dialkylamino-phenylphosphonous acids.[14,15] Similar cleavage of the phosphorus–carbon bond occurs in the reduction of trichloromethyl-phosphonous dichloride with either silane or phosphine, leading to the formation of chloroform.

Experimental.—Trichloromethylphosphonous dichloride was prepared by heating white phosphorus and carbon tetrachloride in a sealed tube at 157° for 100 hr.[16] The waxy solid (m. p. 49·6—50°) was volatile *in vacuo* at room temperature, and was completely trapped out at −30° in the fractionation train of the vacuum system, but gave carbonyl chloride on exposure to air.

Aqueous hydrolysis. Trichloromethylphosphonous dichloride (4·926 mmoles) dissolved only very slowly when shaken in a sealed tube with about 2 ml. of water at room temperature, but solution was complete after 2 days. Removal of volatile components *in vacuo* and freeze-drying for 30 hr. gave 9·500 mmoles of hydrogen chloride, indicating that the reaction was 96·5% complete, giving a correspondingly high yield of the involatile, crystalline trichloromethyl-phosphonous acid.

The acids prepared by complete hydrolysis are invariably contaminated with small amounts of phosphorous acid formed by a much slower P–C cleavage, since the equivalent weights are slightly low ($\sim$175). If, however, the reaction is stopped after only 5 hr., and the unreacted trichloromethylphosphonous dichloride is pumped away, freeze-drying gives an acid whose equivalent is 183·2 (Calc. for $CCl_3HPO\cdot OH$: 183·4), m. p. 34°, stable in air for short periods but

[6] Nabi and Sheppard, *J.*, 1959, 3439; Linton and Nixon, *Spectrochim. Acta*, 1959, **15**, 146; Beachell and Katlafsky, *J. Chem. Phys.*, 1957, **27**, 182.
[7] Braunholtz, Hall, Mann, and Sheppard, *J.*, 1959, 868.
[8] Bellamy, " The Infra-red Spectra of Complex Molecules," Wiley, New York, 2nd edn., 1958.
[9] Daasch and Smith, *Ind. Eng. Chem.*, 1951, **23**, 853.
[10] Bell, Heisler, Tannenbaum, and Goldenson, *J. Amer. Chem. Soc.*, 1954, **76**, 5185.
[11] Kangarise, *J. Amer. Chem. Soc.*, 1955, **77**, 1377.
[12] Eméleus, Haszeldine, and Paul, *J.*, 1955, 563.
[13] Eméleus and Smith, *J.*, 1959, 375.
[14] Schenck and Michaelis, *Ber.*, 1888, **21**, 1497.
[15] Marie, *Compt. rend.*, 1902, **134**, 286; Ville, *ibid.*, 1890, **110**, 348.
[16] Perner and Henglein, *Z. Naturforsch.*, 1962, **17b**, 703.

slightly hygroscopic [Found (for typical preparations): C, 6·3, 6·1; H, 2·1, 1·4; Cl, 56·3; P, 16·0, 16·4%; M (in CH_2Cl_2, thermistor method [17]), 582, 544, 582. Calc. for $CCl_3HPO \cdot OH$: C, 6·5; H, 1·1; Cl, 58·0; P, 16·9%; M (for monomer), 183·4].

The sodium or potassium salts were prepared by careful neutralisation of the acid, and freeze-drying for 2 days. There was no noticeable evolution of chloroform but the anlytical data (Found: C, 4·4; H, 1·7; P, 14·25. Calc. for $CCl_3HPO \cdot OK$: C, 5·42; H, 0·5; P, 14·0%) indicated that some cleavage of the P–C bond was occurring at high pH values. This type of behaviour has also been observed in the analogous perfluoroalkylphosphonous acids.[12,13]

When trichloromethylphosphonous acid is heated in an evacuated tube, it easily decomposes to form chloroform, even when mixed with phosphorus pentoxide, which combines with any free water evolved in the decomposition. A sample of the acid which had stood in air for 14 days before heating produced carbonyl chloride in addition to chloroform, but no trichloro-methylphosphine.

Phosphine and silane reactions. Phosphine did not react with trichloromethylphosphonous dichloride at room temperature, and heating only led to a slight darkening of the solid at 160°, with evolution of small amounts of chloroform. Similarly, the dichloride (1·658 mmoles) and silane (2·440 mmoles) did not react at room temperature or at just above the melting point of the dichloride, but after 10 hr. at 100° some brown involatile solid had been formed. Fractionation of the volatile components yielded 1·191 mmoles of unchanged dichloride, 2·096 mmoles of unchanged silane, 0·284 mmoles of silyl chloride, and 0·234 mmoles of chloroform, but again no trichloromethylphosphine.

Infrared spectra were recorded on a Perkin-Elmer Infracord spectrometer. The nuclear magnetic resonance spectrum was recorded on a Perkin-Elmer spectrometer operating at 40 Mc./sec. Molecular-weight and microanalytical data were obtained by the analytical department in the University Chemical Laboratory.

[17] Neumayer, *Analyt. Chim. Acta,* 1959, **20**, 519.

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468. *Exchange and Rearrangement Reactions of Phenylallyl p-Chlorobenzoates.*

By J. KEITH ADDY and RICHARD M. NOYES.

THE isomerization of 1-phenylallyl to 3-phenylallyl esters is particularly convenient for the study of allylic rearrangements because the equilibrium lies far to the right and the extent of reaction can be followed easily by ultraviolet spectrophotometry. If the

$$Ph \cdot CHX \cdot CH \dot{:} CH_2 \text{ (RX)} \longrightarrow Ph \cdot CH \dot{:} CH \cdot CH_2 X \text{ (R'X)}$$

rearrangement involves an ion-pair intermediate, R^+X^-, the rate of exchange with iso-topically labelled X^- ions should be determined by the rate at which the reactants diffuse together. Since the rate constant for a diffusion-controlled process can probably be predicted *a priori* to within an order of magnitude, it was thought that a kinetic study of exchange accompanying allylic rearrangement might provide information about the lifetime of ion-pair intermediates.

Pocker [1a, b] studied the rearrangement of the phenylallyl benzoates and *p*-nitrobenzoates in chlorobenzene at 155°, and used ^{18}O-labelled benzoic acid and benzoates to demonstrate exchange during rearrangement, but he did not study the extent of exchange as a function of concentrations of benzoate salts. The Pocker procedure was cumbersome for detailed kinetic studies because each isotopic analysis required isolation and purification of product. Since *p*-chlorobenzoate can be labelled with a radioactive tracer, studies with it offered advantages. It also appeared that ion-pair lifetime would be enhanced in a

[1] Pocker, *J.*, 1958, (*a*) p. 4318; (*b*) p. 4323.

solvent having a higher dielectric constant than that of chlorobenzene, and *N*-methyl-2-pyrrolidone was finally selected (see Experimental section).

3-Phenylallyl *p*-chlorobenzoate was virtually stable, for the periods of time involved, in *N*-methylpyrrolidone at 140°. Under the same conditions, 1-phenylallyl *p*-chlorobenzoate both rearranged to the cinnamyl ester and decomposed to *p*-chlorobenzoic acid. Titrations indicated that acid was produced by 15% of the initial material, and spectrophotometric data were consistent with the remaining material's rearranging to 3-phenylallyl ester. The rate constant for the rearrangement was $3 \cdot 83 \times 10^{-6}$ sec.$^{-1}$, corresponding to a half-life of $50 \cdot 3$ hours.

Solutions of both esters also exchanged at 140° with benzylammonium [^{36}Cl]-*p*-chlorobenzoate. With $0 \cdot 2205$M-1-phenylallyl ester and $0 \cdot 1145$M-salt, the exchange rate was $1 \cdot 3 \times 10^{-6}$ mole l.$^{-1}$ sec.$^{-1}$ and the half-life $10 \cdot 8$ hours. With $0 \cdot 2722$M-3-phenylallyl ester and $0 \cdot 1781$M-salt, the exchange rate was $2 \cdot 3 \times 10^{-6}$ mole l.$^{-1}$ sec.$^{-1}$ and the half-life $9 \cdot 0$ hours.

Kinetic behaviour during more than two half-lives demonstrated that exchange was not accompanied significantly by side-reactions such as nucleophilic displacement of *p*-chlorobenzoate by amine. If the exchanges are first-order in each of the reacting species, the indicated rate constants are $5 \cdot 1 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$ for the 1-phenylallyl ester and $4 \cdot 8 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$ for the 3-phenylallyl ester. Since the esters differ considerably in free energy, the near equivalence in exchange rates requires that the two transition states for exchange be not identical. It appears that the 3-phenylallyl ester is exchanging by an S_N2 process and that the equality of apparent exchange rate constants is a coincidence.

We are unable to explain the rapid exchange with the 3-phenylallyl ester, for Pocker [1b] observed little exchnge between 3-phenylallyl benzoate and benzoic acid in chlorobenzene at 155°. Since this rapid 3-phenylallyl exchange renders the intended measurements impossible, we are abandoning studies of this system pending completion of work on other allylic rearrangements.

