208. *The Chemical Effects of γ-Radiation on Organic Systems. Part X.*[1] *The Action of Radiation on Benzophenone Oxime.*

By G. A. Swan and P. S. Timmons.

In an attempt to see whether γ-radiation could induce the Beckmann rearrangement, we irradiated a solution of benzophenone oxime in chloroform. We found no evidence of the occurrence of the Beckmann rearrangement, but we obtained benzophenone oxime hydrochloride and diphenylmethylamine hydrochloride (G 0·47). Similar results were obtained in dry, alcohol-free chloroform or in chloroform saturated with water. In one experiment, the temperature was allowed to rise too high during the distillation of the solvent, after the irradiation, with the result that part of the oxime underwent the Beckmann rearrangement under the influence of the hydrogen chloride formed during the irradiation. However, apart from benzanilide, we also isolated a compound believed to be 1-benzoyl-2-diphenylmethyl-1-phenylhydrazine,[2] presumably formed by interaction of diphenylmethylamine (produced during the irradiation) with benzanilide (or an intermediate).

Experimental.—Arrangements for the irradiations and dosimetry were as described in Part I.[3]

A solution of benzophenone oxime (23 g.) in chloroform (245 ml.) was irradiated for 72·5 hr. (total dose $1{\cdot}18 \times 10^{23}$ ev), and the solution was evaporated to dryness at 40°/10 mm. The residue was exhaustively extracted with ether (1 l.), the bulk of it dissolving; evaporation of the extract left a residue which, when dried at 100°/10 mm., had m. p. 150—155° (decomp.) (1·6 g.) and consisted of a mixture of diphenylmethylamine hydrochloride with (mainly) the less stable benzophenone oxime hydrochloride. When an ethanolic solution of this mixture was diluted with ether, the former component was precipitated and collected (0·2 g.); it had m. p. 293° (sealed capillary) (Found: C, 71·25; H, 6·55; N, 6·4. Calc. for $C_{13}H_{13}N,HCl$: C, 71·1; H, 6·35; N, 6·35%). This was converted into diphenylmethylamine picrate, m. p. 208° (Found: C, 55·45; H, 3·65; N, 13·3. Calc. for $C_{13}H_{13}N,C_6H_3N_3O_7$: C, 55·35; H, 3·9; N, 13·6%). The solution from which diphenylmethylamine hydrochloride had been filtered yielded benzophenone oxime.

In an experiment in which the solution was allowed to become too hot during the distillation of the chloroform, the product isolated consisted of 1-benzoyl-2-diphenylmethyl-1-phenylhydrazine, m. p. 145—146° (0·13 g.) (Found: C, 82·6; H, 6·25; N, 7·6. Calc. for $C_{26}H_{22}N_2O$: C, 82·55; H, 5·8; N, 7·4%). This yielded a picrate, m. p. 223—225° (Found: C, 63·05; H, 4·6; N, 11·2. Calc. for $C_{26}H_{22}N_2O,C_6H_3N_3O_7$: C, 63·25; H, 4·1; N, 11·55%), and a hydrochloride (Found: C, 74·7; H, 5·35. Calc. for $C_{26}H_{23}ClN_2O$: C, 75·2; H, 5·5%). The molecular weight of the picrate, as determined from the ultraviolet absorption,[4] was 587 (Calc. for $C_{26}H_{22}N_2O,C_6H_3N_3O_7$: *M*, 607).

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[1] Part IX, Parrack, Swan, and Timmons, *J.*, 1962, 924.
[2] Grammaticakis, *Compt. rend.*, 1939, **208**, 1910.
[3] Swan and Timmons, *J.*, 1958, 4669.
[4] Cunningham, Dawson, and Spring, *J.*, 1951, 2305.

209. *Tervalent Manganese Complexes of* 2,2'-*Bipyridyl* 1,1-*Dioxide.*

By R. S. NYHOLM and A. TURCO.

WE investigated[1] recently the oxidation of bivalent manganese salts with persulphate in the presence of 2,2'-bipyridyl and reported the isolation of a cationic complex $[Bipy_2MnO_2MnBipy_2][ClO_4]_3$ (where Bipy = 2,2'-bipyridyl). This complex contains ter- and quadri-valent manganese and is one of the few compounds in which manganese(III) occurs in a cation; as pointed out by Sidgwick,[2] manganese(III) usually occurs in the anion, one of the exceptions being the $[Mn(Acetylacetone)_2(H_2O)_2]^+$ ion.[3]

Some time ago several complexes of metals with 2,2'-bipyridyl 1,1-dioxide ($BipyO_2$) were reported.[4] In particular the compound $[Mn(BipyO_2)_3][ClO_4]_2,2H_2O$ was described and was said to be very unstable, decomposing on storage to a black powder. This decomposition is apparently due to aerial oxidation since we find that this compound is stable in an inert atmosphere. Partly in order to confirm the formula for this manganese-(III—IV) compound, and partly because of the potentialities of the dioxide for stabilising higher oxidation states, we have investigated the dioxide derivatives. Although we considered that oxidation of the bipyridyl to the dioxide was unlikely under the conditions used in the preparation of the $[Bipy_2MnO_2MnBipy_2]^{3+}$ cation it could not be ruled out. When the latter was treated with alkali the bipyridyl could be extracted with chloroform, suggesting that the chelate group was present as such in the original compound, but characterisation of the manganese(III) complexes of the dioxide was considered essential to establish this conclusively.

We obtained the persulphate and perchlorate of the cation $[Mn(BipyO_2)_3]^{3+}$ by treating aqueous manganous sulphate in the presence of the dioxide with persulphate; addition of perchlorate produces the perchlorate complex instead. The magnetic moments of these compounds (respectively 5·00 and 4·97 B.M.) indicate four unpaired electrons, in agreement with the values usually found for spin-free manganese(III) complexes (4·85—5·0 B.M.). The conductance in nitromethane of the compound $[Mn(BipyO_2)_3](ClO_4)_3,3H_2O$ indicates a uni-tervalent electrolyte (see Table; the values for the corresponding ferric and manganous compounds are also given). Attempts to prepare the anhydrous compounds were unsuccessful, some of the water molecules being held very strongly; since the metal atom is already six-co-ordinate if the three chelate groups are each attached in two positions, it is not considered that the water molecules are co-ordinated to the metal. The compounds are stable indefinitely in the solid state but are easily hydrolysed in water, particularly in dilute solution.

Experimental.—2,2'-*Bipyridyl* 1,1-*dioxide*. This was prepared by Simpson's method,[4] by oxidation of 2,2'-bipyridyl with hydrogen peroxide in acetic acid. It formed white needles, m. p. 308—310° (decomp.).

Tri-(2,2'-*bipyridyl* 1,1-*dioxide*)*manganese*(III) *persulphate*. Potassium persulphate (3·2 g., 0·012 mole) was added to a solution of the dioxide (4·0 g., 0·021 mole) and manganese(II) sulphate tetrahydrate (1·56 g., 0·007 mole) in water (60 ml.) at 75°. The yellow solution gradually became dark-red. After 10 min. at 75°, potassium persulphate (3·0 g.) was added and the solution heated further for a few minutes. The crude product, contaminated with some white crystals, was filtered off after the mixture had been cooled and was obtained free from by-products (microscope) by careful washing with water (4 × 4 ml.). The dark-red crystals (2·2 g.) were washed with ethanol, dried with ether, and stored in desiccator. Infrared spectra indicated that water was still present after 12 hours' heating at 90° under a vacuum in

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[1] Nyholm and Turco, *Chem. and Ind.*, 1960, 74.

[2] Sidgwick, " The Chemical Elements and their Compounds," Oxford, 1950, Vol. II, p. 1274.

[3] Simpson, Thesis, Sydney, Australia, 1959; personal communication from J. V. Quagliano.

[4] Cartledge. *J. Amer. Chem. Soc.*, 1952, **74**, 6015.

the presence of phosphorus pentoxide (loss in weight, 5·8%). The *compound* absorbs this 5·8% of water in a moist atmosphere {Found: C, 34·8; H, 3·4; N, 8·7; Mn, 5·6; S, 9·6. $[\mathrm{Mn}(\mathrm{C_{30}H_{24}N_6O_6})](\mathrm{S_2O_8})_{1\cdot5},4\mathrm{H_2O}$ requires C, 36·8; H, 3·25; N, 8·6; Mn, 5·6; S, 9·8%}.

