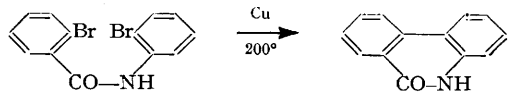
154. *2-Bromo-4- and -5-methylbenzoic Acid and Some Related Compounds.*

By M. S. Gibson.

It was desired to prepared phenanthridones by the general method :



As intermediates, 2 : 2′-dibromo-4-methylbenzanilide and 2 : 2′-dibromo-5-methylbenzanilide have been prepared, but under the conditions of the Ullmann reaction gave only amorphous products. Whilst the main project was unsuccessful, the preparation of the intermediate acids has indicated a number of discrepancies in the literature.

Experimental.—Some analyses are by Mr. F. C. Hall.

2-*Bromo*-4-*methylbenzoic acid.* A solution of 2-bromo-4-methylbenzonitrile [1] (10 g.) and potassium hydroxide (4 g.) in aqueous ethanol was boiled for 6 hr. Ethanol was removed *in vacuo*, and the residual solution decolorised with charcoal. On cooling, the solution deposited needles, m. p. 171—173°. Acidification of the filtrate precipitated 2-bromo-4-methylbenzoic acid, which crystallised from aqueous ethanol in needles, m. p. 141—142°. Claus and Kunath [2] give m. p. 140°.

Crystallisation of the solid, m. p. 171—173°, from a large volume of water afforded needles of 2-bromo-4-methylbenzamide, m. p. and mixed m. p. 175—176° (Found : C, 45·1; H, 3·8; N, 6·7; Br, 37·1. Calc. for C_8H_8ONBr : C, 44·9; H, 3·7; N, 6·5; Br, 37·4%); Claus and Kunath,[2] however, record the m. p. 137°.

2-*Bromo*-N-o-*bromophenyl*-4-*methylbenzamide*, prepared from *o*-bromoaniline by the Schotten–Baumann method, crystallised from ethanol in needles, m. p. 145—146° (Found : C, 45·9; H, 3·0; N, 3·9. $C_{14}H_{11}ONBr_2$ requires C, 45·5; H, 3·0; N, 3·8%). An attempt to convert the anilide into 6-methylphenanthridone by copper powder at 200—220° yielded only amorphous material.

2-*Bromo*-5-*methylaniline.*—The following method of reduction of 2-bromo-5-methylnitrobenzene was more convenient than that of Borsche and Scriba.[3] Iron filings (100 g.) were added during 20 min. to a boiling solution of the nitro-compound (120 g.) in ethanol (280 c.c.) and concentrated hydrochloric acid (6 c.c.) with vigorous shaking. After 2 hours' boiling, sodium hydroxide was added, the mixture distilled in steam, and the distillate discarded until it became turbid. The amine (90 g.) which then distilled was isolated by means of ether and converted into the nitrile without purification. The acetyl derivative formed needles (from aqueous ethanol), m. p. 123—124° (Found : C, 47·0; H, 4·1; N, 6·1; Br, 35·3. Calc. for $C_9H_{10}ONBr$: C, 47·4; H, 4·4; N, 6·1; Br, 35·1%); for this compound, Nevile and Winther [4] give m. p. 113·7—114·6°.

2-*Bromo*-5-*methylbenzoic acid.* A solution of 2-bromo-5-methylbenzonitrile [3] (10 g.) and potassium hydroxide (4 g.) in aqueous ethanol was boiled for 6 hr. The acid was isolated in the normal manner, and after crystallisation from water, formed needles, m. p. 137—138° (Found : C, 44·9; H, 3·6. Calc. for $C_8H_7O_2Br$: C, 44·7; H, 3·3%) (Claus [5] gives m. p. 154—155°; Borsche and Herbert [6] record m. p. 135°; the latter workers hydrolysed the nitrile by acid but alkaline hydrolysis has been found to give a cleaner product).

2-*Bromo*-N-o-*bromophenyl*-5-*methylbenzamide* separated from ethanol in needles, m. p. 118—119° (Found : C, 45·6; H, 3·1; N, 3·9; Br, 43·1. $C_{14}H_{11}ONBr_2$ requires C, 45·5; H, 3·0; N, 3·8; Br, 43·4%). In an Ullmann reaction, this anilide gave an amorphous product.

4-*Bromo*iso*phthalic acid.* Potassium permanganate (1·6 g.) in water (30 c.c.) was slowly added to a boiling solution of 2-bromo-5-methylbenzoic acid (1 g.) in dilute sodium hydroxide solution. The mixture was boiled for 3 hr., cooled, and saturated with sulphur dioxide. Crystallisation of the precipitated acid from aqueous ethanol afforded needles, m. p. 303—304°

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[1] Lindemann and Pabst, *Annalen*, 1928, **462**, 24.
[2] Claus and Kunath, *J. prakt. Chem.*, 1889, **39**, 485.
[3] Borsche and Scriba, *Annalen*, 1939, **541**, 283.
[4] Nevile and Winther, *Ber.*, 1880, **13**, 962.
[5] Claus, *J. prakt. Chem.*, 1892, **46**, 20.
[6] Borsche and Herbert, *Annalen*, 1941, **546**, 277.

(Found: C, 39·4; H, 2·1. Calc. for $C_8H_5O_4Br$: C, 39·2; H, 2·0%). For this acid, Claus[5] records m. p. 287°; Schöpff[7] reports m. p. 283°. 4-Bromo*iso*phthalic acid, prepared from *m*-xylene by bromination, followed by oxidation with potassium permanganate,[7] and twice crystallised from ethanol in which it is moderately soluble, afforded 4-bromo*iso*phthalic acid as needles, m. p. 302—303°. A mixed m. p. with the above-mentioned specimen showed no depression.

The award of a maintenance grant by the Department of Scientific and Industrial Research is gratefully acknowledged.

DYSON PERRINS LABORATORY, OXFORD. [*Received, August* 15*th*, 1955.]

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[7] Schöpff, *Ber.*, 1891, **24**, 3771.

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155. *The Isolation of Octadec*-8 : 10 : 12-*trienoic Acid from Marigold-seed Oil.*

By JOHN McLEAN and A. H. CLARK.