Experimental.—Reagents. 1-Phenylallyl alcohol was prepared [1] from acraldehyde and phenylmagnesium bromide. 1-*Phenylallyl* p-*chlorobenzoate*, prepared by reaction with *p*-chlorobenzoyl chloride in dry pyridine, had b. p. 139—141°/0·25 mm., $\lambda_{max.}$ (in ethanol) 241 mμ (ε 19,200) (Found: C, 70·1; H, 4·6; Cl, 13·0. $C_{16}H_{13}ClO_2$ requires C, 70·4; H, 4·8; Cl, 13·0%). The 3-*phenylallyl ester*, prepared similarly, formed needles, m. p. 46° (from 95% aqueous ethanol), $\lambda_{max.}$ (in ethanol) 247 mμ (ε 32,700) (Found: C, 70·9; H, 5·1; Cl, 13·0%).

p-Toluidine was diazotized, and [^{36}Cl]-*p*-chlorotoluene was prepared by a Sandmeyer reaction with labelled cuprous chloride. Labelled *p*-chlorobenzoic acid was then prepared by permanganate oxidation. Since its tetrabutylammonium salt was unstable under our reaction conditions, the benzylammonium salt was prepared by direct neutralization with the amine.

Solvents. Any solvent needed to be non-solvolysing, to boil above about 150°, to have a moderately high dielectric constant, and to be transparent near 250 mμ. Dimethylformamide met these requirements, but the phenylallyl esters underwent excessive decomposition in it under the conditions necessary for rearrangement. Di-2-chloroethyl ether was unsatisfactory because benzoate salts appeared to displace chloride ion from the solvent. *N*-Methyl-2-pyrrolidone was suggested by Professor V. Boekelheide of this department. It was dried (K_2CO_3) and distilled at 94—97°/15 mm.

Procedures. The rearrangement was followed spectrophotometrically at 250 mμ by adding known amounts of solution to absolute ethanol. At this wavelength, the 1-phenylallyl and 3-phenylallyl esters had ε 13,000 and 32,100, respectively. A solution from an exchange run was diluted with a five-fold excess of diethyl ether and extracted with ice–water. This removed the benzoate salt and left the ester in the ether layer. The radioactivity in the aqueous layer was measured with a thin-walled Geiger tube.

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OREGON,
EUGENE, OREGON, U.S.A.   [*Received, October 4th*, 1963.]

469. *S-Acylmethyl OO'-Dialkyl Phosphoro-thioates and -dithioates.*

By R. J. W. CREMLYN.

THESE compounds were synthesised as potential systemic insecticides. The first group (Table 1), $R \cdot CO \cdot CH_2 \cdot S \cdot P:X(OR')_2$ (R = alkyl or aryl, R' = Me or Et, X = O or S), were prepared by phosphorylation of the corresponding chloro- or bromo-methyl ketones. The second group (Table 2) are the oximes, semicarbazones, and phenylhydrazones of these compounds. Many organophosphorus compounds are active as systemic insecticides

TABLE 1.

The compounds $R \cdot CO \cdot CH_2 \cdot S \cdot P:X(OR')_2$.

R	X	R'	B. p./mm.	n_D (Temp.)	Formula	Found (%) P	Found (%) S	Reqd. (%) P	Reqd. (%) S
1. Me	O	Et	98°/0·01	1·4730 (19°)	$C_7H_{15}O_4PS$	13·7	14·6	13·7	14·2
2. Me	S	Me	—	1·5270 (26)	$C_5H_{11}O_3PS_2$	14·6	30·5	14·6	30·1
3. Ph	O	Et	148—150/0·17	1·5540 (22)	$C_{12}H_{17}O_4PS$	11·3	11·6	10·9	11·2
4. Ph	S	Me	175—180/0·30	1·6045 (22)	$C_{10}H_{13}O_3PS_2$	10·8	23·2	11·2	23·5
5. Ph·CH$_2$	O	Et	156—158/0·20	1·5270 (20)	$C_{13}H_{19}O_4PS$	10·2	10·2	10·2	10·5
6. ,,	S	Me	164—168/0·28	1·5730 (21)	$C_{11}H_{15}O_3PS_2$	10·6	21·7	10·6	22·0
7. 4-Cl·C$_6$H$_4$	O	Et	—	1·5520 (23)	$C_{11}H_{16}ClO_4PS$	8·8	9·3	9·2	9·5
8. ,,	S	Me	—	1·5920 (19)	$C_{10}H_{12}ClO_3PS_2$	9·9	21·1	10·0	20·7
9. 4-Ph·C$_6$H$_4$	O	Et	*	—	$C_{18}H_{21}O_4PS$	8·1	9·1	8·5	8·8
10. ,,	S	Me	M. p. 55—58	—	$C_{16}H_{17}O_3PS_2$	8·8	17·9	8·9	18·2
11. 4-MeO·C$_6$H$_4$	O	Et	—	1·3766 (26)	$C_{14}H_{19}O_5PS$	9·0	10·2	9·4	9·8
12. 4-Me·C$_6$H$_4$	O	Et	—	—	$C_{13}H_{19}O_4PS$	9·7	10·1	10·2	10·5
13. ,,	S	Me	—	—	$C_{11}H_{15}O_3PS_2$	10·4	21·9	10·6	22·0
14. (3-NO$_2$, 4-NH$_2$, 5-Br)C$_6$H$_2$	O	Et	*	—	$C_{12}H_{16}BrN_2O_6PS$	6·9	7·2	7·3	7·5
15. ,,	S	Me	—	—	$C_{10}H_{12}BrN_2O_5PS_2$	6·8	14·9	7·5	15·4
16. 4-NO$_2$·C$_6$H$_4$	O	Et	—	—	$C_{12}H_{16}NO_6PS$	8·9	9·6	9·3	9·6
17. NO$_2$·C$_6$H$_4$	S	Me	M. p. 78—80	—	$C_{10}H_{12}NO_5PS_2$	9·2	19·2	9·6	19·8
18. (2-MeO, 5-Cl)-C$_6$H$_3$	O	Et	—	1·5470 (22)	$C_{13}H_{18}ClO_5PS$	8·9	9·3	9·1	9·95
19. ,,	S	Me	—	—	$C_{11}H_{14}ClO_4PS_2$	8·9	18·6	9·1	18·8

* Low-melting solid. Other analyses (Found value first, Required in parentheses): (7) Cl, 11·1 (10·6); (14) N, 6·1 (6·6); (15) N, 7·4 (6·7); (16) N, 4·6 (4·2); (17) N, 4·7 (4·4); (18) Cl, 9·9 (10·1); (19) Cl, 10·0 (10·4).

TABLE 2.

The derivatives $Me \cdot C(:NR) \cdot CH_2 \cdot S \cdot P:X(OR')_2$.

R	X	R'	M. p.	Formula	Found (%) N	Found (%) P	Found (%) S	Reqd. (%) N	Reqd. (%) P	Reqd. (%) S
OH..............	O	Et	Liquid	$C_7H_{16}NO_4PS$	5·2	12·4	12·9	5·7	12·8	13·2
OH..............	S	Me	,,	$C_5H_{12}NO_3PS_2$	5·8	14·0	28·6	6·1	13·5	27·9
NH$_2$·CO·NH.........	O	Et	98—101°	$C_8H_{18}N_3O_4PS$	14·4	10·4	10·9	14·8	10·9	11·3
NH$_2$·CO·NH.........	S	Me	128—130	$C_6H_{14}N_3O_3PS_2$	15·6	11·6	23·6	15·5	11·4	23·6
2,4-(NO$_2$)$_2$C$_6$H$_3$·NH	O	Et	94—96	$C_{13}H_{19}N_4O_7PS$	13·9	7·4	7·8	13·8	7·6	7·8
2,4-(NO$_2$)$_2$C$_6$H$_3$·NH	S	Me	Liquid	$C_{11}H_{15}N_4O_6PS_2$	14·0	7·7	16·0	14·2	7·9	16·2
NH$_2$·CS·NH.........	S	Me	Liquid	$C_6H_{14}N_3O_2PS_3$	14·4	11·0	32·8	15·0	10·8	33·4

owing to their ease of translocation and their ability to interfere with the normal mechanism of nerve transmission.[1] Unfortunately, the most efficient phosphorus insecticides are generally highly toxic to mammals, and, in the development of less toxic and more selective insecticides, several compounds have been described [2,3] in which the phosphorus atom is linked to electrophilic groups through one or more methylene groups; the compounds described here fall into this general pattern.