Tri-(2,2′-*bipyridyl* 1,1-*dioxide*)*manganese*(III) *perchlorate.* A mixture of potassium persulphate (3·0 g., 0·011 mole) and sodium perchlorate (15 g.) in water (60 ml.) was stirred for a few minutes and cooled to 0°. The supernatant liquor was separated by centrifugation and added in small portions to a solution of the dioxide (3·84 g., 0·020 mole) and manganous sulphate tetrahydrate (1·35 g., 0·006 mole) in water (45 ml.) 90°. After 10 min. more solid sodium perchlorate (30 g.) was added and the temperature was kept at 80° for further 5—10 min. The solution was cooled to 30° and filtered. The dark-red crystals (2·3 g.) were washed with water, ethanol, and ether and stored in a desiccator.

Before this procedure was adopted, several preparations were found to consist of a mixture of green and red crystals. Attempts to obtain the green free from the red compound were unsuccessful.

Infrared spectra of this *salt* indicated the presence of water, part of which is lost at 110° (loss in weight 2·1% in 10 hr.) {Found: C, 37·5; H, 3·4; N, 8·8; Mn, 5·6; Cl, 10·75. $[\mathrm{Mn}(\mathrm{C_{30}H_{24}N_6O_6})](\mathrm{ClO_4})_3,3\mathrm{H_2O}$ requires C, 37·05; H, 3·1; N, 8·65; Mn, 5·65; Cl, 10·95%}.

Molar conductivity in nitromethane at 20°.

Compound	Concn. (10^{-4}M)	Conductivity (cm.^{2} ohm^{-1} mole^{-1})	Compound	Concn. (10^{-4}M)	Conductivity (cm.^{2} ohm^{-1} mole^{-1})
$[\mathrm{Mn}(\mathrm{BipyO_2})_3](\mathrm{ClO_4})_2,2\mathrm{H_2O}$ [3]	1·45	200	$[\mathrm{Mn}(\mathrm{BipyO_2})_3](\mathrm{ClO_4})_3,3\mathrm{H_2O}$	1·24	288
	2·45	192		2·02	275
	10·10	164		8·42	227
$[\mathrm{Fe}(\mathrm{BipyO_2})_3](\mathrm{ClO_4})_3,3\mathrm{H_2O}$ [3]	1·23	298			

Magnetic susceptibilities. These were determined by the Gouy method at 15°. The χ values for $[\mathrm{Mn}(\mathrm{BipyO_2})_3](\mathrm{S_2O_8})_{1\cdot5},4\mathrm{H_2O}$ and $[\mathrm{Mn}(\mathrm{BipyO_2})_3](\mathrm{ClO_4})_3,3\mathrm{H_2O}$ were, respectively, 10·48 and 10·46 × 10^{-6} c.g.s. units.

Analysis. Manganese was determined by heating the compound (1 pt.) with anhydrous sodium carbonate (3 pt.), the manganese then being estimated gravimetrically as pyrophosphate. The same procedure led to reduction of the perchlorate (catalysed by manganese oxides), and the chloride ion was then estimated gravimetrically as silver chloride. The persulphate was determined as barium sulphate.

The authors are indebted to Professor J. V. Quagliano for helpful discussions.

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210. *The Reaction of Dialkyl Phosphites with Cupric Chloride.*

By T. D. SMITH.

THE general methods available for preparation of dialkyl phosphorochloridates are [1] (1) reaction with phosphorus oxychloride, (2) treatment of trialkyl phosphates with phosphorus oxychloride, (3) reaction of dialkyl phosphites with chlorine,[2] sulphuryl

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[1] Kosolapoff, " Organo-phosphorus Compounds," John Wiley & Sons, Inc., New York, 1950.

[2] McCombie, Saunders, and Stacey, *J.*, 1945, 380.

chloride,[3] *N*-chlorosuccinimide,[4,5] or *N*,2,4-trichloroacetanilide.[5] The literature contains many references to the use of anhydrous cupric chloride in the chlorination of hydrocarbons. Recently[6] the reaction of cupric chlorides with aromatic hydrocarbons was investigated, cupric bromide and toluene yielding bibenzyl with evolution of hydrogen bromide as a result of a free-radical reaction with participation of benzyl radicals. We have found that under heterogeneous conditions in, for example, carbon tetrachloride anhydrous cupric chloride reacted readily with dialkyl phosphites to yield cuprous chloride and dialkyl phosphorochloridates with evolution of hydrogen chloride: $2CuCl_2 + (RO)_2P(O)H \longrightarrow 2CuCl + (RO)_2P(O)Cl + HCl$. Reaction of anhydrous cupric chloride alone with dialkyl phosphite was very vigorous, though, contrary to the reaction of cupric halides with aromatic hydrocarbons,[6] anhydrous cupric bromide reacted much less readily. The product was isolated by the method outlined by McCombie *et al.*[2] and characterised by formation of the dialkyl *N*-phenylphosphoroamidate.

Experimental.—*Diethyl phosphorochloridate.* Diethyl phosphite (5·4 g.) in carbon tetrachloride (200 ml.) was stirred in dry air in the presence of anhydrous cupric chloride (11·0 g.) at ~100° for 4 hr. The solution then gave no reaction with cacotheline.[7] The mixture was filtered off, the filtrate shaken with lead carbonate (15 g.), the carbon tetrachloride distilled off, and diethyl phosphorochloridate obtained by distillation under reduced pressure (5·0 g., 74%) (Found: Cl, 20·6. Calc. for $C_4H_{10}ClO_3P$: Cl, 20·5%). This ester was readily identified by conversion into diethyl *N*-phenylphosphoramidate[2] which, recrystallised twice from water, had m. p. 96° (Found: C, 52·3; H, 7·4; N, 6·3. $C_{10}H_{16}NO_3P$ requires C, 52·4; H, 7·0; N, 6·1%). Di-isopropyl *N*-phenylphosphoramidate, m. p. 121°, was also prepared from it.

To establish that cuprous chloride was formed, anhydrous cupric chloride was treated with a two-fold excess of dimethyl phosphite, and the white solid product washed with carbon tetrachloride and cyclohexane and heated at 120° under reduced pressure (Found: Cl, 35·6. Calc. for CuCl: Cl, 35·8%). The yields for dimethyl, di-isopropyl, and di-n-butyl phosphite were 83%, 71%, and 64%, respectively.

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[*Received, September 28th,* 1961.]

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[3] Ford-Moore, Lermit, and Stratford, *J.*, 1953, 1776.
[4] Goldwhite and Saunders, *J.*, 1955, 2040.
[5] Kenner, Todd, and Weymouth, *J.*, 1952, 3675.
[6] Nonhabel, *Proc. Chem. Soc.*, 1961, 306.
[7] Smith, *Analyt. Chim. Acta*, 1960, **22**, 249.

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211. *A Nuclear Magnetic Resonance Study of Hydrogen Bonding of Some Amines.*

By J. Feeney and L. H. Sutcliffe.

This Note provides the detailed experimental results in support of a preliminary communication[1] on hydrogen-bonding equilibria of some amines. The Table given previously is reproduced for convenience. The association shift was taken as the difference between the chemical shift of the amino-hydrogen nuclei at infinite dilution (pure monomer) and the constant value observed for the liquid amine just above its melting point.

Diluting or heating amines caused the ^1H resonance of the hydrogen nuclei of the amino-group to move to high fields. It is interesting that the sharp amine band of the pure

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[1] Feeney and Sutcliffe, *Proc. Chem. Soc.*, 1961, 118.

liquid amine lies within the CH_3 multiplet. The changes of chemical shift brought about by diluting or cooling the amine were measured with a precision of ±1%, utilising some other band in the spectrum as a reference, usually the central line of a methyl group triplet. An internal reference such as tetramethylsilane was avoided because of the large chemical-shift difference between it and the amine-resonance signal. Unless ring compounds are formed, the chemical shift of the *n*-mer will have a contribution from non-hydrogen-bonded hydrogen atoms. To obtain the roughly constant association shift shown in the last column of Table 1, the same ratio of hydrogen-bonded to non-hydrogen-bonded amine-hydrogen atoms would have to prevail for each compound. This unlikely state of affairs can be taken as some indication of the formation of cyclic *n*-mers in the three amines listed.

TABLE 1.

The chemical shifts (c./sec.) of the monomer and the *n*-mer species measured from the room-temperature NH_2 band.

	Monomer shift at room temp. (f_1)	*n*-Mer shift just above the m. p. (f_n)	Association shift
Monoethylamine	17·7	−22·1	39·8
Diethylamine	22·4	−17·2	39·6
Isobutylamine	—	−35	>35
Ammonia [2]	—	—	42

Table 2 lists the results for the variation of the chemical-shift difference with concentration of monoethylamine and diethylamine at 25°C. The data were treated by the method devised by Saunders and Hyne[3] from the theory developed by Gutowsky and Saika.[4] The exchange process between hydrogen-bonded and non-hydrogen-bonded species is sufficiently rapid to prevent observation of separate resonance bands. If it is assumed that the time-averaged absorption band results from interchange between the monomer and a single *n*-mer, then the ratio of monomer to *n*-mer in equilibrium can be calculated by using the following equations:[3]

TABLE 2.