EXTRACTION of the crushed seeds of Scots Marigold (*Calendula officinalis*) with light petroleum gives a relatively high yield (24%) of oil, the ultraviolet absorption spectrum of which suggests that about 56% of it is a conjugated trienoic acid (or ester). Attempts directly to isolate the trienoic acid were unsuccessful because of the ease with which it autoxidised. When refluxed with alcoholic potassium hydroxide in the presence of traces of sulphur, the oil gives an acid fraction (approx. 30%) which readily yields a crystalline acid, $C_{18}H_{30}O_2$, m. p. 77—78°, identified as octadec-8 : 10 : 12-trienoic acid as described below. Hydrogenation of the acid over Raney nickel gives stearic acid in high yield. The presence of three conjugated double bonds is established by the ultraviolet spectrum which shows maxima at 2580, 2680, and 2800 Å (ε 44,100, 59,100, 45,600), in this respect resembling the isomeric β-elæostearic acid[1] (maxima at 2590, 2680, and 2800 Å). Oxidation of the acid with potassium permanganate gives a mixture from which hexanoic acid (as its *p*-bromophenacyl ester) and suberic acid were isolated.

Octadec-8 : 10 : 12-trienoic acid, m. p. 77—78°, readily forms an adduct with maleic anhydride, the infrared absorption spectrum of which includes bands at 958 and 687 cm.$^{-1}$, the former attributed to an exocyclic *trans*-disubstituted ethylenic bond and the latter to the *cis*-disubstituted double bond in a hydroaromatic ring. The ease with which maleic anhydride forms an adduct with the trienoic acid proves, in our opinion, that the conjugated double bonds directly involved are orientated *trans-trans*, thus leading to the view that the octadec-8 : 10 : 12-trienoic acid is the all-*trans*-isomer. In this respect, it is related to β-elæostearic acid (all-*trans*-octadec-9 : 11 : 13-trienoic acid).[2] α-Elæostearic acid (the *cis-trans-trans*-isomer) is converted into its β-isomer (all-*trans*) by treatment with alkali in the presence of sulphur[3] and we assume that a similar change has occurred during the isolation of all-*trans*-octadec-8 : 10 : 12-trienoic acid from marigold-seed oil.

Experimental.—Ultraviolet spectra were measured in EtOH and infrared spectra were determined in CS_2 solutions.

Marigold-seed oil. Marigold seed (2 lb.) was extracted continuously with light petroleum (b. p. 60—80°) to remove the outer wax coating (1·5 g.). The seed was crushed and again extracted continuously with light petroleum. Removal of the solvent gave a pale green oil (219 g.), having absorption: max. at 2620, 2710, and 2820 Å ($E^{1\%}_{1\,\text{cm.}}$ 1000 at 2710 Å).

*all-*trans*-Octadec-*8 : 10 : 12-*trienoic acid.* A mixture of marigold-seed oil (34 g.), potassium hydroxide (13·6 g.), ethanol (140 c.c.), and sulphur (0·7 g.) was refluxed for 1½ hr. The alcohol was removed by distillation, water being added continuously to avoid concentration of alkali, and the non-saponifiable matter extracted with ether (500 c.c.). The aqueous phase was

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[1] Ahlers and Gunstone, *Chem. and Ind.*, 1954, 1291.

[2] Paschke, Tolberg, and Wheeler, *J. Amer. Oil Chemists' Soc.*, 1953, **30**, 97; Bickford, du Pré, Mack, and O'Connor, *ibid.*, p. 376.

[3] Thomas and Thomson, *J. Amer. Chem. Soc.*, 1934, **56**, 898.

acidified with hot 2N-sulphuric acid (250 c.c.), and the precipitated acids were washed with hot water and finally with ice water. Four crystallisations from ethanol (90%) and one from light petroleum gave all-trans-*octadec*-8 : 10 : 12-*trienoic acid* (1·7 g.) as plates, m. p. 77—78° (Found : C, 77·5; H, 10·9. $C_{18}H_{30}O_2$ requires C, 77·65; H, 10·9%). Light absorption : Max. at 2580, 2680, 2800 Å (ε respectively 44,100, 59,100, and 45,600). The *maleic anhydride adduct*, prepared by refluxing the acid with excess of maleic anhydride in toluene for 1 hr., separated as rosettes, m. p. 71°, from light petroleum (Found : C, 70·4; H, 8·7. $C_{22}H_{32}O_5$ requires C, 70·2; H, 8·6%).

Hydrogenation. Octadec-8 : 10 : 12-trienoic acid (0·3 g.) in ethyl acetate was shaken with hydrogen over Raney nickel. Isolation in the usual manner followed by crystallisation from light petroleum gave stearic acid (0·2 g.), m. p. and mixed m. p. 69—70°.

Oxidation. The trienoic acid (5 g.) in water (1540 c.c.) containing potassium hydroxide (1 g.) was treated with 4·8% aqueous potassium permanganate (580 c.c.) during 2 hr. with stirring. The mixture was kept at room temperature for 48 hr. and then treated with sulphur dioxide. The solution was distilled down to 50 c.c., the distillate being collected in 5% aqueous sodium hydroxide (50 c.c.). Acidification of the distillate and extraction with ether gave hexanoic acid, identified as the *p*-bromophenacyl ester, m. p. and mixed m. p. 72° (Found : C, 53·5; H, 5·8. Calc. for $C_{14}H_{17}O_3Br$: C, 53·7; H, 5·5%). The aqueous residue in the distillation flask deposited crude suberic acid (2·8 g.) on cooling. Repeated crystallisation from benzene gave the pure acid, m. p. and mixed m. p. 138—139° (*p*-bromophenacyl ester, m. p. 145°, phenacyl ester, m. p. and mixed m. p. 103°).

The authors thank Dr. Eglinton for the infrared spectra, and Mr. McCorkindale for the microanalyses.

THE ROYAL TECHNICAL COLLEGE, GLASGOW. [*Received, September 8th,* 1955.]

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156. *The Stability of* H_2^+ *and* OH^+ *in Aqueous Solutions.*

By C. A. COULSON.

SINCE the original suggestion by Weiss [1] it has become recognised that the positive ion H_2^+ may act as a centre capable of co-ordinating water molecules in aqueous solution, and in recent months many applications of this concept have been made.[2,3] It has also been suggested by various authors [4] that possibly the positive ion OH^+ might possess a similar stability in aqueous solution. This suggestion is made a little more plausible by the fact that both H_2^+ and OH^+ are found in the mass spectrograph. It is true that in the conventional heterolytic reaction theory of hydroxylation we are more accustomed to the anion OH^- than the cation OH^+. But the possible biological, radiochemical, and pure chemical interests of this problem seem to warrant a discussion of the comparative efficiencies of H_2^+ and OH^+ in the co-ordination of a shell of water molecules. The purpose of the present note is to suggest why, although a final decision cannot yet be reached, it seems unlikely that OH^+ would behave analogously to H_2^+.