Experimental.—The phenacyl and substituted-phenacyl chlorides were prepared from the appropriate acyl chloride by treatment with ethereal diazomethane, followed by hydrogen

[1] Metcalf, " Organo-Phosphorus Insecticides," Interscience, New York, 1955.
[2] Lorenz, U.S.P. 2,843,588/1958; U.S.P. 2,758,115/1956.
[3] B.P. 801,523; B.P. 804,761/1958.

chloride [4] (cf. ref. 5). The phenacyl bromides were obtained by bromination of the corre-sponding acetophenone with bromine in chloroform.[6]

OO′-Dimethyl S-phenacyl phosphorodithioate. Sodium dimethyl phosphorodithioate (8·2 g.) dissolved in acetone (30 c.c.) was added dropwise to a stirred solution of phenacyl chloride (7 g.) in acetone (100 c.c.). Sodium chloride immediately began to be precipitated, and, when addition was complete, the suspension was boiled under reflux for 3 hr., and filtered, and the acetone evaporated *in vacuo.* The residual oil was extracted with benzene (150 c.c.), and the extract washed with water and aqueous sodium carbonate, dried (Na_2SO_4), and evaporated. Vacuum distillation gave the *product* as an orange liquid (3 g.). The above details are illustrative of the general phosphorylation procedure adopted.

[4] Bradley and Schwarzenbach, *J.*, 1928, 2904.
[6] Clibbins and Nierenstein, *J.*, 1915, **107**, 1491.
[6] Kindler and Blaas, *Ber.*, 1944, **77**, 585.

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470. *Alkylation of the Aromatic Nucleus. Part XI.[1] Isomer Distribution in the Benzylation of Toluene.*

By P. R. ADAMS and W. J. HICKINBOTTOM.

ALKYLATION of toluene by the thermal decomposition of alkyl sulphonates in an excess of toluene gives a high proportion of *meta*-substitution; 17% for cyclohexylation,[1] 21% for cyclopentylation,[2] and about 30% for cyclohexylmethylation.[3] In contrast, benzyl-ation by this method gives no appreciable amount of *meta*-substituted product.[3] Olah *et al.*,[4] using benzyl chloride with aluminium chloride–nitromethane catalyst, reported that the product contained 4·5% of *m*-benzyltoluene. On the other hand, Brown and Bolto,[5] in the benzylation of toluene with gallium bromide and benzyl bromide, calculated that, at zero-reaction time, 19·4% of *m*-benzyltoluene was formed.

It is desirable to study the benzylation of toluene more closely to explain these differences. The reaction of toluene with benzyl alcohol in the presence of boron trifluoride, sulphuric acid, or phosphoric acid was examined to determine the isomer distribution in the product. No isomerisation of the benzyltoluenes occurred under the conditions used except when aluminium chloride was present. The results are given in the Table, with those of the other workers. In all these benzylations, where isomerisation

Yields (%) of *o*-, *m*-, and *p*-benzyltoluene.

Reagent	Catalyst	*o*- and *m*-	*p*-	*m*-
$PhCH_2 \cdot OH$	BF_3	48	52	4 ± 1
$PhCH_2 \cdot OH$	H_2SO_4	49	51	<3
$PhCH_2 \cdot OH$	H_3PO_4	50	50	3 ± 1
$PhCH_2 \cdot O \cdot SO_2 \cdot C_6H_4 \cdot Me$ [3]	—	48	52	—
$PhCH_2Cl$ [4]	$AlCl_3$–$MeNO_2$	48	52	4·5
$PhCH_2 \cdot OH$	$AlCl_3$	69	31	43
$PhCH_2Br$ [5]	$GaBr_3$	60·5	39·5	19·4

does not occur, the isomer distribution is remarkably constant, with 3—4% of the *meta*-isomer. It may be concluded that the results of Brown and Bolto do not accurately

[1] Part X, Blackwell and Hickinbottom, *J.*, 1963, 518.
[2] Davies and Hickinbottom, *J.*, 1963, 373.
[3] Blackwell and Hickinbottom, *J.*, 1963, 366.
[4] Olah, Kuhn, and Flood, *J. Amer. Chem. Soc.*, 1962, **84**, 1688.
[5] Brown and Bolto, *J. Amer. Chem. Soc.*, 1959, **81**, 3320.

represent the proportion of *meta*-substitution in benzylations where the possibility of isomerisation is rigidly excluded.

Experimental.—The general procedure was to treat a mixture of benzyl alcohol (0·2 mole) and toluene (1 mole) with the condensing agent. After the reaction was judged to be completed the mixture was poured into water and the product isolated.

The proportion of the *para*-isomer in the product was estimated by vapour-phase chromatography (4 ft. column; 10% Apiezon L on Celite, 100—120 mesh; Pye Argon unit with ionisation detector). No satisfactory separation of *ortho*- and *meta*-isomers could be effected. Relatively large amounts of *meta*-isomer could be determined with sufficient accuracy from the infrared spectrum by the base-line technique,[6] using a peak at 12·85 μ. The estimation of small amounts of *meta*-isomer was achieved by comparison of the infrared spectra of the reaction products with those of artificial mixtures containing 2, 3, 4, 5, 7, and 20% of *meta*-isomer. The presence of 3% of *meta*-isomer was just perceptible. A Grubb-Parsons double-beam grating spectrometer was used for infrared spectroscopy.

With boron trifluoride. After passing boron trifluoride for 30 min. at room temperature the mixture had separated into two layers. The product (43%) had b. p. 144—147°/15 mm., n_D^{20} 1·5712 (Found: C, 93·5; H, 6·4. Calc. for $C_{14}H_{14}$: C, 93·7; H, 6·3%).

With sulphuric acid. The mixture, stirred with sulphuric acid (100 ml.; 80%) at room temperature for 12 hr., gave a product (50%) with b. p. 144—146°/15 mm., n_D^{20} 1·5713 (Found: C, 93·7; H, 6·2%).

With phosphoric acid. Heating with phosphoric acid (100 ml.; 100%) at 70° for 5 hr. gave a product (17 g., 39%) with b. p. 145—147°/15 mm., n_D^{20} 1·5704 (Found: C, 93·5; H, 6·3%).

With aluminium chloride. Benzyl alcohol (21·6 g.) in toluene (50 ml.) was added dropwise to a mixture of anhydrous aluminium chloride (26·5 g.) and toluene. When the reaction had subsided the mixture was heated at 70° for 30 min. and then kept overnight at room temperature; the product (37%) had b. p. 144—152°/15 mm., n_D^{20} 1·5675 (Found: C, 93·1; H, 6·2%).

Pure *o*-benzyltoluene (18·2 g., 0·1 mole), toluene (4·6 g., 0·5 mole), and anhydrous aluminium chloride (13·3 g., 0·1 mole) were stirred together for 5 hr. at room temperature. The product (27%) had b. p. 140—146°/14 mm. and n_D^{20} 1·5679, and contained 30% of *o*-, 37% of *m*-, and 33% of *p*-benzyltoluene.

⁶ Heigl, Bell, and White, *Ind. Eng. Chem., Analyt.,* 1947, **19**, 293.

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471. *Syntheses of Heterocyclic Compounds. Part VII.*[1]
Cyanoethylation of Methyl Groups in Nitrogen Heterocycles.

By E. LATHWOOD and H. SUSCHITZKY.

NUMEROUS examples of the cyanoethylation of active methylene groups are known[2] but little work has been done on active methyl groups in nitrogen heterocycles. In a recent patent[3] various methylpyridines are claimed to react with acrylonitrile in the presence of alkali-metal catalysts but yields are not stated. However, we found this method ineffective even with picoline *N*-oxides. Other workers[4] could not cause acrylonitrile to react with a derivative of 3,4-dihydro-1-methylisoquinoline in presence of sodium ethoxide.

¹ Part VI, Lathwood and Suschitzky, *J.,* 1964, 2426.
² Bruson, *Org. Reactions,* 1949, **5**, 79.
³ U.S.P. 2,868,794/1959.
⁴ Openshaw and Whittaker, *J.,* 1961, 4939.

We have now found that certain methylated nitrogen heterocycles undergo cyano-ethylation in the presence of copper powder and cupric acetate, with acetic acid as solvent, to give butyronitriles (see Table 1). These conditions are similar to those used by Cookson and Mann [5] to cyanoethylate unreactive amines. Only monocyanoethyl compounds were obtained, even on prolonged heating with an excess of reagent, and β-picoline did not react at all.

$$R \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot R'$$

(I)

(II) $CH_2 \cdot CH_2 R$

(III)
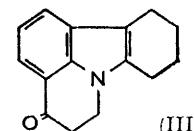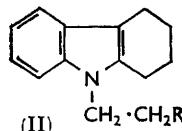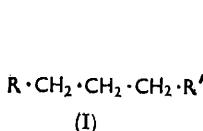
The nitriles (I; R = 2- or 4-pyridyl, R' = CN) derived from α- and γ-picoline were made previously, in similar yields, from 2- and 4-vinylpyridine and acetonitrile.[6,7] We failed to cyclise some of these nitriles with polyphosphoric acid to give cyclic ketones, and obtained acid amides instead. This result is in keeping with the known hydrolytic resistance of amides towards this reagent [8] although chroman-4-ones have been made directly from the appropriate nitriles under these conditions.[9] Neither could the corresponding acids (I; R as in Table 1, R' = CO_2H) be made to cyclise, possibly because quaternisation of the heterocyclic nitrogen atom deactivates the ring to Friedel–Crafts acylation. We also failed to cyclise the nitrile and the amide of the tetrahydrocarbazole (II; R = CN, $CONH_2$), but the corresponding acid (II; R = CO_2H) gave a good yield of the ketone (III), previously made by a much more tedious route.[10]

Experimental.—Cyanoethylations. A mixture of the required methyl-heterocycle (1 mol.), acrylonitrile (0·5 mol.), copper powder (5 g.), cupric acetate (4 g.), and acetic acid (40 ml.) was heated with stirring in an autoclave. The viscous mixture was taken up in chloroform, copper powder removed by filtration, and acetic acid extracted with aqueous sodium carbonate. The butyronitrile (Table 1) was isolated by fractional distillation. An excess of acrylonitrile had no effect on the yields.