Mono- and di-ethylamine in carbon tetrachloride. Chemical shifts (f) (c./sec.) are measured from the central band of the methyl triplet at 40 Mc./sec. (high field positive).

Monoethylamine at 25°.			Diethylamine at 25°.			Diethylamine at −37°.		
Chemical shift	Concn. (C) (M)	log C	Chemical shift	Concn. (C) (M)	log C	Chemical shift	Concn. (C) (M)	log C
9·0	1·21	0·082	22·8	1·51	0·185	20·2	1·47	0·167
3·3	3·32	0·521	22·8	1·97	0·295	18·0	2·19	0·340
4·7	3·36	0·526	20·3	4·42	0·645	16·9	2·57	0·410
0·0	3·69	0·567	20·2	4·44	0·677	14·1	3·38	0·529
−1·1	4·52	0·655	19·8	5·58	0·746	8·1	4·81	0·682
−2·7	7·36	0·867	16·6	6·97	0·843	4	7·36	0·866
−6·3	11·1	1·004	16·2	7·28	0·862			
−7·5	15·95	1·203	15·4	7·60	0·880			
			14·3	7·77	0·890			
			8·4	8·70	0·939			
			0·0	9·70	0·987			

$$f = (f_1 M_1 + n f_n K_n M_1)/C \qquad (1)$$

$$C = M_1 + n K_n M^n_1, \qquad (2)$$

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[2] Schneider, Bernstein, and Pople, *J. Chem. Phys.*, 1958, **28**, 601.

[3] Saunders and Hyne, *J. Chem. Phys.*, 1958, **29**, 1319.

[4] Gutowsky and Saika, *J. Chem. Phys.*, 1953, **21**, 1688.

where f is the observed frequency, f_n is the frequency of the n-mer, K_n is the correspondine association constant, C is the total concentration of all species, and M_1 is the monomer concentration. These simple equations contain too many unknowns to allow a complete solution. However, theoretical curves of log C against f can be constructed for arbitrary values of C, K_n, and n, and these can be compared with the experimental curves. Theoretical curves for the equilibria involving monomer–dimer and monomer–trimer species do not agree with the experimental results for dilution of mono- and di-ethylamine.

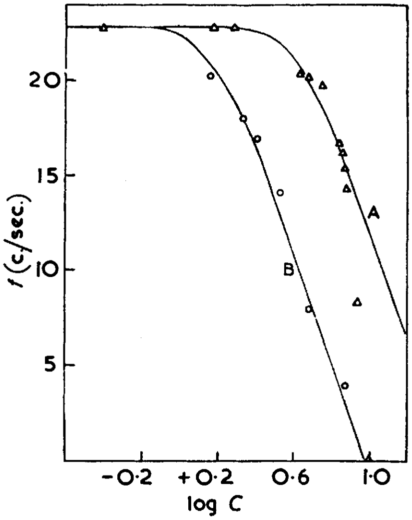

FIG. 1. The variation of the observed chemical shift difference f with the logarithm of the concentration C of diethylamine in carbon tetrachloride, on the basis of a monomer–tetramer equilibrium, at (A) 25° and (B) −37° c. The full lines have been calculated by taking the values of K_n to be $2{\cdot}5 \times 10^{-4}$M^{-3} and $2{\cdot}5 \times 10^{-3}$M^{-3}, respectively.

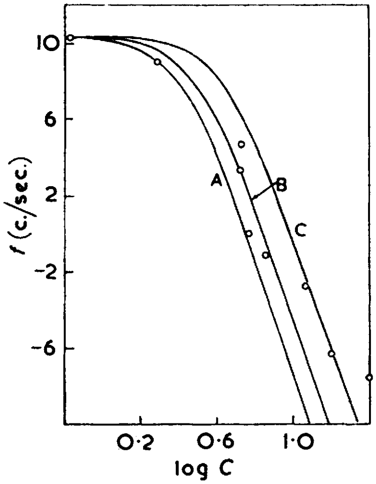

FIG. 2. The variation of the observed chemical-shift difference f with the logarithm of the concentration C of monoethylamine in carbon tetrachloride at 25°c. The full lines have been calculated for K_n values of (A) 5×10^{-3}M^{-3}, (B) $2{\cdot}5 \times 10^{-3}$M^{-3}, and (C) 1×10^{-3}M^{-3}.

A suitable theoretical curve for the dilution of diethylamine resulted when a monomer-tetramer equilibrium was postulated (see Fig. 1 and Table 2).

The rather greater chemical-shift difference observed on dilution of diethylamine enabled more precise data to be obtained than was possible for monoethylamine. The evidence for tetramers is tenuous because curve fitting is insensitive to values of n greater than 4. The deviations occurring at higher amine concentrations could be due to the presence of n-mers greater than tetramers but they might also arise from changes in magnetic susceptibility on changing the medium.[5] Similar theoretical curves to that for a monomer–tetramer equilibrium result if higher aggregates are present and it is impossible unequivocally to exclude their presence from the system by means of the present results. A monomer–tetramer equilibrium was also found to produce theoretical curves most consistent with the experimental results obtained on diluting monoethylamine (see Fig. 2 and Table 2). The formation constants of the assumed tetramers of di- and mono-ethylamine were $2{\cdot}5 \times 10^{-4}$M^{-3} and $2{\cdot}5 \times 10^{-3}$M^{-3}, respectively, at 25°.

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[5] Saunders and Hyne, *J. Chem. Phys.*, 1958, **29**, 253.

Measurements of the effect of dilution on the amine band of diethylamine at —37° were also carried out and the results are given in Fig. 1 and Table 2: the association constant of diethylamine was $5{\cdot}0 \times 10^{-3}\text{M}^{-3}$ at —37°. From the two values of the association constant, the heat of formation of the assumed tetramer was calculated to be —6·8 kcal. per mole of tetramer. Had a higher aggregate been accepted, this overall enthalpy would not be greatly affected and thus the rather low value of —1·7 kcal. per hydrogen bond per mole would have been lowered still further.

Exploratory experiments on aniline revealed no measurable change in chemical shift of the NH_2 group on dilution but the band did become narrower with increased dilution. Line narrowing could be due to a de-association effect not involving hydrogen bonds. The infrared data obtained on the influence of dilution of the N–H stretching frequency of aniline did not provide conclusive evidence for hydrogen bonding.[6]

Experimental.—Materials. Aniline was of " AnalaR " quality. Monoethylamine and diethylamine were of ordinary reagent grade, from Eastman-Kodak Co. and May and Baker Ltd., respectively. Isobutylamine was a Light and Co. product. Small amounts of water drastically affected the nuclear magnetic resonance spectra; therefore the compounds were distilled in a vacuum after being kept over sodium wire for a day. Samples were stored under a vacuum until required.

" AnalaR " carbon tetrachloride was used as solvent without further purification.

Apparatus. ^{1}H resonance spectra were obtained by means of a Varian V4300B NMR spectrometer operating at 40·00 Mc./sec. Temperature-control of the sample was achieved with the aid of a modified Brownstein probe insert.[7]

Experimental procedure. Detailed measurements have been made only on mono- and di-ethylamine because these compounds require some hours before their amine hydrochlorides crystallise:[1,8] nuclear magnetic resonance spectra could be obtained before this salt formation had an observable effect. The solutions were contained in Pyrex sample tubes of 3 mm. internal and 5 mm. external diameter, into which had been inserted a 5 mm. length of Pyrex tubing to facilitate mixing of amine and solvent by shaking. Mixtures of known concentration were made up by weighing but the two components were kept apart by means of an air-bubble until the spectra were about to be recorded, then the sample tube was shaken. Delays between weighing of samples and recording of spectra were kept to a minimum.

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[6] Fuson, Josien, Powell, and Utterback, *J. Chem. Phys.*, 1952, **20**, 145.
[7] Brownstein, *Canad. J. Chem.*, 1959, **37**, 1119.
[8] Collins, *Chem. and Ind.*, 1957, 704.

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212. *Carcinogenic Nitrogen Compounds. Part XXXIII.*[1] *Alkyl-substituted Benzacridines and Benzophenarsazines.*

By N. P. BUU-HOÏ, P. JACQUIGNON, and MICHÈLE MARTY.

As carcinogenicity is known to be enhanced by the introduction of a 5- or 6-isopropyl group into 1,2-benzanthracene,[2] 1,2- and 3,4-benzacridines bearing isopropyl groups in various positions have now been synthesised; the kinship of the cyclohexyl radical to

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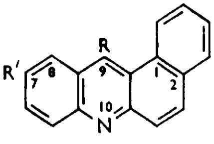
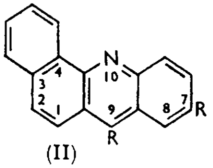
[1] Part XXXII, Buu-Hoï, Périn, and Jacquignon, *J.*, 1961, 146.
[2] Cook, *J.*, 1932, 456; Badger, Cook, Hewett, Kennaway, Kennaway, Martin, and Robinson, *Proc. Roy. Soc.*, 1940, *B*, **129**, 439.