First, we may enquire about possible modes of formation of H_2^+ and OH^+ in aqueous solutions. It is reasonable to suppose that the ions most frequently formed in water by the passage of an ionising particle are H_2O^+ and H_2O^-. It is true that incident neutrons may eject protons from H_2O, but each of these recoil protons will itself ionise a large number of other water molecules before coming to rest. With fast neutrons the number of protons (and therefore residual OH radicals and ions) produced in this primary fashion may only be of the order of 10^{-4} times the number of ions subsequently produced by these recoil protons and associated secondary electrons. We therefore restrict our attention to the primary species H_2O^+ and H_2O^-. Now the positive ion OH^+ could hardly be formed directly from H_2O^-. So far as OH^+ is concerned, therefore, we need only consider H_2O^+.

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[1] Weiss, *Nature*, 1950, **165**, 728.

[2] *E.g.* : Rigg, Stein, and Weiss, *Proc. Roy. Soc.*, 1952, *A*, **211**, 375; Rigg and Weiss, *J. Chem. Phys.*, 1952, **20**, 1194; *J.*, 1952, 4198; Hart, *Radiation Res.*, 1954, **1**, 53; Allen, *ibid.*, p. 85; Hart, *J. Amer. Chem. Soc.*, 1954, **76**, 4198; Sworski, *ibid.*, p. 4687.

[3] Dewhurst, Samuel, and Magee, *Radiation Res.*, 1954, **1**, 60.

[4] Cf. ref. 3, p. 67.

In the presence of water this radical would presumably break up in either of the following ways, which are almost equally energetic in the gas phase :

$$H_2O^+ \longrightarrow OH + H^+$$
$$H_2O^+ \longrightarrow OH^+ + H$$

(There is, however, a possibility that H_2O^+ may itself have a certain stability in aqueous solutions.) If OH^+ is created in this process, there is the possibility (see below) of its disappearance in an electron-transfer reaction

$$OH^+ + H_2O \longrightarrow OH + H_2O^+$$

or alternatively in the reaction

$$OH^+ + H_2O \longrightarrow H_3O^+ + O$$

leading to a strongly hydrated proton and possible formation of oxygen gas, O_2, for whose existence there is experimental evidence. On the basis of these considerations alone, therefore, it is not very likely that OH^+ would appear in an aqueous system.

For H_2^+, the situation is rather different. There appears no possibility of primary formation of H_2^+ (except perhaps $H_2O^+ \longrightarrow H_2^+ + O$) and it is presumed that H_2^+ in aqueous system is formed by the interaction :

$$H + H^+ \rightleftharpoons H_2^+$$

which could also be written (cf. Weiss [1]) as :

$$H + H_3O^+ \rightleftharpoons H_4O^+$$

so that this species is in continuous equilibrium with the hydrogen ions in the solution. There is no difficulty, therefore, in explaining the origin of H_2^+.

Next, let us compare the ions H_2^+ and OH^+ as regards their power of co-ordinating water molecules. Co-ordination of H_2O molecules around a positive ion is largely due to attraction, by the electrostatic field of the ion, of the negative end of the H_2O molecules—in this case the region of predominantly negative charge surrounding the oxygen atoms. Now at sufficiently large distances this electrostatic field will be effectively the same for both OH^+ and H_2^+, since it depends simply on the total positive charge. But at closer distances, which are necessary if full use is to be made of this electrostatic field, these two ions will behave quite differently towards approaching water molecules. There appear to be at least four ways in which this difference may be expected from our present knowledge of the electronic structure of the ions themselves.

(1) The H_2^+ molecule has only one electron, and this is almost entirely found in regions between the nuclei, hardly ever on the further sides. The accurate curve [5] in Fig. 1 shows the density distribution along the central axis of the molecule. Thus from many points of view the H_2^+ ion will behave as if it were a single bare proton, split into two halves, separated by about 1 Å. There is no effective screening of the nuclei by the one electron that does exist, and water molecules can therefore approach quite close to the two nuclei. This may be seen very clearly if we recall that, with a reasonable definition of the volume of a molecule, the volume of H_2^+ is considerably less even than that of atomic hydrogen. The charge-cloud pattern of H_2^+ is shown rather schematically in Fig. 2.

(2) The ion OH^+, on the other hand, has acquired its positive charge by losing one of the non-bonding electrons of the oxygen atom. There remain two electrons in the bond, so that, as comparisons of accurate electron-density diagrams for H_2^+ and H_2 show, there is now a considerable electronic density on the remote side of the hydrogen nucleus; thus an approaching water molecule would have little tendency to co-ordinate at this end of the ion. But if such a molecule came near the other end it would not be able to get very close before experiencing repulsions due to overlapping of its charge cloud with that of the oxygen atom.

[5] Burrau, *Kgl. danske Videnskab. Selskab, Mat.-fys. Medd.*, 1927, **7**, 1.

Thus we may argue that the effective radius of the oxygen atom in OH^+ is greater than that of the hydrogen atoms in H_2^+, and the co-ordinating power correspondingly less. A schematic charge-cloud pattern is shown in Fig. 3.

(3) The situation just described is actually rendered a little more unfavourable to co-ordination because, on account of the resultant positive charge near the oxygen nucleus, the electrons of the O–H bond will be drawn in a little towards the oxygen atom, and will partly neutralise this charge.

(4) Our last point arises out of a consideration of the ionisation potentials of H_2O and OH. These are 12·6 and 13·6 —13·8 ev respectively,[6] showing that it is easier to remove an electron (usually a non-bonding electron) from H_2O than OH. As a result the reaction

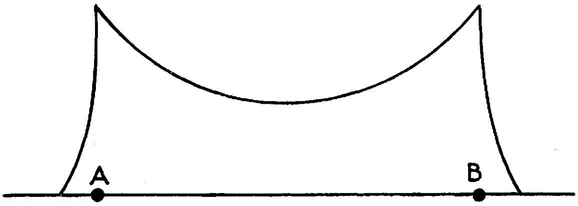


FIG. 1. *Charge-cloud along the axis of* H_2^+ (*after Burrau* [5]).

FIG. 2. *Charge-cloud for* H_2^+. *Almost all the charge lies within the contour shown. This contour approaches very closely to the nuclei* A *and* B *on the sides remote from each other. There is symmetry around the axis* A–B.