TABLE 1.

Preparation of the butyronitriles (I; R' = CN) by cyanoethylation in an autoclave at 150°.

R	Time (hr.)	B. p.	Yield * (%)	Found (%) N	Formula	Required (%) N
2-Pyridyl †	18	100°/1·5 mm.	5	—	—	—
4-Pyridyl ‡	13	122/1 mm.	14	—	—	—
2-Quinolyl.....................	8	160/1 mm.	46·3	13·9	$C_{13}H_{12}N_2$	14·3
4-Quinolyl.....................	8	190/2 mm.	33	14·2	,,	14·3
1-Isoquinolyl	22	156/2·5 mm.	47	13·9	,,	14·3
3,4-Dihydro-1-isoquinolyl	12	154/0·8 mm.	67	13·85	$C_{13}H_{14}N_2$	14·1

* Based on the heterocycle.   † Lit.,[6] b. p. 96—97°/1 mm.   ‡ Lit.,[7] b. p. 123—125°/1 mm.

Attempted cyclisation of nitriles. Heating of the quinolylbutyronitriles with polyphosphoric acid under various conditions gave only amides, in high yield. 4-(2-*Quinolyl*)*butyramide* had m. p. 172° (Found: C, 72·9; H, 6·6. $C_{13}H_{14}N_2O$ requires C, 72·9; H, 6·5%), and 4-(4-*quinolyl*)-*butyramide* had m. p. 135° (Found: C, 72·9; H, 6·1%). The propionitrile (II; R = CN) [11] gave, on heating for 2·5 hr. at 100° with polyphosphoric acid, the *amide* (73%), m. p. 122° (Found: C, 74·5; H, 7·7. $C_{15}H_{18}N_2O$ requires C, 74·4; H, 7·4%).

[5] Cookson and Mann, *J.*, 1949, 67.
[6] Magnus and Levine, *J. Amer. Chem. Soc.*, 1956, **78**, 4127.
[7] Profft and Steinke, *Chem. Ber.*, 1961, **94**, 2267.
[8] Denton and Suschitzky, *J.*, 1963, 4741.
[9] Heininger, U.S.P. 2,792,407/1957.
[10] Clemo and Perkin, *J.*, 1924, 1608.
[11] Whitmore, Mosher, Adams, Taylor, Chapin, Weisel, and Yanko, *J. Amer. Chem. Soc.*, 1944, **66**, 725.

Attempted cyclisation of acids. The nitriles (2 g.) listed in Table 1 were hydrolysed with aqueous sodium hydroxide (20%; 30 ml.) in ethanol (10 ml.) for 8 hr., to give the corresponding acids (Table 2) in 60—70% yield. None of the acids could be cyclised by heating with polyphosphoric acid under various conditions. Only the tetrahydrocarbazolepropionic

TABLE 2.

4-Substituted butyric acids (I; R′ = CO_2H).

		Found (%)			Required (%)	
R	M. p.	C	H	Formula	C	H
2-Pyridyl	85° *	—	—	—	—	—
4-Pyridyl	125 †	—	—	—	—	—
2-Quinolyl	140	72·5	6·25	$C_{13}H_{13}NO_2$	72·55	6·1
4-Quinolyl	145	72·3	6·7	,,	,,	,,
1-Isoquinolyl	126	72·0	6·7	,,	,,	,,

* Doering and Weil, *J. Amer. Chem. Soc.*, 1947, **69**, 2461, give m. p. 85°. † Cejka, Ferles, Chládek, Labský, and Zelinka, *Coll. Czech. Chem. Comm.*, 1961, **26**, 1429, give m. p. 126—127°.

acid (II; R = CO_2H) (2 g.), m. p. 118° (lit.,[12] m. p. 118—119°), obtained from the nitrile as described above, cyclised with polyphosphoric acid (25 g.) when heated at 140° for 50 min. The mixture was poured into water, and the tarry residue filtered off and taken up in chloroform. Removal of the solvent left the ketone (III) (72%), m. p. 132—134° (lit.,[10] 135—136°) (Found: C, 80·1; H, 7·1. Calc. for $C_{15}H_{15}NO$: C, 79·9; H, 6·7%). Its phenylhydrazone had m. p. 190° (lit.,[10] 190—191°).

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[12] Smith, *J. Amer. Chem. Soc.*, 1950, **72**, 4313.

472. *π-1-Methylcyclohexadienyltricarbonylmanganese.*

By D. JONES and G. WILKINSON.

RECENT X-ray structural studies[1] have shown that the phenyl group in π-cyclopentadienyl-1-phenylcyclopentadienecobalt is in the *exo*-position with respect to the metal atom. This result now makes it reasonable to assume that in all the substituted cyclopentadiene complexes[2] such as π-$C_5H_5CoC_5H_5CCl_3$, the substituent on the ring is in the *exo*-position rather than in the *endo*-position originally postulated; the assignments of the nuclear magnetic resonance spectra of the protons on the $>$CHR group must therefore be revised. The original postulation was made on the ground that in the substituted complexes, the low intense C–H stretching frequency in the infrared spectrum (designated C–H_α), appearing in the unsubstituted cyclopentadiene complexes, was absent. The structure of the phenyl-substituted complex suggests that the absence of this band is due to the bending away from the metal atom of the $>$CHPh group through rehybridization at the C_2 and C_5 carbon atoms of the cyclopentadiene ring, so that the bonding of the diene to the metal is best regarded as being through two σ-bonds plus a donor π-bond from the double bond between C_3 and C_4 [cf. discussion in ref. 2(*a*)]. This bending away so increases the distance between the metal atom and the *endo* hydrogen atom that the hydrogen-bonding type of interaction observed[2a] in the unsubstituted complexes, which gives rise to the low intense C–H_α stretching frequency, cannot occur.

[1] Churchill and Mason, *Proc. Chem. Soc.*, 1963, 112; *Acta Cryst.*, in the press.
[2] (*a*) Green, Pratt, and Wilkinson, *J.*, 1959, 3753; (*b*) *J.*, 1960, 989; Davison, Green, and Wilkinson, *J.*, 1961, 3172.

A similar argument was also made for π-cyclohexadienyl metal complexes [3] where the unsubstituted species showed a low intense C–H$_\alpha$ stretching frequency, whereas the substituted derivatives (formulated with *endo*-substituents) did not. In view of the similarities in preparation, chemical properties, and spectra of the cyclopentadiene and π-cyclohexadienyl compounds, it now seems reasonable to reformulate the latter as having *exo*-substituents. X-Ray structural studies [4] on a π-cyclohexadienyl complex are not yet sufficiently advanced to allow a decision on either the extent of rehybridization at ring carbon atoms, which would imply both σ- and π-components to the bonding, or on the orientation of substituents. However, the nuclear magnetic resonance spectra of the previously unreported π-1-methylcyclohexadienyltricarbonylmanganese and other substituted π-cyclohexadienyl derivatives are in accord with *exo*-substitution. Whether the π-cyclohexadienyl ring has five planar carbon atoms in a delocalized system or whether there is some rehybridization with σ-components in the metal-to-ring bonding can only be shown by X-ray studies. In either case, the sixth carbon atom can be more or less in the plane of the others, or can be bent out of the plane. For unsubstituted compounds, there will be two possible structures with the $>$CH$_\alpha$ or H$_\beta$ group pointing towards the metal atom [as in (I)] or away from it [as in (II)]. For 1-substituted compounds there could be four isomers since substitution can be *exo* or *endo*.
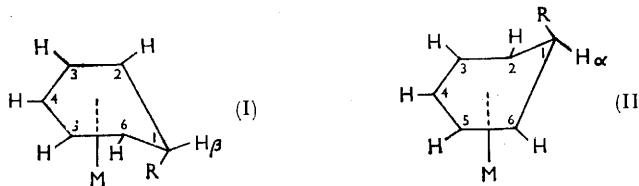
For the unsubstituted compounds, the methylene protons couple differently to H$_2$ and H$_6$, and this was explained [3b] on the basis that these protons will make different dihedral angles with H$_2$ and H$_6$. For the substituted compounds with a $>$CHR group, the remaining proton is coupled to H$_2$ and H$_6$ with the following J values: π-C$_6$H$_5$C$_6$H$_6$Mn(CO)$_3$, 5·5 c./sec.; π-C$_6$H$_5$C$_6$H$_6$(π-C$_5$H$_5$)Fe, 6·5 c./sec.; (π-C$_6$H$_5$C$_6$H$_6$)$_2$Ru, 6·0 c./sec.; and π-CH$_3$C$_6$H$_6$Mn(CO)$_3$, 6·0 c./sec.; these values thus indicate a dihedral angle of *ca.* 30°. Thus the nuclear magnetic resonance data are compatible with either the structure (I) with the substituent *endo* or structure (II) with the substituent *exo*. In view of the evidence for the *exo*-substitution in cyclopentadiene complexes, the structure (II) now seems to be clearly preferable for these cyclohexadienyl complexes.