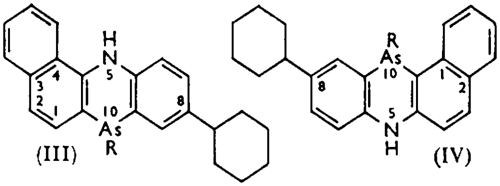
isopropyl suggested the preparation also of cyclohexylbenzacridines. The intermediates used were *p*-isopropyl- and *p*-cyclohexyl-aniline, which were converted into the corresponding *N*-arylnaphthylamines [3] and thence by Bernthsen condensations [4] into 9-alkyl-7-isopropyl- and 9-alkyl-7-cyclohexyl-1,2- (I) and -3,4-benzacridines (II); benzacridines not substituted in position 9 were obtained by condensation of *p*-isopropyl- and *p*-cyclohexyl-aniline with α- and β-naphthol in presence of paraformaldehyde.[5]



(I)



(II)



(III) (IV)

Condensation of the two *N*-*p*-cyclohexylphenylnaphthylamines with arsenic trichloride afforded the dihydrobenzophenarsazines (III and IV; R = Cl); replacement of the chlorine atom by methyl and ethyl groups was easily achieved with the appropriate Grignard reagents, to give the dihydrobenzophenarsazines (III and IV; R = Me or Et).

Experimental.—M. p.s were taken on a Maquenne block.

7-Isopropyl-3,4-benzacridine (II; R = H, R' = Pr^i). To a boiling mixture of *p*-isopropylaniline (9 g.) and α-naphthol (10 g.), paraformaldehyde (7 g.) was added in small portions, and the product boiled for a few minutes. The orange-red oil, b. p. 275—280°/25 mm., obtained on fractionation *in vacuo*, was converted into a *picrate*, m. p. 102°, orange prisms, m. p. 242° (decomp. >218°) (from chlorobenzene) (Found: N, 11·2. $C_{26}H_{30}N_4O_7$ requires N, 11·2%). Basification with aqueous ammonia gave the *acridine*, cream-coloured needles (1·5 g.) (from hexane), b. p. 270°/14 mm. (Found: C, 88·5; H, 6·6; N, 5·4. $C_{20}H_{17}N$ requires C, 88·5; H, 6·3; N, 5·2%).

The following were similarly prepared: 7-Isopropyl-1,2-benzacridine (I; R = H, R' = Pr^i), isolated as a *picrate*, yellow needles, m. p. 268° (decomp. >235°) (from chlorobenzene) (Found: N, 11·1%) (the free acridine crystallised with difficulty from aqueous acetone as solvated crystals, m. p. 60°). *7-Cyclohexyl-3,4-benzacridine*, m. p. 105° (from hexane) (Found: C, 88·8; H, 6·6. $C_{23}H_{21}N$ requires C, 88·7; H, 6·8%) [*picrate*, m. p. 239° (decomp. >180°) (from chlorobenzene) (Found: N, 10·3. $C_{29}H_{24}N_4O_7$ requires N, 10·4%)]. *7-Cyclohexyl-1,2-benzacridine*, m. p. 117° (from heptane) (Found: C, 88·9; H, 6·4%) [*picrate*, m. p. 247° (decomp. >230°) (from chlorobenzene) (Found: N, 10·2%)].

N-p-*Isopropylphenyl-1-naphthylamine*. Prepared from *p*-isopropylaniline (20 g.), α-naphthol (22·5 g.), and iodine (0·2 g.), this *amine* (11 g.) had b. p. 240—244°/18 mm. (Found: C, 87·0; H, 7·3. $C_{19}H_{19}N$ requires C, 87·3; H, 7·3%) and gave a *picrate*, violet needles, m. p. 76—77° (from hexane) (Found: N, 11·7. $C_{25}H_{22}N_4O_7$ requires N, 11·4%).

From this amine, the following benzacridines were obtained with the appropriate acid anhydride: *7-Isopropyl-9-methyl-3,4-benzacridine* (II; R = Me, R' = Pr^i), b. p. 277°/22 mm., yellowish needles, m. p. 142° (from ethanol) (Found: C, 88·1; H, 6·7. $C_{21}H_{19}N$ requires C, 88·4; H, 6·7%) [*picrate*, yellow prisms, m. p. 198° (decomp. >185°) (from chlorobenzene) (Found: N, 10·6. $C_{27}H_{22}N_4O_7$ requires N, 10·9%)]. *9-Ethyl-7-isopropyl-3,4-benzacridine* (II; R = Et, R' = Pr^i), b. p. 280—285°/25 mm., m. p. 113° (Found: C, 88·0; H, 7·1. $C_{22}H_{21}N$ requires C, 88·3; H, 7·1%) [*picrate*, m. p. 231° (decomp. >190°) (Found: N, 10·8. $C_{28}H_{24}N_4O_7$ requires N, 10·6%)]. *7,9-Di-isopropyl-3,4-benzacridine* (II; R = R' = Pr^i), b. p. 288—290°/28 mm., m. p. 85° (Found: C, 88·2; H, 7·4; N, 4·7. $C_{23}H_{23}N$ requires C, 88·2; H, 7·3; N, 4·5%) [*picrate*, m. p. 223° (decomp. >177°) (Found: N, 10·5. $C_{29}H_{26}N_4O_7$ requires N, 10·3%)].

N-p-*Isopropylphenyl-2-naphthylamine*. This *amine*, b. p. 250—252°/22 mm., formed colourless

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[3] Knoevenagel, *J. prakt. Chem.*, 1914, **89**, 1.
[4] Buu-Hoï, *J.*, 1946, 792.
[5] Ullmann and Fetvadjian, *Ber.*, 1903, **36**, 1029; Buu-Hoï, *J.*, 1950, 1146.

prisms, m. p. 68°, from aqueous ethanol (Found: C, 87·2; H, 7·6%), and a *picrate*, violet needles, m. p. 98°, from hexane (Found: N, 11·5%).

From this amine, the following benzacridines were prepared: 7-*Isopropyl*-9-*methyl*-1,2-*benzacridine* (I; R = Me, R′ = Pr^i), yellow oil, b. p. 285°/25 mm. (Found: C, 88·1; H, 6·6%) [*picrate*, m. p. 239° (decomp. >181°) (from chlorobenzene) (Found: N, 10·8%)]. 9-*Ethyl*-7-*isopropyl*-1,2-*benzacridine* (I; R = Et, R′ = Pr^i), b. p. 290°/22 mm. (Found: C, 88·0; H, 7·0%) [picrate, m. p. 190° (decomp. >176°)]. 7,9-*Di-isopropyl*-1,2-*benzacridine* (I; R = R′ = Pr^i), yellowish needles, m. p. 165°, from ethanol (Found: C, 88·2; H, 7·4; N, 4·6%) [*picrate*, m. p. 198° (decomp. >170°) (Found: C, 63·5; H, 4·9. $C_{29}H_{26}N_4O_7$ requires C, 63·3; H, 4·8%)].

N-p-*Cyclohexylphenyl*-1-*naphthylamine*. This *amine*, b. p. 280°/20 mm., formed colourless needles, m. p. 116°, from hexane (Found: N, 4·9. $C_{22}H_{23}N$ requires N, 4·7%); with picric acid, these gave a violet colour in hexane, but the picrate decomposed on crystallisation. N-p-*Cyclohexylphenyl*-2-*naphthylamine* formed leaflets, m. p. 101°, from hexane (Found: N, 4·7%) and a *picrate*, violet needles, m. p. 113° (from hexane) (Found: N, 10·6. $C_{28}H_{26}N_4O_7$ requires N, 10·6%). From these secondary amines, the following benzacridines were obtained: 7-*Cyclohexyl*-9-*methyl*-3,4-*benzacridine*, m. p. 204° (from ethanol) (Found: C, 88·6; H, 7·1; N, 4·4. $C_{24}H_{23}N$ requires C, 88·9; H, 6·9; N, 4·3%) [*picrate*, m. p. 212° (decomp. >185°) (from ethanol) (Found: N, 10·4. $C_{30}H_{26}N_4O_7$ requires N, 10·1%)]. 7-*Cyclohexyl*-9-*ethyl*-3,4-*benzacridine*, m. p. 172° (Found: C, 88·4; H, 7·0; N, 4·3. $C_{25}H_{25}N$ requires C, 88·5; H, 7·4; N, 4·1%) [*picrate*, m. p. 187° (decomp. >180°) (Found: N, 9·8. $C_{31}H_{28}N_4O_7$ requires N, 9·9%)]. 7-*Cyclohexyl*-9-*ethyl*-1,2-*benzacridine*, m. p. 138° (Found: C, 88·4; H, 7·4; N, 4·1%) [picrate, m. p. 228° (decomp. >212°) (from chlorobenzene)].