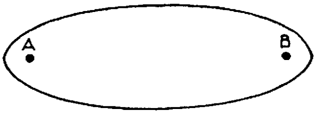
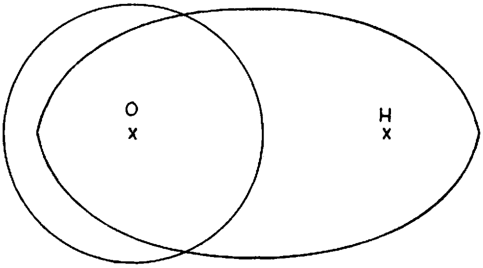


FIG. 3. *Charge-cloud for* OH^+. *Almost all the bonding charge lies in the ellipsoidal contour; almost all non-bonding charge lies within the spherical contour. There is symmetry around the axis* O–H.



$$H_2O + OH^+ \longrightarrow H_2O^+ + OH$$

in the vapour phase will go in the direction shown by the arrow. Consequently one may expect that co-ordination of water molecules around an OH^+ ion would soon transform that ion into a neutral radical OH, with the formation of an H_2O^+ ion instead.

None of the discussion just given makes it absolutely certain that OH^+ does not exist in a state co-ordinated with water molecules. But, taken collectively, it suggests that such stability as a hydrated OH^+ might possess in this way is distinctly less than that of a hydrated H_2^+.

The writer acknowledges the benefit of discussions with Dr. J. Weiss, who brought the problem to his attention, and pointed out the need for a clarification of the issues involved.

MATHEMATICAL INSTITUTE, OXFORD.

[*Received, June 6th*, 1955.]

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[6] Tsuchiya, *J. Chem. Phys.*, 1954, **22**, 1784; Price and Sugden, *Trans. Faraday Soc.*, 1948, **44**, 108; Robertson, *ibid.*, 1952, **48**, 228.

157. *The Preparation and Properties of Some Plutonium Compounds. Part III.* X-Ray Diffraction Studies of Plutonium Hydride.*

By B. J. McDonald and J. B. Fardon.

As far as is known to us there are no published data on the crystal structure of plutonium hydrides. Reference is made to hydrides PuH_2 and PuH_3 by Cunningham,[1] the formulæ being deduced by gas-displacement and dissociation-pressure methods. It is also stated that the dihydride forms a solid solution with the trihydride.

The plutonium–hydrogen system has recently been investigated[2] and in conjunction with this work we have examined powder diffraction patterns of the resultant plutonium hydride.

All the samples examined showed the same powder pattern. This consisted of a strong face-centred cubic phase with lattice parameter 5·34 Å and a very weak system which was probably hexagonal with parameters *a* 3·78, *c* 6·76 Å.

The chemical formula[2] of these samples, $PuH_{2\cdot7}$, admits the following interpretations of the observed diffraction patterns: (*a*) the cubic and the hexagonal phase represent two plutonium hydrides, which would require 70% of PuH_3 and 30% of PuH_2. This is not considered likely because the hexagonal pattern observed is too weak and represents only about 5—10% of the whole. (*b*) The strong cubic phase represents a solid solution of PuH_3 in PuH_2 as suggested by Bakes and Johns,[3] and the hexagonal phase is an impurity; this cannot be verified since no reference data on PuH_2 and PuH_3 are available. (*c*) The strong cubic phase represents a solid solution of hydrogen in PuH_2, the additional hydrogen atoms occupying some of the interstitial positions and the hexagonal phase being either an impurity or possibly PuH_3.

The hexagonal phase does not correspond to any of the known allotropes of plutonium or to any oxide of plutonium, data for all these having been examined since they are the most likely impurities.

It is suggested, therefore, that the cubic phase is a solid solution of either PuH_3 or hydrogen in PuH_2 and that the hexagonal phase may be another plutonium hydride, possibly PuH_3.

Experimental.—Preparation of the plutonium hydride is described by Brown *et al.*,[2] special precautions being taken to prevent contamination or oxidation of the product, which was a very finely divided black powder. It was photographed after binding with Canada balsam, in a 19 cm. camera (to be described elsewhere).

None of the samples photographed gave a sharp diffraction pattern, showing that the particle size was less than 1 μ (uranium hydride also shows this effect). The consequent diffuseness of the high-angle lines prevented very accurate measurements of the lattice parameter. Tables 1 and 2 give the data obtained. The intensities were estimated visually, relatively to the strongest line in the complete pattern (*d* 3·08 Å).

Table 1. *Cubic phase.*

Line no.	*d* (Å)	*hkl*	Relative intensity	Line no.	*d* (Å)	*hkl*	Relative intensity	Line no.	*d* (Å)	*hkl*	Relative intensity
1	3·08	111	100	6	1·33	400	10	11	0·9435	440	20
2	2·67	200	40	7	1·23	331	50	12	0·9028	531	50
3	1·89	220	70	8	1·19	420	40	13	0·8897	600, 442	50
4	1·61	311	80	9	1·090	422	50	14	0·8430	620	30
5	1·54	222	30	10	1·027	333, 511	50				

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* Part II, *J.*, 1955, 4196.

[1] Cunningham, "The Actinide Elements," McGraw-Hill, New York, 1954.

[2] Brown, Ockenden, and Welch, *J.*, 1955, 3932.

[3] Baker and Johns, reported by Johns, L.A.D.C. 277, Sept. 1944; M.D.D.C. 717, Feb. 1947, declassified Feb. 1947.

TABLE 2. *Hexagonal phase.*

Line no.	*d* (Å)	*hkl*	Relative intensity	Line no.	*d* (Å)	*hkl*	Relative intensity
1	3·38	002	5	4	2·36	102	5
2	3·27	100	5	5	1·85	103	10
3	2·94	101	20	6	1·64	112	5

The lattice parameter of the cubic phase was calculated by using the Nelson–Riley extrapolation [4] on results from several different samples. The results (5·340 Å for 3 samples, 5·341 and 5·342 for one each) give a calculated density 10·6.

Some difficulty was experienced in indexing the hexagonal phase owing to the very faint lines and consequent uncertainty in the *d* values, particularly the first two. It is thought that the indices given are correct. They were obtained by using Bunn charts (cf. above).

The samples of plutonium hydride used in this work were prepared by Mrs. H. M. Ockenden and we acknowledge helpful discussions with Mrs. Ockenden and G. A. Welch on many points in this work. Thanks are offered to the Managing Director of this Group for permission to publish this paper.

U.K. ATOMIC ENERGY AUTHORITY (INDUSTRIAL GROUP),
WINDSCALE WORKS, CUMBERLAND.

[*Received, June* 10*th*, 1955.]

[4] Nelson and Riley, *Proc. Phys. Soc.*, 1945, **57**, 160.