Experimental.—Analyses by the Microanalytical Laboratory, Imperial College. Nuclear magnetic resonance spectra were measured at 56·4 Mc./sec. on a Varian Associates model 4300 spectrometer, using conventional methods and tetramethylsilane as internal reference.

π-1-*Methyl-cyclohexadienyltricarbonylmanganese.* Benzenetricarbonylmanganese perchlorate (5 g.) was slowly added to a solution of methyl-lithium (0·6 g. Li) in diethyl ether (50 ml.) at −20°. The mixture was stirred and allowed to warm to 25°, when a yellow colour developed in the solution. After stirring under reflux for 10 hr., the ether was evaporated *in vacuo* and the residue extracted with carbon disulphide (20 ml.). Filtration and evaporation of the solvent left a red solid which on purification by vacuum sublimation at 100° gave orange crystals of the *compound* (0·5 g.), m. p. 90° [Found: C, 51·8; H, 4·3%; *M* (ebullioscopic in benzene), 240. C$_{10}$H$_9$MnO$_3$ requires C, 51·7; H, 3·9%; *M*, 232]. The compound has a camphor-like odour and is stable in air. It is soluble in benzene, carbon disulphide, and carbon tetrachloride; a solution in the last solvent decomposed completely in air in 3—4 days. The compound is not affected by triphenylmethyl tetrafluoroborate.

The nuclear magnetic resonance spectrum, in CCl$_4$ solution, was as follows: τ 4·34, intensity 1,

[3] (*a*) Winkhaus, Pratt, and Wilkinson, *J.,* 1961, 3801; (*b*) Jones, Pratt, and Wilkinson, *J.,* 1962, 4458.

[4] Mason, personal communication.

triplet, H_4 split by $H_3 + H_5$ (J 5·5 c./sec.); τ 5·31, intensity 2, triplet with additional structure, $H_3 + H_5$ split by H_4 and H_2 or H_6 (J 6·0 c./sec.); τ 6·85, intensity 2, triplet with additional structure, $H_2 + H_6$ split by H_α and H_3 or H_5 (J 6·5 c./sec.); τ 7·42 (centre), intensity 1, sextuplet H_α split by methyl protons (J 6·5 c./sec.) and $H_2 + H_6$ (J 6·0 c./sec.); τ 9·57 (centre), intensity 3, doublet, methyl protons split by H_α (J 6·5 c./sec.).

473. *Preparation and Some Reactions of 2-Hydroxy-3-3′-hydroxy-propyl-5-methoxyacetophenone.*

By A. O. FITTON and G. R. RAMAGE.

THE acetylation of 6-methoxychroman (I; $R = Me$, $R' = H$) by the complex of boron trifluoride and acetic acid was recently shown to yield 7-acetyl-6-hydroxychroman (I; $R = H$, $R' = Ac$) as main product.[1] A second product has now been identified as 2-hydroxy-3-3′-hydroxypropyl-5-methoxyacetophenone (II). This compound, whose infrared spectrum displayed typical chelation of the *o*-hydroxyacyl system together with alcoholic hydroxyl absorption, was cyclised in concentrated sulphuric acid or polyphosphoric acid to 8-acetyl-6-methoxychroman (III; $R = H$). This was reduced to 8-ethyl-6-methoxychroman, which was then synthesised unambiguously.
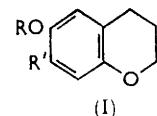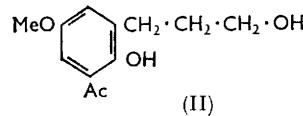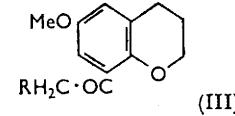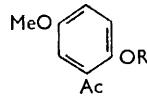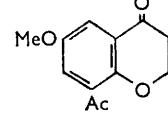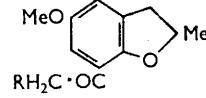
2-Hydroxy-5-methoxyacetophenone[2] (IV; $R = H$) was condensed with β-chloropropionic acid and the resulting β-(2-acetyl-4-methoxyphenoxy)propionic acid (IV; $R = CH_2 \cdot CH_2 \cdot CO_2H$) cyclised in polyphosphoric acid to yield 8-acetyl-6-methoxychroman-4-one (V). This on Clemmensen reduction gave 8-ethyl-6-methoxychroman, identical with the sample previously prepared.

The related 7-acetyl-5-methoxy-2-methylcoumaran (VI; $R = H$) was conveniently obtained by the action of polyphosphoric acid on 2-allyloxy-5-methoxyacetophenone (IV; $R = CH_2 \cdot CH \colon CH_2$), the structure being consistent with its proton magnetic resonance spectrum.

Claisen condensation of 2-hydroxy-3-3′-hydroxypropyl-5-methoxyacetophenone (II) with ethyl oxalate yielded 8-(β-ethoxycarbonyl-β-oxopropionyl)-6-methoxychroman (III; $R = CO \cdot CO_2Et$) also obtained by condensation of 8-acetyl-6-methoxychroman with ethyl oxalate.

Similarly, Claisen condensation of 7-acetyl-5-methoxy-2-methylcoumaran with ethyl oxalate yielded 7-(β-ethoxycarbonyl-β-oxopropionyl)-5-methoxy-2-methylcoumaran (VI; $R = CO \cdot CO_2Et$).

[1] Fitton and Ramage, *J.*, 1962, 4870.
[2] Mauthner, *Math. naturwiss. Anz. ungar. Akad. Wiss.*, 1938, **57**, 245.

Experimental.—*2-Hydroxy-3-3′-hydroxypropyl-5-methoxyacetophenone* (II). A mixture of 6-methoxychroman (3·28 g.) and boron trifluoride–acetic acid complex (40% w/w; 15 ml.) was heated under a dry atmosphere with frequent shaking during 1 hr., then added to water (50 ml.) before being basified with 10% aqueous sodium hydroxide. Filtration followed by acidification of the filtrate with concentrated hydrochloric acid and crystallisation of the product gave 7-acetyl-6-hydroxychroman (1 g.).

To the mother-liquor from the crystallisation was added water, and the precipitated oil was extracted with ether. The residue from the evaporation of the dried ($MgSO_4$) extract on fractionation gave *2-hydroxy-3-3′-hydroxypropyl-5-methoxyacetophenone* (0·5 g.) as a pale yellow oil, b. p. 148—153°/0·4 mm., which slowly solidified. Crystallisation from light petroleum (b. p. $<40°$) yielded fine needles, m. p. 39—40° (Found: C, 64·0; H, 6·9. $C_{12}H_{16}O_4$ requires C, 64·3; H, 7·2%).

It formed a *2,4-dinitrophenylhydrazone* as red needles (from acetic acid), m. p. 211—213° (Found: C, 53·5; H, 5·1. $C_{18}H_{20}N_4O_7$ requires C, 53·5; H, 5·0%).

8-Acetyl-6-methoxychroman (III; R = H). A solution of 2-hydroxy-3-3′-hydroxypropyl-5-methoxyacetophenone (0·5 g.) in concentrated sulphuric acid (5 ml.) was kept for 48 hr. before being added to water (50 ml.). The mixture was basified with 10% aqueous sodium hydroxide and then extracted with ether. The extract was dried ($MgSO_4$) and evaporated to give a residue which on crystallisation from light petroleum (b. p. 40—60°) yielded *8-acetyl-6-methoxychroman* (0·2 g.) as prisms, m. p. 62—63·5° (Found: C, 70·1; H, 6·6. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%).

It formed a *2,4-dinitrophenylhydrazone* as orange needles, m. p. 155—156·5°, from ethanol (Found: C, 55·6; H, 4·5. $C_{18}H_{18}N_4O_6$ requires C, 55·9; H, 4·7%).