10-*Chloro*-8-*cyclohexyl*-5,10-*dihydro*-3,4-*benzophenarsazine* (III; R = Cl). *N*-*p*-Cyclohexylphenyl-1-naphthylamine (6 g.) and arsenic trichloride (3·7 g.) in *o*-dichlorobenzene (15 c.c.) were refluxed for 2 hr. and the solid obtained on cooling was recrystallised from chlorobenzene, giving the *dihydrobenzophenarsazine* as orange-yellow prisms (4·5 g.), m. p. 228° (decomp. >218°), whose solutions in sulphuric acid were brown-red (Found: C, 64·5; H, 5·2. $C_{22}H_{21}AsClN$ requires C, 64·5; H, 5·1%). Reaction of methylmagnesium iodide (2 mol.) gave 8-*cyclohexyl*-5,10-*dihydro*-10-*methyl*-3,4-*benzophenarsazine* (III; R = Me) as colourless needles, m. p. 155°, from methanol, whose solutions in sulphuric acid were orange (Found: N, 3·7. $C_{23}H_{24}AsN$ requires N, 3·6%). With ethylmagnesium iodide, 8-*cyclohexyl*-10-*ethyl*-5,10-*dihydro*-3,4-*benzophenarsazine* (III; R = Et) was obtained, colourless needles, m. p. 124° (hexane) (Found: C, 71·4; H, 6·5; N, 3·5. $C_{24}H_{26}AsN$ requires C, 71·5; H, 6·5; N, 3·5%).

10-*Chloro*-8-*cyclohexyl*-5,10-*dihydro*-1,2-*benzophenarsazine* (IV; R = Cl), prepared from *N*-*p*-cyclohexylphenyl-2-naphthylamine, formed orange-yellow prisms (4 g.), m. p. 222° (decomp. >213°) from chlorobenzene (Found: C, 64·3; H, 5·2%); 8-*cyclohexyl*-5,10-*dihydro*-10-*methyl*-1,2-*benzophenarsazine* (IV; R = Me), colourless leaflets (from ethanol), had m. p. 189° (Found: N, 3·9%); 8-*cyclohexyl*-10-*ethyl*-5,10-*dihydro*-1,2-*benzophenarsazine* (IV; R = Et), colourless needles (from ethanol), had m. p. 133° (Found: C, 71·6; H, 6·5; N, 3·5%).

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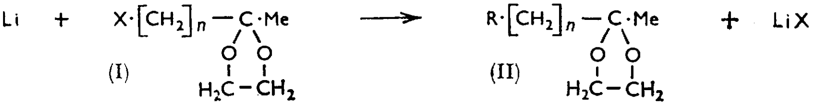
213. *The Reaction of Organolithium Compounds with Some Halogeno-ketals.*

By GURNOS JONES.

WE have described[1] the reaction between organolithium compounds and some halogeno-acetals which gives good yields of acetals:

$$RLi + X{\cdot}[CH_2]_n{\cdot}CH(OEt)_2 \longrightarrow R{\cdot}[CH_2]_n{\cdot}CH(OEt)_2 + LiX$$

This reaction was particularly successful with halogenopropionaldehyde diethyl acetals. As some pyridyl ketones were required for another investigation we have now studied the reaction between organolithium compounds and some halogeno-ketals, namely, those from 4-chloro- and 4-bromo-butan-2-one (I; X = Cl or Br, $n = 2$) and from 5-chloro- and 5-bromo-pentan-2-one (I; X = Cl or Br, $n = 3$). The general reaction was:



(I) (II)

In these experiments, as with the halogeno-acetals, a 2 : 1 molar ratio of organolithium compound to halogen compound was used. The ketals (II) formed were identified by their infrared absorption and by hydrolysis and preparation of derivatives of the ketone. All showed a characteristic group of bands in the region 1030—1225 cm.$^{-1}$. The three principal regions of absorption were at 1220—1225, 1110—1150, and at 1045—1065 cm.$^{-1}$, the last of these being the strongest; medium to strong absorption bands were at 945—955 and 860—870 cm.$^{-1}$. Bergmann and Pinchas reported[2] that ketals and acetals show absorption at 1158—1190, 1124—1143, 1063—1098, and 1038—1056 cm.$^{-1}$.

The results of these experiments are grouped in Tables 1 and 2. 2-Pyridylmethyl-lithium and any of the four halogeno-ketals gave high yields ($\not<70\%$) of the ketals (II; R = 2-$C_5H_4N{\cdot}CH_2$). Since the ketals were readily hydrolyzed by dilute acids, these reactions give the best reported syntheses of 5-2′-pyridylpentan-2-one and 6-2′-pyridylhexan-2-one. With other organolithium compounds the yields were lower, and more variation was observed between the chloro- and the bromo-ketals.

Experimental.—The ethylene ketals of 4-chloro- and 4-bromo-butan-2-one were prepared as described by Schinz and Williman,[3] except that the reduction of the ethylene ketal of acetoacetic ester was performed with lithium aluminium hydride instead of with sodium in ethanol. 5-Chloro-[4] and 5-bromo-pentan-2-one[5] were synthesized from α-acetyl-γ-butyrolactone and converted into the ethylene ketals as described by Cawley[6] and by Grob and Moesch,[7] respectively. All ketals were dried over calcium chloride and distilled before use.

6-2′-Pyridylhexan-2-one. A filtered solution of 2-pyridylmethyl-lithium prepared[8] from bromobenzene (0·2 mole), lithium (0·4 mole), and 2-picoline (0·2 mole) in ether (200 ml.) was stirred under dry nitrogen while 5-bromopentan-2-one ethylene ketal (0·1 mole) was added dropwise. Much heat was evolved and the addition was made at a rate sufficient to maintain

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[1] Jones and Law, *J.*, 1958, 3631.
[2] Bergmann and Pinchas, *Rec. Trav. chim.*, 1952, **71**, 161.
[3] Schinz and Williman, *Helv. Chim. Acta*, 1949, **32**, 2153.
[4] Cannon, Ellis, and Leal, *Org. Synth.*, Vol. XXXI, p. 74.
[5] Boon, U.S.P. 2,370,392/1945, B.P. 558,286/1943.
[6] Cawley, B.P. 728,446/1955.
[7] Grob and Moesch, *Helv. Chim. Acta*, 1959, **42**, 78.
[8] Woodward and Kornfeld, *Org. Synth.*, Coll. Vol. III, p. 413.

TABLE 1.

Reactions of ethylene ketals of $X{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$.

Reagent	X	Product: ketal of	Yield (%)	B. p./mm.
$2\text{-}C_5H_4N{\cdot}CH_2Li$	Cl	5-2′-Pyridylpentan-2-one [a]	70	157—160°/14
,,	Br		78	160—166°/18
PhLi	Cl	4-Phenylbutan-2-one [b]	41	141°/17
,,	Br		38	130—140°/17
Bu^nLi	Cl	Octan-2-one [c]	32	90—94°/17

[a] Ketone picrate, m. p. 112° (Found: C, 49·25; H, 3·9. Calc. for $C_{16}H_{16}N_4O_8$; C, 49·0; H, 4·1%) (lit.,[10] m. p. 111·5°). [b] Ketone 2,4-dinitrophenylhydrazone, m. p. 126—127° (lit.,[11] m. p. 126—126·5°). [c] Ketone 2,4-dinitro-phenylhydrazone, m. p. 58° (lit.,[12] m. p. 58°); semicarbazone, m. p. 121—122° (lit.,[13] m. p. 123°).

TABLE 2.

Reactions of ethylene ketals of $X{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$.

Reagent	X	Product: ketal of	Yield (%)	B. p./mm.
$2\text{-}C_5H_4N{\cdot}CH_2Li$	Cl	6-2′-Pyridylhexan-2-one	76	167—173°/15
,,	Br		80	171—174°/19
PhLi	Cl	5-Phenylpentan-2-one [a]	16 [b]	144—150°/15
,,	Br		58	150—152°/16
Pr^iLi	Cl	—	— [c]	
,,	Br	—	— [d]	

[a] Ketone, m. p. 128—132°/18 mm.; semicarbazone, m. p. 127—128° (lit.,[14] 127°). [b] 67% of chloro-ketal recovered; prep. in boiling benzene gave the same yield (30% of chloro-ketal recovered). [c] Recovered 88% of chloro-ketal. [d] Recovered 85% of bromo-ketal.

gentle boiling. The mixture then boiled for 10 min. without external heating. It was boiled for a further 4 hr. and left overnight. The cooled mixture was hydrolyzed by addition of a mixture of dilute aqueous ammonia and ammonium chloride, the ether layer was separated, and the aqueous layer twice extracted with further small portions of ether. The combined ethereal extracts were dried (Na_2SO_4) and distilled. The *ketal* (17·7 g., 80%) boiled at 171—174°/19 mm., 114—115°/0·4 mm. (Found: C, 70·8; H, 8·8; N, 6·3. $C_{13}H_{19}NO_2$ requires C, 70·5; H, 8·65; N, 6·3%).