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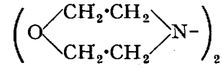
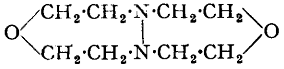
158. *The Reaction of Di-(2-chloroethyl) Ether with Hydrazine.*

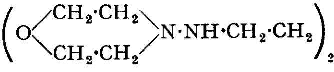
By W. V. FARRAR.

ACCORDING to a patent [1] di-(2-hydrazinoethyl) ether (not characterised) can be prepared by the reaction of di-(2-chloroethyl) ether with excess of hydrazine in ethanol. This could not be confirmed; the only product isolated was 4-aminomorpholine.[2]

When the reaction was conducted in water, the main product was still 4-aminomorpholine, but 5—10% of di-4-morpholinyl (I) was also isolated, together with minor quantities of another base (isolated as dipicrate) whose analysis corresponded to di-(2-4′-morpholinylaminoethyl) ether (III). Di-4-morpholinyl has m. p. 103°: the unlikely formula (II) is excluded by an alternative synthesis from 4-aminomorpholine and di-(2-chloroethyl) ether. It is probably identical with "polydehydromorpholine," m. p. 105—106° (corr.), which Henry and Dehn [3] obtained by the action of alkali on 4-chloromorpholine; the attempts of these authors to demonstrate the presence of an NH group are unconvincing; their α-naphthyl *iso*cyanate derivative is clearly not a chemical individual, and their supposed acetyl derivative is probably acetomorpholide.


(I)


(II)


(III)

Experimental.—*Reaction in ethanol.* Hydrazine hydrate (60 g.) and ethanol (200 c.c.) were refluxed, and di-(2-chloroethyl) ether (30 g.) added during 1 hr.; refluxing was continued for a further 1·5 hr. The product (2 layers) was distilled to small bulk, then taken up in water, and excess of hydrazine precipitated by the addition of sulphuric acid (98 g. of hydrazine sulphate recovered). The filtrate was evaporated to a syrup and stirred with cold ethanol, giving 4-*aminomorpholine sulphate* (25 g.), plates (from aqueous ethanol), m. p. 242° (decomp.) (Found: N, 18·5. $C_4H_{10}ON_2,H_2SO_4$ requires N, 18·5%). The picrate was very soluble, but a *compound* was precipitated when hydrazine was present, consisting of 1 mol. each of 4-aminomorpholine, hydrazine hydrate, and picric acid: it formed bright yellow needles, m. p. 180—185° (decomp.),

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[1] Dreyfus, B.P. 594, 453.

[2] Knorr and Browndson, *Ber.*, 1902, **35**, 4414.

[3] Henry and Dehn, *J. Amer. Chem. Soc.*, 1950, **72**, 2280.

from aqueous ethanol (Found: N, 25·85, 25·3. $C_4H_{10}ON_2 + N_2H_6O + C_6H_3O_7N_3$ requires N, 25·7%).

The ultimate mother-liquors from the sulphate crystallisation (above) were treated with benzaldehyde, giving a benzylidene derivative, m. p. 79—84°, which did not depress the m. p. of 4-benzylideneaminomorpholine (m. p. 88—89°). No appreciable amounts of any other hydrazine with unsubstituted amino-groups can therefore be present.

Reaction in water. Di-(2-chloroethyl) ether (100 g.), hydrazine sulphate (52 g.), sodium hydroxide (64 g.), and water (650 c.c.) were refluxed for 15 hr. The product was acidified, extracted with ether, basified with aqueous sodium hydroxide, and again extracted with ether. The latter extracts were dried (Na_2SO_4) and evaporated, leaving a sticky crystalline residue; washing with cold ether left *di-4-morpholinyl* (3—5 g.). Recrystallisation from light petroleum (b. p. 60—80°) gave prisms, m. p. 103° (Found: C, 56·0; H, 9·3; N, 16·45. $C_8H_{16}O_3N_2$ requires C, 55·8; H, 9·35; N, 16·3%). Di-4-morpholinyl is freely soluble in most solvents, including water, from which it can be partially salted out; it is slightly volatile in steam and reduces ammoniacal silver nitrate. It will not quaternise with methyl iodide, a behaviour also found with 4-phenylmorpholine. The salts are in general very soluble, except the *picrate*, large pale yellow prisms (from ethanol or water), m. p. 218° (Found: C, 41·35; H, 4·7; N, 17·6. $C_{12}H_{19}O_9N_5$ requires C, 41·8; H, 4·75; N, 17·4%).

Treatment of the washings of the crude dimorpholinyl with ethanolic picric acid, followed by water, gave a different *picrate* (*ca.* 2 g.), eventually obtained as bright yellow needles m. p. 184° (decomp.), from water (Found: C, 39·05; H, 4·4; N, 19·05. $C_{24}H_{32}O_{17}N_{10}$ requires C, 39·3; H, 4·4; N, 19·1%). The free base appeared to be a water-soluble oil, but was not characterised.

Addition of acetic acid to the alkaline aqueous portion from the reaction, followed by benzaldehyde, gave a precipitate of 4-benzylideneaminomorpholine (36 g.). Solutions of 4-aminomorpholine, after a few hours in air, do not show certain characteristic reactions, *e.g.*, formation of the benzylidene derivative, or Schotten–Baumann benzoylation. Reaction can be started by adding a trace of reducing agent, *e.g.*, sodium sulphite, or by boiling the solution (perhaps to expel dissolved oxygen) and cooling, before adding the other reagent.

Di-4-morpholinyl was also formed (13% yield) when 4-aminomorpholine sulphate (7·5 g.), di-(2-chloroethyl) ether (7 g.), sodium hydroxide (6 g.), and water (50 c.c.) were refluxed for 12 hr.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, DYESTUFFS DIVISION,
HEXAGON HOUSE, BLACKLEY, MANCHESTER, 9.
[Received, August 25th, 1955.]

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159. *Heptadecafluorodecahydroquinoline and Perfluorotetradecahydroanthracene.*

By R. N. HASZELDINE and F. SMITH.