β-*(2-Acetyl-4-methoxyphenoxy)propionic Acid* (IV; R = $CH_2·CH_2·CO_2H$). To a solution of 2-hydroxy-5-methoxyacetophenone (33·2 g.) and potassium hydroxide (11·2 g.) in water (30 ml.) was added a solution of β-chloropropionic acid (10·9 g.) and potassium carbonate (13·8 g.) in water (30 ml.). The mixture was heated during 15 min., then cooled, acidified with concentrated hydrochloric acid, and extracted with ether. The ethereal solution was extracted repeatedly with saturated sodium hydrogen carbonate solution, and the combined extracts were acidified with concentrated hydrochloric acid. The precipitated β-*(2-acetyl-4-methoxyphenoxy)-propionic acid* was filtered off and on crystallisation from water gave fawn needles (0·65 g.), m. p. 104—105° (Found: C, 60·2; H, 5·9. $C_{12}H_{14}O_5$ requires C, 60·5; H, 5·9%).

8-Acetyl-6-methoxychroman-4-one (V). β-(2-Acetyl-4-methoxyphenoxy)propionic acid (2·4 g.) was stirred with polyphosphoric acid (30 g.) during 1 hr. at $\not> 40°$. The mixture was added to water (100 ml.) and the precipitated solid was filtered off. The residue was washed with sodium hydrogen carbonate solution, dried, and crystallised from light petroleum (b. p. 60—80°). *8-Acetyl-6-methoxychroman-4-one* (0·73 g.) was obtained as yellow needles, m. p. 99—100° (Found: C, 65·5; H, 5·4. $C_{12}H_{12}O_4$ requires C, 65·5; H, 5·5%).

8-Ethyl-6-methoxychroman. (a) 8-Acetyl-6-methoxychroman-4-one (1 g.) was heated under reflux with a mixture of amalgamated zinc wool (5 g.) and constant-boiling hydrochloric acid (15 ml.) during 1 hr. The cooled liquid was decanted from excess of zinc and then extracted with ether. Distillation of the residue from the dried ethereal extract yielded *8-ethyl-6-methoxychroman* (0·2 g.) as an oil, b. p. 105—110°/0·6 mm. (Found: C, 74·7; H, 8·7. $C_{12}H_{16}O_2$ requires C, 74·9; H, 8·4%).

(b) Similar reduction of 8-acetyl-6-methoxychroman yielded a product with an identical infrared spectrum to that of the above 8-ethyl-6-methoxychroman.

2-Allyloxy-5-methoxyacetophenone (IV; R = $CH_2·CH{:}CH_2$). A mixture of 2-hydroxy-5-methoxyacetophenone (16·6 g.), allyl bromide (18·2 g.), and anhydrous potassium carbonate (13·8 g.) in acetone (100 ml.) was stirred under reflux during 36 hr., then cooled and filtered. The filtrate was evaporated, and the solution formed by dissolving the residue in ether was washed successively with 2N-sodium hydroxide and water and then dried ($MgSO_4$). Fractionation yielded *2-allyloxy-5-methoxyacetophenone* (15·7 g.) as a pale yellow oil, b. p. 99—102°/0·1 mm., which solidified and crystallised from light petroleum (b. p. 40—60°) as plates, m. p. 36—37° (Found: C, 70·1; H, 6·8. $C_{12}H_{14}O_4$ requires C, 69·9; H, 6·8%).

2-Allyloxy-5-methoxyacetophenone formed a *2,4-dinitrophenylhydrazone* as plates, m. p. 155—156°, from ethanol (Found: C, 55·8; H, 4·8. $C_{18}H_{18}N_4O_4$ requires C, 55·9; H, 4·7%).

7-Acetyl-5-methoxy-2-methylcoumaran (VI; R = H). 2-Allyloxy-5-methoxyacetophenone (14 g.) was stirred with polyphosphoric acid (140 g.) during 1 hr. at $\not> 40°$, and then added to

water (500 ml.). The mixture was extracted with ether, and the ethereal layer was washed successively with 2N-sodium hydroxide and water. Fractionation of the dried (MgSO₄) extract yielded 7-*acetyl-5-methoxy-2-methylcoumaran* (5·6 g.), b. p. 121—125°/0·7 mm., which solidified and crystallised from light petroleum (b. p. 40—60°) as prisms, m. p. 66—68° (Found: C, 70·1; H, 6·8. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%).

It formed a 2,4-*dinitrophenylhydrazone*, as needles, m. p. 209—210°, from acetic acid (Found: C, 55·9; H, 4·5. $C_{18}H_{18}N_4O_6$ requires C, 55·9; H, 4·7%).

8-(β-*Ethoxycarbonyl* - β - *oxopropionyl*) -6- *methoxychroman* (III; R = CO·CO₂Et). (*a*) To sodium ethoxide [from sodium (0·5 g.)] in ethanol (25 ml.) was added 2-hydroxy-3-3′-hydroxy-propyl-5-methoxyacetophenone (1·12 g.) in diethyl oxalate (3 ml.). The mixture was refluxed during 1·5 hr., cooled, and added to dry ether (250 ml.). The salt was filtered off and added to 2N-hydrochloric acid (10 ml.). Filtration of the precipitate followed by crystallisation from ethanol yielded 8-(β-*ethoxycarbonyl-β-oxopropionyl*)-6-*methoxychroman* (0·5 g.) as needles, m. p. 106—108° (Found: C, 62·5; H, 5·6. $C_{16}H_{18}O_6$ requires C, 62·7; H, 5·9%).

(*b*) To sodium ethoxide [from sodium (0·05 g.)] in ethanol (5 ml.) was added 8-acetyl-6-methoxychroman (0·2 g.) in ethyl oxalate (2 ml.). The resulting solution was refluxed during 6·5 hr. and then cooled, and the product was isolated and purified as above. 8-(β-Ethoxy-carbonyl-β-oxopropionyl)-6-methoxychroman (50 mg.) was obtained, identical with the above material.

7-(β-*Ethoxycarbonyl-β-oxopropionyl*)-5-*methoxy-2-methylcoumaran* (VI; R = CO·CO₂Et). To sodium ethoxide [from sodium (0·21 g.)] in ethanol (8 ml.) was added 7-acetyl-5-methoxy-2-methylcoumaran (0·6 g.) in ethyl oxalate (2 ml.). The resulting mixture was heated under reflux during 4 hr. Isolation of the product as in the above experiment gave 7-(β-*ethoxy-carbonyl-β-oxopropionyl*)-5-*methoxy-2-methylcoumaran* which crystallised from ethanol as plates (0·2 g.), m. p. 122—123° (Found: C, 62·6; H, 5·6. $C_{16}H_{18}O_6$ requires C, 62·7; H, 5·9%).

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                        SALFORD, LANCS.   [*Received, November 18th, 1963.*]

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474. *Organometallic Compounds of Group II. Part V.*[1]
Magnesium Isopropoxide, a Metastable Metal-organic Rubber.

By D. BRYCE-SMITH and B. J. WAKEFIELD.

MAGNESIUM isopropoxide has not hitherto been reported, possibly because magnesium [2] and magnesium hydride are markedly unreactive towards propan-2-ol. We have now obtained this compound by reaction of n-butylmagnesium isopropoxide [3] with propan-2-ol. When freshly isolated, the product was an involatile white porous rubber. On standing under dry nitrogen at room temperature, it became easily friable and lost all rubber-like character. The friable form of magnesium isopropoxide is insoluble in methylcyclohexane, benzene, and ether, and only sparingly soluble in propan-2-ol. The character of the meta-stable freshly-prepared material is consistent with its formulation as an essentially linear polymer possibly having very limited cross-linking; for such a polymer, some or all of the magnesium atoms must have a co-ordination number of less than six. Structure (I) represents a feasible repeating unit where magnesium is four co-ordinate, and Bradley's prediction of a trimeric structure (III) in such cases appears to be inapplicable.[4] Structure (I) is analogous to (II) which has been proposed for a metastable crystalline form of magnesium chloride having very strong electron-acceptor properties, which like the alkoxide, is prepared by replacement of alkyl groups in an unsolvated organomagnesium

[1] Part IV, Bryce-Smith and Skinner, *J.*, 1963, 577.
[2] Bryce-Smith, Wakefield, and Blues, *Proc. Chem. Soc.*, 1963, 219.
[3] Bryce-Smith and Wakefield, *Proc. Chem. Soc.*, 1963, 376.
[4] Bradley, " Metal-organic Compound," American Chemical Society, 1959, pp. 24, 25.

compound.[5]   The insolubility and involatility of the non-rubbery form of magnesium isopropoxide render improbable any covalently bonded trimeric structure such as (III); in any event, structure (III) seems to be seriously overcrowded.   We prefer to believe that a tendency for the co-ordination number of magnesium to increase from four to six provides the driving force for a structural reorganisation.   Bradley pointed out that this

(I : X = OPr^i)
(II : X = Cl)

(III)
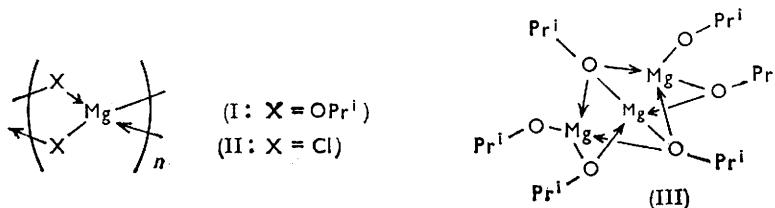
would lead to the formation of a " giant polymer." [4]   Other cases are known where light-metal alkoxides undergo a change in structure with time.[6,7]   Magnesium isopropoxide seems to provide the first example of a rubber in which a true metal forms an integral part of the structure.   The above considerations suggest that beryllium isopropoxide might also be a rubber, and we are investigating its preparation.