The ketal (2·7 g.) was heated in N-hydrochloric acid (25 ml.) on a boiling-water bath for 1 hr., then cooled and extracted with ether, and the aqueous layer was basified and again extracted with ether. The second ethereal extract was dried (Na_2SO_4) and evaporated, and the residue distilled, to give 6-2′-pyridylhexan-2-one, b. p. 138—140°/17 mm. (1·1 g., 51%) (lit.,[9] b. p. 106°/0·7 mm.). The *ketone picrate* crystallized from ethanol as yellow needles, m. p. 101° (Found: C, 50·4; H, 4·4; N, 13·4. $C_{17}H_{18}N_4O_8$ requires C, 50·3; H, 4·5; N, 13·8%).

The above procedure was used in the experiments recorded in Tables 1 and 2, except that with other lithium compounds the chloro- or bromo-ketal was added all at once.

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[9] Gautier, Marszak, and Miocque, *Bull. Soc. chim. France*, 1958, 415.

[10] Doering and Weil, *J. Amer. Chem. Soc.*, 1947, **69**, 2461.

[11] Burnett, Marks, and Moc, *J. Amer. Chem. Soc.*, 1953, **75**, 985.

[12] Allen, *J. Amer. Chem. Soc.*, 1930, **52**, 2955.

[13] Michael, *J. Amer. Chem. Soc.*, 1919, **41**, 417.

[14] Prevost and Robert, *Bull. Soc. chim. France*, 1944, **11**, 225.

214. *The Preparation of Some Substituted Tricyclohexyl- and Trimethyl-phenylstannanes.*

By C. Eaborn and J. A. Waters.

We describe below the preparation of some new tricyclohexylphenylstannanes [$X\cdot C_6H_4\cdot Sn(C_6H_{11})_3$, where X = *m*-Me, *p*-Et, *p*-Pr^i, *p*-Bu^t, *o*-Ph, *p*-Ph, *p*-F, *p*-Cl, *m*-Cl, *p*-OMe, *m*-OMe, *p*-CO_2H, *p*-NMe_2, *p*-Br, *p*-$NMe_3^+I^-$, and *p*-$(C_6H_{11})_3Sn$] and phenyltrimethylstannanes ($X\cdot C_6H_4\cdot SnMe_3$, where X = *p*-Me, *p*-Cl, and *m*-Cl), and of *p*-methoxyphenyltriphenylstannane.

Experimental.—General. Emphasis was on obtaining pure products rather than high yields.

Bromotrimethylstannane.[1] Bromine (35·5 g.) was added during 2 hr. with stirring to tetramethylstannane (40·0 g.) at 0°. The mixture was stirred for 2 hr. more, and then fractionated to give bromotrimethylstannane (39 g., 66%), b. p. 159°.

Preparations from Grignard reagents. The Grignard reagent was prepared in ether from the appropriate aryl bromide (0·065 mole). Bromotricyclohexyl-,[2] bromotrimethyl-, or iodotriphenyl-stannane[3] (0·050 mole in each case) in ether was added during 20 min. and the mixture was refluxed, for 12 hr. unless otherwise stated. Treatment with 5% aqueous ammonium chloride was followed by separation, washing, and drying (Na_2SO_4) of the ethereal layer, and removal of the solvent. The residue was fractionated (in the case of the trimethyl compounds) or recrystallized.

Details for the tricyclohexyl compounds are given in the Table. Trimethylphenylstannane, b. p. 88·5°/16 mm., p-*chlorophenyltrimethylstannane*, b. p. 80°/2—3 mm. (Found: C, 39·5; H, 4·6. $C_9H_{13}ClSn$ requires C, 39·3; H, 4·8%), its m-*isomer*, b. p. 96°/3·5 mm. (Found: C, 39·5; H, 4·9%), and p-*methoxyphenyltriphenylstannane*, m. p. 156·5° (from EtOH–C_6H_6) (Found: C, 65·8; H, 4·9. $C_{25}H_{22}OSn$ requires C, 65·7; H, 4·85%), were obtained in 45—50% yield.

Tricyclohexylphenylstannanes, $X\cdot C_6H_4\cdot Sn(C_6H_{11})_3$, made from Grignard reagents.

X	M. p.[a]	Reflux time (hr.)	Yield (%)	Found (%) C	Found (%) H	Required (%) C	Required (%) H
H	191° (*A*/*B*)	3	35	—	—	—	—
p-Me [b]	111 (*A*)	3	30	65·2	8·5	65·4	8·8
m-Me	104 (*A*)	24	88	65·4	8·7	65·4	8·8
p-Et	89 (*A*)	18	52	66·4	9·0	66·0	8·9
p-Bu^t	139·5 (*A*/*B*)	8	90	67·3	9·1	67·1	9·2
p-Cl	116 (*A*/*B*)	12	75	60·1	8·0	60·1	7·8
m-Cl	109·5 (*A*)	12	70	59·8	7·7	60·1	7·8
p-Br	124 (*A*)	12	60	55·2	7·7	55·0	7·1
p-F	155 (*A*/*B*)	4	58	62·3	8·1	62·2	8·05
p-OMe	102·5 (*A*)	12	80	63·2	8·5	63·2	8·5
m-OMe	76·5 (*P*)	12	82	63·2	8·4	63·2	8·5
p-Ph	118 (*A*/*E*)	12	64	68·7	8·3	69·1	8·1

[a] Letters in parenthesis denote recrystallization medium, *viz.*: *A*, EtOH; *B*, C_6H_6; *E*, EtOAc; *P*, light petroleum, b. p. 60—80°. Not new.

Preparations from organolithium reagents. Bromotricyclohexyl- or bromotrimethylstannane (1 mol.) was refluxed for 12 hr. with the aryl-lithium made from the appropriate aryl bromide (1·2 mol.) and lithium (2·8 g.-atom) in ether. Residual lithium was filtered off, and

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[1] Cf. Kraus and Sessions, *J. Amer. Chem. Soc.*, 1925, **47**, 2361.

[2] Krause and Pohland, *Ber.*, 1924, **57**, 532.

[3] Chambers and Scherer, *J. Amer. Chem. Soc.*, 1926, **48**, 1054.

working-up as for the preparations from Grignard reagents gave *trimethyl-*p*-tolylstannane* (35%), b. p. 80·5°/3 mm. (Found: C, 47·4; H, 6·3. $C_{10}H_{16}Sn$ requires C, 47·1; H, 6·3%), *tricyclohexyl-*p*-isopropyl-* (35%), m. p. 74° (from EtOH) (Found: C, 66·4; H, 9·1. $C_{27}H_{44}Sn$ requires C, 66·5; H, 9·1%), *-*p*-tricyclohexylstannyl-* (46%), m. p. 336—340° (from $CHCl_3$) (Found: C, 62·2; H, 8·8. $C_{42}H_{70}Sn_2$ requires C, 62·1; H, 8·7%), and *-*p*-dimethylamino-phenylstannane* (69%), m. p. 148° (from EtOH) (Found: C, 63·9; H, 8·7. $C_{26}H_{43}NSn$ requires C, 63·95; H, 8·9%).

A solution of the *p*-dimethylamino-compound (4·5 g.) and methyl iodide (13 g.) in ethanol (250 ml.) was kept in the dark for 3 days. Removal of the liquids and recrystallization of the residue from benzene gave the *methiodide* (88%), m. p. 164° (Found: C, 51·1; H, 7·4. $C_{27}H_{46}INSn$ requires C, 51·4; H, 7·4%).

p-Chlorophenyltricyclohexylstannane (7 g.), lithium (0·5 g.), and ether (200 ml.) were boiled together for 2 hr., and the mixture was added to a slurry of solid carbon dioxide and ether. After removal of the excess of carbon dioxide and of ether, the residue was treated with water and then extracted with light petroleum. The organostannane was taken from the petroleum into dilute alkali, and then precipitated by addition of dilute acid. Recrystallization from light petroleum gave *p-carboxyphenyltricyclohexylstannane* (35%), m. p. 177° (Found: C, 61·6; H, 7·8. $C_{25}H_{38}O_2Sn$ requires C, 61·4; H, 7·8%).