THE cobalt fluoride technique, used earlier for the preparation of monocyclic nitrogenous perfluoro-compounds,[1] has now been applied to the preparation in low yield of heptadecafluorodecahydroquinoline. Appreciable cleavage of the nitrogenous ring occurs when quinoline is passed over cobalt trifluoride, since perfluoro(-*n*-propyl*cyclo*hexane), perfluoro-(methyl*cyclo*hexane), and perfluoro*cyclo*hexane were also produced. Perfluoro*cyclo*hexylamine was not detected and it is clear that fission of the C–N bond occurs preferentially at the ring junction. Analysis distinguishes between heptadecafluorodecahydroquinoline and a compound such as perfluoro-(3-*cyclo*hexylpropyl)difluoramine whose formation might have followed C–N fission. The boiling points of heptadecafluorodecahydroquinoline (130°) and perfluorotetrahydronaphthalene (142°) are similar and again illustrate that replacement of carbon in a fluorocarbon by nitrogen has only a slight effect on the boiling point.[1] Heptadecafluorodecahydroquinoline is stable to aqueous alkali, aqueous acid, potassium permanganate, zinc and refluxing ethanol, mercury, and ultraviolet light, and the N–F bond is thus not reactive.

Perfluorotetradecahydroanthracene has also been obtained; McBee and Bechtol[2]

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[1] Haszeldine, *J.*, 1950, 1966; 1951, 102.
[2] McBee and Bechtol, *Ind. Eng. Chem.*, 1947, **39**, 380.

fluorinated anthracene, but the analytical data and physical properties of their product suggest the presence of appreciable impurity.

Experimental.—Fluorination of quinoline. The apparatus and techniques used have been described earlier.[3] Quinoline (284 g.), passed over cobalt trifluoride (equivalent to 175 g. of available fluorine) at 400° at an average rate of 10 g./hr., gave liquid products (158 g.). These were extracted with ethanol,[3] and then distilled (P_2O_5) through a packed column to give perfluoro*cyclo*hexane (1 g.) (Found: *M*, 298), b. p. 50—55°; perfluoro(methyl*cyclo*hexane) (1 g.) (Found: *M*, 351), b. p. 75—76°; and a fraction (51 g.), b. p. 120—135°. The identity of the perfluoro*cyclo*hexane and perfluoro(methyl*cyclo*hexane) was confirmed spectroscopically. The fraction, b. p. 120—135°, was treated with uranium hexafluoride and then redistilled through a 28-plate column to give perfluoro(propyl*cyclo*hexane) (1·5 g.) (Found: C, 23·9%; *M*, 447. Calc. for C_9F_{18}: C, 24·0%; *M*, 450), b. p. 124·2—125·2°, n_D^{25} 1·294, spectroscopically identical with a known sample,[3] and *heptadecafluorodecahydroquinoline* (15·5 g., 2%), b. p. 130·4, n_D^{25} 1·302 [Found: C, 24·6; N, 2·9, 3·2, 3·1; F, 72·1%; *M*, 444, 454. C_9NF_{17} requires C, 24·3; N, 3·1; F, 72·6%; *M*, 445. Calc. for perfluoro-(3-*cyclo*hexylpropyl)difluoramine: C, 22·4; N, 2·9; F, 74·7%; *M*, 483], shown spectroscopically to be free from C–H bonds.

Fluorination of anthracene. Anthracene (56 g.), was added in 5-g. portions (7·5 hr.) to a cobalt trifluoride reaction vessel (400 g. of available fluorine) heated to 350° at the inlet and 450° at the outlet. Distillation of the product gave perfluorotetradecahydroanthracene (10% yield) [Found: C, 26·6; F, 72·4%; *M* (ebullioscopic in perfluoromethyl*cyclo*hexane), 630. Calc. for $C_{14}F_{24}$: C, 26·9; F, 73·1%; *M*, 624], b. p. 205—206°, m. p. 155° (sealed tube), as a white shining solid which readily sublimed at 60°/760 mm., and was spectroscopically free from C–H bonds.

A. E. Hills Laboratories, University of Birmingham.
University Chemical Laboratory, Cambridge.

[*Received, September 8th*, 1955.]

[3] Haszeldine and Smith, *J.*, 1950, 3617, 2689,

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160. *Adsorption of Binary Liquid Mixtures on Solid Adsorbents.*

By G. S. Mill.

Considering the adsorption of two completely miscible liquids, A and B, on a solid surface, Elton [1] derived an equation for the calculation of the mole fraction of B on the surface. He gave this equation originally as

$$x_B{}^s = n_B{}^s/(n_A{}^s + n_B{}^s) = \frac{Ax_B - a_A(n_A + n_B)\Delta x_B}{A + (n_A + n_B)(a_B - a_A)\Delta x_B} \quad . \quad . \quad . \quad . \quad (1)$$

where $n_A{}^s$ and $n_B{}^s$ are the numbers of moles of A and B in the surface layer at equilibrium, n_A and n_B are the total numbers of moles of A and B present in the system, x_B is the mole fraction of B in the bulk liquid at equilibrium, Δx_B is defined as $x_B - x_B{}^0$ where $x_B{}^0$ is the mole fraction of B before adsorption, a_A and a_B are the effective areas occupied per mole of A and B, and A is the area of the surface available for adsorption.

This equation was later [2] corrected to:

$$x_B{}^s = n_B{}^s/(n_A{}^s + n_B{}^s) = \frac{A(x_B + \Delta x_B) - a_A(n_A + n_B)\Delta x_B}{A + (n_A + n_B)(a_B - a_A)\Delta x_B} \quad . \quad . \quad . \quad (2)$$

The original equation [eqn. (1) above] is correct, and incidentally can be obtained by a simpler method than that employed by Elton. The general equation describing the adsorption of two miscible liquids, A and B, on a solid surface was first given by Williams [3] and can be written in the form:

$$(n_A + n_B)\Delta x_B = n_A{}^s x_B - n_B{}^s(1 - x_B) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Elton's equation (1) was

$$n_A{}^s a_A + n_B{}^s a_B = A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

[1] Elton, *J.*, 1951, 2958.
[2] Errata, *J.*, 1952, March, xiii; Elton, *J.*, 1952, 1955.
[3] Williams, *Medd. K. Vetenskapsakad. Nobelinst.*, 1913, **2**, No. 27.

If equations (3) and (4) are then solved for $n_A{}^s$ and $n_B{}^s$ and the resulting expressions are substituted in the equation $x_B{}^s = n_B{}^s/(n_A{}^s + n_B{}^s)$, equation (1) above results. The mistake in Elton's derivation (as corrected by him) is algebraic and lies in the steps involved between his equations (9) and (10).

THE RICE INSTITUTE, HOUSTON, TEXAS. [*Received, September 12th*, 1955.]

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161. *Reaction of Tellurium Dioxide and Selenium Tetrafluoride: Preparation of Tellurium Tetrafluoride.*

By R. CAMPBELL and P. L. ROBINSON.