Feasible alternative routes to magnesium isopropoxide can be envisaged, *e.g.*, alcoholysis of a dialkylmagnesium compound with propan-2-ol, oxidation of di-isopropylmagnesium, and alkoxide exchange between propan-2-ol and (say) magnesium methoxide.

Experimental.—All operations were carried out in dry, oxygen-free nitrogen.   Magnesium powder (Magnesium Elektron Ltd., Grade 4) was sieved to a particle size of less than 89 μ, and was used within six months of its original grinding by the manufacturers.

Unsolvated n-butylmagnesium chloride.   (This procedure is a modification of one previously described by Bryce-Smith and Cox,[8] and was developed in conjunction with Mr. E. T. Blues.) A portion (5 ml.) of a solution of 1-chlorobutane (18·6 g.) in methylcyclohexane (20 ml.) was added to magnesium powder (6·0 g.) in refluxing methylcyclohexane (50 ml.).   Reaction was initiated by adding a few mg. of iodine, and the rest of the chloride solution was then steadily added dropwise, with stirring, during 30 min., to the refluxing mixture.   Heating was continued for 30 min. after the temperature of reflux had reached 100°.   Yields averaged 75% (as from butane evolved on hydrolysis).

n-Butylmagnesium isopropoxide.   Dry propan-2-ol (4·5 g.) in methylcyclohexane (50 ml.) was added at 100° to the n-butylmagnesium chloride in methylcyclohexane, prepared as above, and the mixture was heated, with stirring, under reflux for 2 hr. to precipitate all chloride from solution.   Methylcyclohexane (50 ml.) was added and the mixture was allowed to cool.   After 17 hr. at room temperature, the clear supernatant liquid was decanted, and was estimated (from base formed on hydrolysis) to contain 0·040 mole of Bu^{n}MgOPr^i.   This procedure is one of three recently reported.[3]

Magnesium isopropoxide.   Dry propan-2-ol (2·4 g., 0·040 mole) was added to the foregoing solution of n-butylmagnesium isopropoxide (0·040 mole).   The mixture was heated under reflux for 30 min.   The solvent was decanted, and the residual insoluble white gel was washed several times with methylcyclohexane.   Removal of residual solvent up to 150°/1 mm. gave *magnesium isopropoxide* as a white porous rubbery mass, involatile under these conditions. After 16 hr. under dry nitrogen at room temperature and atmospheric pressure, the material had lost all rubbery character, and was friable; it did not re-form a rubber when heated at 150° [Found: Mg, 16·9%; Equiv. (from base formed by hydrolysis), 72·2. $C_6H_{14}MgO_2$ requires Mg, 16·8%; Equiv., 72·25].   Precise determination of isopropoxyl from the propan-2-ol

[5] Bryce-Smith, *Bull. Soc. chim. France*, 1963, 1418; cf. Blues and Bryce-Smith, *Proc. Chem. Soc.*, 1961, 245.
[6] Mehrotra, *J. Indian Chem. Soc.*, 1953, **30**, 585; 1954, **31**, 85.
[7] Shiner, Whittaker, and Fernandez, *J. Amer. Chem. Soc.*, 1963, **85**, 2318.
[8] Bryce-Smith and Cox, *J.*, 1961, 1175.

formed on hydrolysis was difficult, but a procedure based on the use of Agulhon's reagent (stated to have an accuracy of $\pm 5\%$) [9] gave a figure of 79% ($C_6H_{14}MgO_2$ requires C_3H_7O, 83%).

[9] Wild, " Estimation of Organic Compounds," Cambridge University Press, 1953, p. 67.

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475. *Heterocyclic Polyfluoro-compounds. Part III.*[1]
1H-Decafluoropiperidine.

By R. E. BANKS, W. M. CHENG, and R. N. HASZELDINE.

PERFLUORO-2,3,4,5-TETRAHYDROPYRIDINE, prepared by defluorination of undecafluoropiperidine with mild steel at 500°/1 atm.,[1] combines readily with anhydrous hydrogen fluoride to give 1*H*-decafluoropiperidine, the first secondary perfluorocycloalkylamine to be characterised:
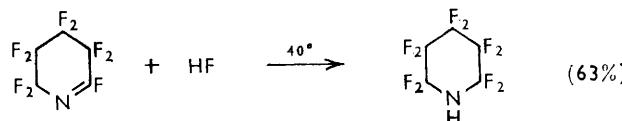
This reaction is analogous to that used to prepare bistrifluoromethylamine, the only other secondary perfluoroamine:[2,3]

$$CF_3 \cdot N{:}CF_2 + HF \longrightarrow (CF_3)_2 NH$$
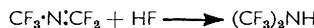
1*H*-Decafluoropiperidine is a colourless liquid, b. p. 73·4°, whose vapour shows strong infrared absorption at 3448 and 1481 cm.$^{-1}$, attributable to N–H stretching and bending vibrations, respectively [cf.[4] $(CF_3)_2NH$, 3460 and 1499 cm.$^{-1}$]. It loses hydrogen fluoride slowly when stored in a Pyrex vessel at room temperature, and rapidly in the presence of moisture, to yield perfluoro-2,3,4,5-tetrahydropyridine; further reaction with water follows the scheme reported earlier.[1] Like bistrifluoromethylamine,[3,5] 1*H*-decafluoropiperidine reacts with a mixture of concentrated nitric acid and trifluoroacetic anhydride to yield the corresponding perfluoro-*N*-nitroamine.

Experimental.—Preparation of 1H-*decafluoropiperidine.* Analytically pure perfluoro-2,3,4,5-tetrahydropyridine [1] (1·18 g., 4·82 mmoles) and anhydrous hydrogen fluoride (0·19 g., 9·50 mmoles) were heated in a 16 ml. stainless-steel autoclave at 40° for 6 days. The product was passed over powdered sodium fluoride to remove the excess of hydrogen fluoride, and the recovered material was fractionated to yield 1H-*decafluoropiperidine* (0·80 g., 3·02 mmoles, 63%) (Found: C, 22·8; H, 0·4; N, 5·2%; *M*, 262. $C_5HF_{10}N$ requires C, 22·6; H, 0·4; N, 5·3%; *M*, 265).

The vapour pressure of 1*H*-decafluoropiperidine, measured over the range 0—40°, is given by the equation $\log_{10} p$ (cm.) = 6·804 − 1706/*T*. The calculated b. p. is 73·4°, the Trouton constant is 22·5, and the latent heat of vaporisation is 7810 cal. mole^{-1}.

[1] Part II, Banks, Cheng, and Haszeldine, *J.*, 1962, 3407.
[2] Barr and Haszeldine, *J.*, 1955, 2532.
[3] Young, Tsoukalas, and Dresdner, *J. Amer. Chem. Soc.*, 1958, **80**, 3604.
[4] Barr and Haszeldine, *J.*, 1955, 4169.
[5] Dinwoodie and Haszeldine, *J.*, 1964, in the press.

Nitration of 1H-*decafluoropiperidine.* 1H-Decafluoropiperidine (1·20 g., 4·53 mmoles) was added slowly (15 min.) to a mixture of concentrated nitric acid (1 ml.) and trifluoroacetic anhydride (10 ml.) held at 0° in a Pyrex flask fitted with a reflux condenser cooled to $-72°$. The mixture was allowed to warm slowly to room temperature, then was heated under reflux for 30 min., cooled to $-5°$, and carefully neutralised with sodium carbonate; a few drops of water were added periodically during the last operation to prevent the mixture solidifying. The volatile product, separated *in vacuo* and condensed at $-196°$, was washed successively with 2N-aqueous sodium hydroxide (5 ml.) and water (5 ml.) and then dried (P_2O_5) to give *decafluoro*-1-*nitropiperidine* (0·58 g., 1·87 mmoles, 41%) (Found: C, 19·1; N, 9·2%; *M*, 312. $C_5F_{10}N_2O_2$ requires C, 19·4; N, 9·0%; *M*, 310), showing strong absorption in the infrared region (vapour spectrum) at 1667 and 1686 cm.$^{-1}$ (doublet), which can be attributed to the presence of the nitro-group [cf.[3,5] $(CF_3)_2N\cdot NO_2$, 1670 cm.$^{-1}$].

The vapour pressure of decafluoro-1-nitropiperidine, measured over the range 10—70°, is given by the equation $\log_{10} p$ (cm.) $= 6\cdot177 - 1545/T$. The calculated b. p. is 86·7°, the Trouton constant is 19·7, and the latent heat of vaporisation is 7070 cal. mole^{-1}.