Preparations by the Wurtz–Fittig reaction. A solution of bromotricyclohexylstannane (20 g.) and 2-chlorobiphenyl (16 g.) in light petroleum (b. p. 60—80°) (150 ml.) was boiled with sodium wire (6 g.) for 7 hr. Filtration through glass wool, treatment with water, and separation, washing, drying (Na_2SO_4), and concentration of the organic layer left a solid which recrystallized from ethanol–benzene (9 : 1) to give *tricyclohexyl-*o*-biphenylylstannane* (60%), m. p. 110—111° (Found: C, 69·0; H, 8·3. $C_{30}H_{42}Sn$ requires C, 69·1; H, 8·1%).

Tricyclohexylphenylstannane, m. p. 191°, was prepared analogously in 75% yield.

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THE UNIVERSITY, LEICESTER. [*Received, October 12th*, 1961.]

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215. *Transition-metal Fluorocarbon Complexes. Part II.*[1] *A Stabilized Fluorocarbanion.*

By G. W. PARSHALL and G. WILKINSON.

IT has recently been shown that fluoride ion is a catalyst for the rearrangement of fluoro-olefins.[2] The products of these reactions can be explained on the assumption that fluoride ion has added to the olefinic bond to give, initially, a fluorinated carbanion. We now report a fluoride adduct in which a perfluorocarbanion is stabilized by co-ordination to a transition-metal atom in a carbonyl complex.

When the colourless solutions of tricarbonyl octafluorocyclohexa-1,3-dieneiron [1] in tetrahydrofuran or formamide is treated with cæsium fluoride at room temperature, there is a slow reaction and the solution becomes yellow. From this solution can be isolated hygroscopic pale yellow crystals which are soluble in water, tetrahydrofuran, and formamide, giving air-stable solutions. Metathesis of the cæsium salt with tetramethylammonium chloride in aqueous solution gives the sparingly soluble tetramethylammonium

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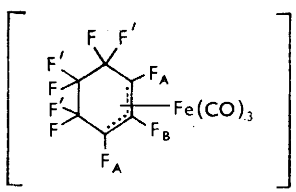
[1] Part I, Hoehn, Pratt, Watterson, and Wilkinson, *J.*, 1961, 2738.

[2] Miller, Fried, and Goldwhite, *J. Amer. Chem. Soc.*, 1960, **82**, 3091; Miller, Frass, and Resnicke, *ibid.*, 1961, **83**, 1767.

salt. Interaction of the diene complex with fluoride ion can hence be written: $\pi\text{-}C_6F_8Fe(CO)_3 + F^- = [\pi\text{-}C_6F_9Fe(CO)_3]^-$; and the stable anion can be regarded as the first example of a perfluoro-π-allylic complex, the π-nonafluorocyclohexenyl tricarbonylferrate ion (I).



(I)

The infrared and ^{19}F nuclear magnetic resonance spectra support the proposed structure. The former for the cæsium salt in mulls shows strong carbonyl stretching peaks at 2080 and 1997 cm.$^{-1}$, which are at somewhat low frequencies, as would be expected for a negatively charged species, compared with the neutral tricarbonyl complex.[1] There is also weaker olefinic absorption at 1657 cm.$^{-1}$. For the tetramethylammonium salt the frequencies are shifted to 2073, 1981, and 1620 cm.$^{-1}$, respectively. The high-resolution nuclear magnetic resonance data are tabulated. Two peaks assignable to the fluorine atoms attached to the carbon toms of the π-allylic system appear at high field. The larger of them is assigned to the two equivalent fluorine atoms (F_A) on the terminal carbons of the π-allylic system and, as expected, appears as a doublet due to coupling with the lone central fluorine atom (F_B). The smaller peak is unfortunately not well resolved. The lower-field peaks are assigned to the " aliphatic " fluorine atoms of the ring and fall at approximately the same resonance position as the corresponding fluorine resonances in $C_6F_8Fe(CO)_3$.[1] The two lowest-field peaks appear to be a doublet (J ~223 c./sec.) produced by interaction with the triplet (J 217 c./sec.). The larger splittings are attributed to the interaction of the non-equivalent fluorines on the same carbon atom as was noted earlier for $C_6F_8Fe(CO)_3$.[1]

^{19}F nuclear resonance spectrum of $Cs[\pi\text{-}C_6F_9Fe(CO)_3]$.

Chemical shifts in c./sec. on high-field side of benzotrifluoride internal reference (measurements made on a Varian spectrometer V–4311 at 56·45 Mc./sec. in spinning Pyrex tubes of 5 mm. outside diameter).

Formamide solution	Tetrahydrofuran solution	Relative area	Structure	J (c./sec.)
1935	1985	1·2	Doublet	45
2167	2200	1·8	Doublet	45
3103	3100	3·0	Triplet	217
3910 (F^-)	—			
7718	7065	1·9	Doublet	*ca.* 50
8064	7940	1·4	Unresolved	

Experimental.—Microanalyses by the Microanalytical Laboratories of Imperial College and the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co. Infrared spectra were taken on a Perkin–Elmer model 21 instrument with sodium chloride optics.

Cæsium and tetramethylammonium tricarbonyl-π-nonafluorocyclohexenylferrate. A solution of tricarbonyl octafluorocyclohexa-1,3-dieneiron (1·0 g.) in dry, freshly distilled tetrahydrofuran (12 ml.) was added to anhydrous cæsium fluoride (2·0 g.) in a 35-ml. Carius tube. The tube was sealed and was agitated at room temperature for 2 days. The resulting yellow solution was filtered and the solvent removed in a vacuum to leave the cæsium salt of the anion in essentially quantitative yield. Owing to the very hygroscopic nature of the salt and the difficulty in removal of cæsium fluoride, analyses of the product are not too satisfactory. To an aqueous solution of the salt was added an excess of a saturated solution of tetramethylammonium chloride. The precipitated *salt* was filtered off and dried in a vacuum (Found: C, 34·2, 35·1; H, 3·65, 2·6; F, 35·25. $C_{13}H_{12}F_9FeNO_3$ requires C, 34·2; H, 2·65; F, 37·4%).

We are indebted to the International Nickel Co. (Mond) Ltd. and Imperial Smelting Corporation for generous gifts of iron carbonyl and perfluorocyclohexa-1,3-diene, respectively, and to Dr. L. Pratt for assistance with nuclear magnetic resonance measurements.

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216. *Some Derivatives of* 5,6-*Dibenzyloxyindole.*

By R. M. Acheson, A. R. Hands, and L. J. King.

5,6-Dibenzyloxyindole [1] with dimethylamine and formaldehyde gave 5,6-dibenzyloxygramine, which was reduced with sodium hydroxide and zinc dust to 5,6-dibenzyloxyskatole. The gramine methosulphate with sodium cyanide gave 5,6-dibenzyloxyindol-3-ylacetonitrile, hydrolysis of which gave a tar whence 5,6-dibenzyloxyindol-3-ylacetic acid was isolated as its methyl ester. Attempts to hydrolyse this ester with aqueous sodium hydroxide gave only tars.

The product from 5,6-dibenzyloxygramine methiodide and ethyl sodioacetamidomalonate [2] was hydrolysed and decarboxylated to give *N*-acetyl-5,6-dibenzyloxytryptophan.

5,6-Dibenzyloxyindole and nitroethylene gave 5,6-dibenzyloxy-3-2′-nitroethylindole. This was reduced catalytically with Raney nickel and palladised charcoal, but neither 5,6-dibenzyloxy- nor 5,6-dihydroxy-tryptamine could be isolated as the picrate or creatinine sulphate, respectively.

Attempts were made to debenzylate 5,6-dibenzyloxyskatole and methyl 5,6-dibenzyloxyindol-3-ylacetate by hydrogenation at 5 atm. over palladised charcoal, but the compounds were recovered quantitatively. When Adams platinum catalyst was used, the recoveries were 30—70%, the remainder of the materials being tars. In no case was a dihydroxyindole derivative isolated.

Experimental.—Chromatographic alumina was prepared as described earlier.[3]

5,6-*Dibenzyloxygramine.* Glacial acetic acid (2·0 ml.), 40% aqueous formaldehyde (1·0 ml.), and 5,6-dibenzyloxyindole (m. p. 114°; [1] 2·8 g.) were added successively to 33% ethanolic dimethylamine (1·5 ml.) at 0°. After 12 hr. at room temperature the mixture was poured into ice–water (50 ml.) and filtered from unchanged 5,6-dibenzyloxyindole (0·10 g.). The filtrate was basified with 20% aqueous potassium carbonate and extracted with ether (5 × 75 ml.). Evaporation of the dried ($MgSO_4$) extracts gave a gum which was extracted at 100° with light petroleum (b. p. 100—120°; 3 × 100 ml.). Cooling the extracts gave 5,6-*dibenzyloxygramine* (2·75 g., 84%) as prisms, m. p. 124° (Found: C, 77·4; H, 6·7; N, 7·5. $C_{25}H_{26}N_2O_2$ requires C, 77·7; H, 6·8; N, 7·2%).