TELLURIUM TETRAFLUORIDE was reported by Hartley, Henry, and Whytlaw-Gray [1] as a white solid resulting from the reduction of the hexafluoride with elementary tellurium. (Berzelius [2] mistakenly thought he had made it from hydrofluoric acid and tellurium dioxide, and Moissan [3] by the action of fluorine on tellurium; Prideaux [4] showed the latter must have had hexafluoride.) The reduction of the hexafluoride was subsequently investigated in these laboratories and is described by Peacock,[5] who gave details of an apparatus which allowed the reduction to take place in alumina and the tetrafluoride subsequently to be transferred to glass for storage. Colourless, needle-shaped crystals of the pure substance were obtained; but the method involved a reaction-time of four days and allowed only a small quantity to be made per run. Junkins, Bernhardt, and Barber,[6] carrying out the same reaction later in a nickel vessel for periods of over 100 hr., obtained a product of average composition Te, 62·06; F, 36·04%. Neither the reduction of hexafluoride nor the action of nitryl fluoride on tellurium [7] furnishes a method of preparing the tetrafluoride comparable in convenience with that now described.

The ease with which selenium tetrafluoride is converted into the oxyfluoride, $SeOF_2$, and the fact that the latter is readily volatilised, b. p. 126°, led us to examine its reaction with the tellurium oxides. The trioxide appears to be unreactive at least up to the boiling point of selenium tetrafluoride, b. p. 93°, but at about 80° the dioxide reacts smoothly and quantitatively according to the scheme $TeO_2 + 2SeF_4 \longrightarrow TeF_4 + 2SeOF_2$. In this way the whole of the dioxide is converted into tetrafluoride which can readily be recovered in a pure crystalline condition by evaporating the excess of selenium tetrafluoride and the selenium oxyfluoride.

Experimental.—Selenium tetrafluoride, readily preparable in bulk, was distilled from a break-seal storage bulb into a carefully dried, evacuated train of bulbs, the stem of the first, which carried the dry tellurium dioxide, being drawn down for subsequent removal under vacuum. The liquid was condensed on to the dioxide and the mixture was slowly heated by means of a water-bath. As the temperature approached 80° there was a vigorous but steady reaction and the tellurium dioxide dissolved. The temperature was raised until the liquid began to reflux under its own vapour pressupe and kept at that point for 15 min., after which the selenium tetrafluoride and oxyfluoride were distilled into another bulb, the last traces being removed from the residue by keeping it at 100° and 10^{-2} mm. for 1 hr. The product was wholly crystalline (Found: Te, 62·6; F, 37·1. Calc. for TeF_4: Te, 62·7; F, 37·3%).

The authors acknowledge grants for material and maintenance (R. C.) from the United Kingdom Atomic Energy Authority.

KING'S COLLEGE, NEWCASTLE UPON TYNE, 1. [*Received, September 14th*, 1955.]

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[1] Hartley, Henry, and Whytlaw-Gray, *Nature*, 1938, **142**, 952.
[2] Berzelius, *Schweigger's J.*, 1812, **6**, 311.
[3] Moissan, *Ann. Chim. Phys.*, 1891, **24**, 239.
[4] Prideaux, *J.*, 1906, **89**, 316.
[5] Peacock, Ph.D. Thesis, Univ. Durham, 1951.
[6] Junkins, Bernhardt, and Barber, *J. Amer. Chem. Soc.*, 1952, **74**, 5749.
[7] Aynsley, Hetherington, and Robinson, *J.*, 1954, 1119.

162. *Preparation and Some Properties of 2 : 2′-Dibromodiphenylamine.*

By Emrys R. H. Jones and Frederick G. Mann.

Failure attended our attempts to prepare 2 : 2′-dibromodiphenylamine by (*a*) heating *o*-bromoaniline and its hydrochloride (1 mol. each) at 235—240° in open or sealed tubes, (*b*) heating *o*-chloronitrobenzene (1 mol.) and *o*-bromoaniline (1·5 mol.) with potassium carbonate and copper bronze at 170° for various times up to 12 hr., (*c*) heating *o*-bromophenol [1] with 1 and 2 equivs., respectively, of *o*-bromoaniline and zinc chloride at 250° for 8 hr., (*d*) boiling a mixture of *o*-chloronitrobenzene and *o*-bromo-*N*-sodioacetanilide in xylene for 3 hr., and (*e*) acylating or methylating the intermediate 2 : 2′-dinitrodiphenylamine [2] under a variety of conditions. The methods (*a*), (*b*), and (*c*) gave only intractable tars, and the product from method (*d*) when worked up yielded *o*-bromoacetanilide in 50% recovery.

The amine was ultimately prepared by using the Chapman rearrangement.[3] *o*-Bromobenzanilide was converted by phosphorus pentachloride into *N*-*o*-bromophenylbenzimidoyl chloride (I), which with sodium *o*-bromophenoxide gave *o*-bromophenyl *N*-*o*-bromophenylbenzimidoate (II). This ester, when suitably heated, rearranged to *N*-benzoyl-2 : 2′-dibromodiphenylamine (III), which on alkaline hydrolysis gave 2 : 2′-dibromodiphenylamine; this exists in dimorphic forms, m. p. 37° and 61°.

$$\begin{array}{ccccc} \mathrm{Br{\cdot}C_6H_4{\cdot}N{:}CClPh} & \longrightarrow & \mathrm{Br{\cdot}C_6H_4{\cdot}N{:}CPh{\cdot}O{\cdot}C_6H_4Br} & \longrightarrow & \mathrm{(Br{\cdot}C_6H_4)_2N{\cdot}COPh} \\ \mathrm{(I)} & & \mathrm{(II)} & & \mathrm{(III)} \end{array}$$

This amine resisted methylation: it was unaffected when its solution in formic acid–formaldehyde was boiled for 7 hr., and when heated with methyl sulphate at 100° for 1 hr. It rapidly decomposed to a black tar when its solution in methyl sulphate was boiled.

It underwent ready lithiation when its ethereal solution was treated with *n*-butyllithium in light petroleum. Carboxylation of the product afforded diphenylamine-2 : 2′-dicarboxylic acid in 84% yield.

2 : 2′-Dilithiodiphenyl ether condenses with phenyldichlorophosphine to give 10-phenylphenoxphosphine [4] in 63% yield, but the lithium derivative of diphenylamine reacted with the phosphine to give a sticky solid, presumably a polymer, which had an indefinite m. p., was freely soluble in chloroform and benzene and very sparingly soluble in most solvents, could not be obtained crystalline, and could not be broken down by pyrolysis [5] (at atmospheric or reduced pressure) to simpler, identifiable compounds. Its solution in boiling methyl iodide gave an intractable gummy product.