THE CHEMISTRY DEPARTMENT, FACULTY OF TECHNOLOGY,
UNIVERSITY OF MANCHESTER.   [*Received, January 22nd, 1964.*]

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476.   *Dibenzylphenylphosphine Sulphide and* 1,2-*Dibenzyl-*
1,2-*diphenyldiphosphine Disulphide.*

By P. C. CROFTS and K. GOSLING.

REACTIONS of thiophosphoryl chloride with alkylmagnesium halides are known to afford relatively minor amounts of trialkylphosphine sulphides, the main products isolated being tetra-alkyldiphosphine disulphides;[1] tertiary phosphine sulphides are, however, obtained nearly quantitatively from thiophosphoryl chloride and phenylmagnesium bromide, and as the main product from thiophosphoryl chloride and benzylmagnesium chloride.[2] We now report the formation of both the diphosphine disulphide (I) and the tertiary phosphine sulphide (II) from the reaction between phenylphosphonothioic dichloride and benzyl-magnesium chloride. Evidence for the structure of (I) was obtained from its cleavage with bromine[3] and conversion of the resulting phosphinothioic bromide into the *p*-toluidide (III), similar treatment of tetramethyldiphosphine disulphide having yielded dimethyl-phosphinothioic *p*-toluidide.
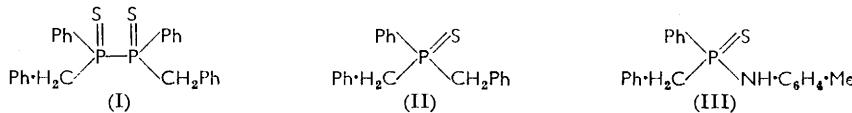
Dibenzylphenylphosphine sulphide (II) was also prepared from phenylphosphine by reaction with potassium or sodium in liquid ammonia, followed successively by treatment with benzyl chloride and sulphur. An attempt to avoid the use of phenylphosphine by preparing disodium phenylphosphide from phenylphosphonous dichloride and an excess of sodium,[4] followed by treatment with benzyl chloride and sulphur as before, gave the

[1] Kabachnik and Shepeleva, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1949, 56; Christen, van der Linde, and Hooge, *Rec. Trav. chim.*, 1959, **78**, 161; Issleib and Tzschach, *Chem. Ber.*, 1959, **92**, 704; Kuchen and Buchwald, *Angew. Chem.*, 1959, **71**, 162.
[2] Strecker and Grossmann, *Ber.*, 1916, **49**, 63; Crofts and Fox, unpublished work.
[3] Maier, *Chem. Ber.*, 1961, **94**, 3051.
[4] Horner, Beck, and Hoffmann, *Chem. Ber.*, 1959, **92**, 2088.

diphosphine disulphide (I). This suggested that disodium 1,2-diphenyldiphosphide had been produced in the first stage; P–P bonds are known to be formed by incomplete reduction of organophosphorus chlorides,[5] and also to be cleaved by further treatment with alkali metals,[6] and repetition of the reaction sequence, allowing more time for the reduction, gave the phosphine sulphide (II) as expected.

The diphosphine disulphide (I) may be either the ($\pm$)- or the *meso*-isomer; X-ray crystallography showed the number of molecules in the unit cell to be equal to the number of equivalent general positions, and hence provided no information about the molecular symmetry.

Experimental.—Reaction of phenylphosphonothioic dichloride with benzylmagnesium chloride. Phenylphosphonothioic dichloride (10·5 g.) in ether (20 ml.) was added during 1·5 hr. to benzyl-magnesium chloride [from benzyl chloride (25·4 g.) and magnesium (4·7 g.)] in ether (120 ml.). After 3·5 hr. under reflux, ice and dilute sulphuric acid were added, followed by chloroform to dissolve a white solid in the organic layer. This layer was separated, the solvents were distilled off, and the sludgy residue steam-distilled, to give bibenzyl (2·6 g.) and a solid residue which after four recrystallisations from light petroleum (b. p. 60—80°)–ethyl acetate afforded *1,2-dibenzyl-1,2-diphenyldiphosphine disulphide* (4·8 g., 24%), m. p. 189·5—190·5° [Found: C, 67·9; H, 5·2; S, 13·6%; M (cryoscopic in benzene), 480. $C_{26}H_{24}P_2S_2$ requires C, 67·5; H, 5·2; S, 13·9%; M, 462]. The mother-liquor from the first recrystallisation was evaporated, and the residue recrystallised five times from light petroleum (b. p. 60—80°)–chloroform and once from ethanol, to give *dibenzylphenylphosphine sulphide* (1·1 g., 10%), m. p. 150·5—151·5° (Found: C, 75·0; H, 5·7; S, 10·3. $C_{20}H_{19}PS$ requires C, 74·5; H, 5·7; S, 10·0%).

Phosphinothioic p-toluidides from diphosphine disulphides. A 0·25M-solution of bromine in carbon tetrachloride was added dropwise with stirring to a suspension of tetramethyldiphosphine disulphide (2·2 g.) in carbon tetrachloride (50 ml.) until a clear solution was obtained. *p*-Toluidine (6·0 g.) in carbon tetrachloride (100 ml.) was added, the mixture was filtered, and the filtrate washed with water and dried. Most of the solvent was evaporated, light petroleum (b. p. 60—80°) was added, and the precipitated solid was recrystallised from carbon tetra-chloride, to give *dimethylphosphinothioic p-toluidide*, m. p. 119—120° (Found: C, 54·8; H, 7·4; N, 6·7; P, 15·4; S, 16·1. $C_9H_{14}NPS$ requires C, 54·2; H, 7·1; N, 7·0; P, 15·5; S, 16·1%).

Treatment of 1,2-dibenzyl-1,2-diphenyldiphosphine disulphide as above, and recrystallisation of the product from light petroleum (b. p. 60—80°)–chloroform, yielded *benzylphenylphos-phinothioic p-toluidide*, m. p. 190·5—191° (Found: C, 71·0; H, 6·0; N, 4·3; P, 9·2; S, 9·6. $C_{20}H_{20}NPS$ requires C, 71·2; H, 5·9; N, 4·2; P, 9·2; S, 9·5%).

Dibenzylphenylphosphine sulphide from phenylphosphine. Phenylphosphine (6·6 g.) was added during 30 min. to a stirred solution of potassium (4·7 g.) [or of sodium (2·7 g.)] in liquid ammonia (200 ml.). After 1·5 hr., the ammonia was evaporated in a stream of nitrogen, and gradually replaced by toluene (200 ml.). Benzyl chloride (15·2 g.) in toluene (30 ml.) was added during 2·5 hr. at 20°, and the mixture was heated to 50° for 30 min. Sulphur (1·9 g.) in toluene (40 ml.) was added at 20° and the mixture was again heated to 50° for 30 min., cooled, and filtered. The filtrate was washed with water, dried (Na_2SO_4), and evaporated under reduced pressure, leaving a residue which was recrystallised twice from ethanol, to give dibenzylphenyl-phosphine sulphide (7·8 g., 40%), m. p. and mixed m. p. 150·5—151·5°.

Experiments using phenylphosphonous dichloride. (a) *Formation of 1,2-dibenzyl-1,2-di-phenyldiphosphine disulphide.* Phenylphosphonous dichloride (10·7 g.) was added to sodium (10·0 g.) covered with di-n-butyl ether (150 ml.) under nitrogen. The mixture was heated under reflux for 1·5 hr., and cooled, the bright yellow suspension was decanted from the excess of sodium, benzyl chloride (15·2 g.) in di-n-butyl ether (30 ml.) was added, and the mixture was heated under reflux for 1 hr. Sulphur (1·92 g.) in di-n-butyl ether (20 ml.) was added and the mixture was heated under reflux for 3 hr., cooled, and filtered. Evaporation of the filtrate yielded 1,2-dibenzyl-1,2-diphenyldiphosphine disulphide, m. p. and mixed m. p. 189·5—190·5° (from ethanol).

(b) *Formation of dibenzylphenylphosphine sulphide.* An experiment essentially as in (a),

[5] Kuchen and Buchwald, *Chem. Ber.*, 1958, **91**, 2871; Issleib and Seidel, *ibid.*, 1959, **92**, 2681.
[6] Kuchen and Buchwald, *Chem. Ber.*, 1959, **92**, 227.

except that the initial heating under reflux was for 3·5 hr., yielded dibenzylphenylphosphine sulphide, m. p. and mixed m. p. 148·5—149·5°, and no diphosphine disulphide.

Crystallography of 1,2-*dibenzyl*-1,2-*diphenyldiphosphine disulphide.* $a = 12·02 \pm 0·02$, $b = 29·00 \pm 0·04$, $c = 6·97 \pm 0·02$ Å, $\beta = 93·2 \pm 0·3°$, $U = 2324$ Å³, $D_m = 1·30$ (by flotation), $Z = 4$, $D_c = 1·29$, $F(000) = 968$.   Space group, $P2_1/c$ (C_{2h}^5, No. 14).   Cu K_α-radiation. single-crystal rotation, oscillation, and Weissenberg photographs.   Optically biaxial.