5,6-Dibenzyloxygramine (1·0 g.) and methyl iodide (10 ml.) were refluxed for 15 min. and then evaporated. The residue was extracted with boiling ethanol (5 × 20 ml.) and dried, to give 5,6-*dibenzyloxygramine methiodide* (1·3 g., 95%), m. p. 178—180° (Found: C, 59·1; H, 5·7; N, 5·0. $C_{26}H_{29}IN_2O_2$ requires C, 59·1; H, 5·5; N, 5·3%).

5,6-*Dibenzyloxyskatole.* Sodium hydroxide (2·0 g.), water (15 ml.), methanol (25 ml.), and 5,6-dibenzyloxygramine (2·0 g.) were refluxed. Zinc dust (1·6 g.) was added during 2 hr. with

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[1] Schlossberger and Kuch, *Chem. Ber.*, 1960, **93**, 1318.

[2] Cf. Snyder and Smith, *J. Amer. Chem. Soc.*, 1944, **66**, 350.

[3] Acheson and Hands, *J.*, 1961, 744.

frequent shaking. After further refluxing (12 hr.) the methanol was removed on a water-bath and the residue was cooled and extracted with chloroform (4 × 30 ml.). Evaporation of the extracts gave a brown tar which was chromatographed on alumina (250 g.) with benzene as eluent. The eluate (600 ml.) gave, on evaporation to dryness and recrystallisation of the residue from light petroleum (b. p. 40—60°), 5,6-*dibenzyloxyskatole* (0·32 g., 18%) as needles, m. p. 123° (Found: C, 80·3; H, 6·2; N, 4·4. $C_{23}H_{21}NO_2$ requires C, 80·4; H, 6·2; N, 4·1%).

5,6-*Dibenzyloxyindol*-3-*ylacetonitrile*. 5,6-Dibenzyloxygramine (2·25 g.) in tetrahydrofuran (12 ml.) and glacial acetic acid (0·14 ml.) was added to methyl sulphate (2·6 ml.) in tetrahydrofuran (4·5 ml.) and glacial acetic acid (0·14 ml.) at 10—15°, and the mixture was left at room temperature for 3 hr. Ether (50 ml.) was added and after 12 hr. the liquid was poured off and the gummy precipitate was washed with ether (3 × 50 ml.) by decantation. Sodium cyanide (1·0 g.) in water (24 ml.) was added, and the mixture was heated at 65—70° for 1 hr., cooled, and extracted with chloroform (3 × 100 ml.). The extracts were dried ($MgSO_4$) and evaporated under reduced pressure at 30° to give a gum which was chromatographed on alumina (150 g.). Elution with benzene (300 ml.) gave, on evaporation and recrystallisation of the residue from ether, 5,6-*dibenzyloxyindol*-3-*ylacetonitrile* (0·98 g., 46%) as rhombic plates, m. p. 113° (Found: C, 78·3; H, 5·5; N, 7·8. $C_{24}H_{20}N_2O_2$ requires C, 78·3; H, 5·5; N, 7·6%).

Methyl 5,6-*dibenzyloxyindol*-3-*ylacetate*. 5,6-Dibenzyloxyindol-3-ylacetonitrile (0·7 g.), ethanol (5 ml.), and potassium hydroxide (1·0 g.) were refluxed for 15 hr., cooled, and acidified with glacial acetic acid. The liquid was poured off the brown tar, which was repeatedly washed with water by decantation and then dissolved in methanol (20 ml.). An ~3% solution of diazomethane in ether was added until a yellow colour persisted; this was discharged by adding 10% methanolic acetic acid. The solution was evaporated to dryness under reduced pressure at 30°, and the residue was extracted with boiling light petroleum (b. p. 60—80°; 5 × 100 ml.). The extracts were evaporated to 100 ml. and cooled, yielding *methyl* 5,6-*dibenzyloxyindol*-3-*ylacetate* (0·49 g., 64%) as prisms, m. p. 100° (Found: C, 74·6; H, 6·0; N, 3·5. $C_{25}H_{23}NO_4$ requires C, 74·8; H, 5·8; N, 3·5%).

Ethyl α-*acetamido*-β-(5,6-*dibenzyloxyindol*-3-*yl*)-α-*ethoxycarbonylpropionate*. Sodium (0·5 g.) was powdered under xylene (25 ml.), which was then replaced by dioxan (40 ml.). Ethyl acetamidomalonate (6·8 g.) was added and the suspension was heated at 92° (bath-temperature) for 14 hr. 5,6-Dibenzyloxygramine methiodide (10 g.) was added and the mixture was refluxed at 108° for 19 hr., then at 125° for 3 hr., and was filtered hot. The solid residue was extracted with boiling dioxan (3 × 50 ml.), and the combined filtrates were evaporated to 35 ml. *in vacuo* and cooled. The solids were filtered off and two recrystallisations from ethyl acetate–light petroleum (b. p. 60—80°; 1 : 1) gave the *propionate* (2·15 g., 15%) as prisms, m. p. 147° (Found: C, 68·7; H, 6·2; N, 5·2. $C_{32}H_{34}N_2O_7$ requires C, 68·8; H, 6·1; N, 5·1%).

N-*Acetyl*-5,6-*dibenzyloxytryptophan*. The preceding ester (2·8 g.), sodium hydroxide (1·0 g.) and water (15 ml.) were refluxed for 4 hr., cooled to 0°, and acidified with concentrated hydrochloric acid. The precipitate of impure acid was collected, suspended in water (50 ml.), refluxed for 3 hr., cooled, and filtered. The solid on two recrystallisations from methanol gave N-*acetyl*-5,6-*dibenzyloxytryptophan* (1·8 g., 78%) as prisms, m. p. 192° (Found: C, 70·3; H, 5·5; N, 6·1. $C_{27}H_{26}N_2O_5$ requires C, 70·7; H, 5·7; N, 6·1%).

5,6-*Dibenzyloxy*-3-2′-*nitroethylindole*. 5,6-Dibenzyloxyindole (4·07 g.) was heated at 114° and nitroethylene (1·4 g.) was added dropwise during 30 min. The heating was continued for 30 min. The cooled mixture was dissolved in benzene (30 ml.) and chromatographed on alumina (250 g.). Elution with benzene (1650 ml.) gave 5,6-dibenzyloxindole (0·9 g., 22%), m. p. 114° (from ether). Further elution with benzene (750 ml.) gave 5,6-*dibenzyloxy*-3-2′-*nitroethylindole* (1·0 g., 20%) as needles, m. p. 108° (from ether) (Found: C, 71·8; H, 5·9; N, 6·8. $C_{24}H_{22}N_2O_4$ requires C, 71·6; H, 5·5; N, 6·9%). In paraffin paste it showed $\nu_{max.}$ at 3480 and 3400 (N–H) and at 1562 and 1341 cm.$^{-1}$ (NO_2).

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217 *Methyl* 4,6-O-*Benzylidene*-α-D-*glucoside* 2,3-*Dibenzenesulphinate; a Correction.*

By J. R. HOLKER and JOHN HONEYMAN.

METHYL 4,6-*O*-BENZYLIDENE-α-D-GLUCOSIDE 2,3-DIBENZENESULPHINATE is claimed[1] to result from treatment of the corresponding 2,3-diacetate with sodium benzenesulphinate in acetic anhydride. The product has now been re-examined since Dr. C. J. M. Stirling pointed out that such displacement of acetate by benzenesulphinate is extremely unlikely. Elementary analysis indicated the product to be a 1 : 1 *adduct* of phenyl benzenethiolsulphonate, readily formed from sodium benzenesulphinate and acetic anhydride,[1] and the diacetate (Found: C, 58·6; H, 5·2; O, 26·0; S, 10·3; *O*-acetyl, 13·2. $C_{18}H_{22}O_8,C_{12}H_{10}O_2S_2$ requires C, 58·4; H, 5·2; O, 26·0; S, 10·4; *O*-acetyl, 14·0%). The complex showed strong infrared absorption at 1750 cm.$^{-1}$ (C=O) in addition to sulphone and sulphoxide bands at 1325 cm.$^{-1}$ and 1150 cm.$^{-1}$, respectively. Finally, the adduct crystallised spontaneously when cold solutions of the components in methanol were mixed. Its identity with material from the previous preparation[1] was confirmed by m. p., mixed m. p., and comparison of infrared spectra.

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[1] Honeyman and Morgan, *J.*, 1955, 3660.