This extensive polymerisation might have been avoided had preliminary protection of the amine group been possible. If so, the reaction would have afforded ready access to 5 : 10-dihydro-10-phenylphenphosphazine and thus indirectly to many of its derivatives. Michaelis and Schenk,[6] and later Sergeev and Kudryashov,[7] prepared the crude 10-chloro-5 : 10-dihydrophenphosphazine by direct condensation of diphenylamine with phosphorus trichloride, and then by hydrolysis obtained the pure 10-hydroxy-derivative. We have investigated this condensation employing a wide variation of trichloride proportions (1·0—2·8 mols.), catalyst, solvent, temperature, and time of heating, but have obtained after hydrolysis only very low yields of the 10-hydroxyphosphazine: moreover the crude condensation product, if prepared on a reasonably large scale, may cause explosions when subsequently extracted with water. Phosphorus trichloride had no action on *N*-methyldiphenylamine, and in this respect resembles arsenic trichloride.[8]

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[1] Merz and Weith, *Ber.*, 1880, **13**, 1299.
[2] Eckert and Steiner, *Monatsh.*, 1914, **35**, 1154.
[3] Chapman, *J.*, 1929, 569; also *J.*, 1922, **121**, 1676; 1925, **127**, 1992; 1927, 1743.
[4] Mann and Millar, *J.*, 1953, 3746.
[5] Cf. Beeby and Mann, *J.*, 1951, 886; Mann, Millar, and Stewart, *J.*, 1954, 2832.
[6] Michaelis and Schenk, *Annalen*, 1890, **260**, 1.
[7] Sergeev and Kudryashov, *J. Gen. Chem.* (*U.S.S.R.*), 1938, **8**, 266.
[8] Burton and Gibson, *J.*, 1926, 450.

Experimental.—N-o-*Bromophenylbenzimidoyl chloride* (I). Powdered *o*-bromobenzanilide (446 g.) was mixed with phosphorus pentachloride (360 g., 1·05 mols.) in a flask through which nitrogen was passed. On this scale the reaction began spontaneously, but on a smaller scale required gentle initial heating. When the vigorous reaction had subsided, the mixture was heated at 100° for *ca.* 10 min., and the phosphorus oxychloride then removed by distillation (water-pump); the residue, distilled at lower pressure, gave the *imidoyl chloride* (I), b. p. 164—168°/2 mm. (408 g., 86%); a sample, further purified by fractionation, had b. p. 123—125°/0·02 mm. (Found: C, 53·0; H, 2·85. $C_{13}H_9NClBr$ requires C, 53·0; H, 3·1%). The m. p. of the pure compound is just below room temperature.

o-*Bromophenyl* N-o-*bromophenylbenzimidoate* (II). *o*-Bromophenol (63 g.) was added to a solution obtained by the interaction of sodium (8·4 g., 1 atom-equiv.) and absolute ethanol (500 c.c.), which was then thoroughly cooled and stirred whilst a solution of the imidoyl chloride (I) (108 g., 1 mol.) in ether (200 c.c.) was added. Next day, the greater part of the solvent was removed by distillation, and the residue poured into water, precipitating the *ester* (II) as an oil which slowly solidified. Recrystallisation from ethanol gave colourless crystals, m. p. 95° (Found: C, 53·0; H, 3·0; N, 3·4. $C_{19}H_{13}ONBr_2$ requires C, 52·9; H, 3·0; N, 3·25%): 76 g., 48% yield.

N-*Benzoyl*-2 : 2′-*dibromodiphenylamine* (III). The exothermic rearrangement of the ester (II) was markedly affected by small changes in the temperature, and the optimum conditions were therefore determined largely by the scale of the experiment. Three results are quoted for illustration. (i) The ester (7·3 g.) was heated for 3 hr. at 265—270° (bath-temp.) and the product digested with boiling ethanol (20 c.c.). The benzoyl derivative (III) which separated on cooling had m. p. 172—177° (4·3 g., 58%). (ii) The ester (40 g.), heated at 155—260°/2·5 hr. and digested with ethanol (90 c.c.), gave the derivative (III), m. p. 175—179° (26 g., 65%). (iii) The ester (35 g.), heated as in (ii) and digested with ethanol (50 c.c.), gave the derivative (III), m. p. 175—179° (30 g., 86%). Recrystallisation from ethanol gave the pure *benzoyl* derivative (III), m. p. 179—180° (Found: C, 53·1; H, 3·3; N, 3·35. $C_{19}H_{13}ONBr_2$ requires C, 52·9; H, 3·0; N, 3·25%).

2 : 2′-*Dibromodiphenylamine.* The derivative (III) (75 g.) was boiled in a solution of potassium hydroxide (150 g.) in water (150 c.c.) and ethanol (750 c.c.) for 8 hr. and then concentrated by distillation, the residue being poured into water. The precipitated oil was extracted with ether, and the dried extract on distillation gave the *amine*, b. p. 135—142°/0·05 mm. (46·0 g., 87%). The amine when first prepared was isolated as colourless crystals, m. p. 37°, by crystallisation from ethanol at −70°: this sample, when set aside for 2 weeks, had changed to yellow crystals, m. p. 61°. All subsequent preparations furnished solely the yellow crystals, m. p. 61°, readily isolated by normal crystallisation from ethanol (Found: C, 44·3; H, 2·8; N, 4·3. $C_{12}H_9NBr_2$ requires C, 44·0; H, 2·8; N, 4·3%).

Lithiation. The amine (5·0 g.) in ether (50 c.c.) was added under nitrogen to a stirred 0·66N-solution of *n*-butyl-lithium in light petroleum (b. p. 40—60°) (120 c.c.; 6 mols. of solute), which after 10 min. was poured on crushed solid carbon dioxide (*ca.* 50 g.). The mixture was ultimately extracted with dilute aqueous potassium hydroxide, which when separated and acidified gave diphenylamine-2 : 2′-dicarboxylic acid, yellow crystals, m. p. 291° (decomp.), from ethanol (Found: C, 65·6; H, 4·6; N, 5·4. Calc. for $C_{14}H_{11}O_4N$: C, 65·3; H, 4·3; N, 5·4%); the yield of recrystallised product was 2·85 g. (84%). Ullmann[9] records the acid as forming yellow crystals, m. p. 295° (decomp.).

Reaction with phenyldichlorophosphine. The amine (5·0 g.) was lithiated by using a 0·83N-solution of *n*-butyl-lithium (57 c.c.; 3·1 mols. of solute) under the above conditions, and then treated with the phosphine (2·74 g., 1 mol.) in ether (25 c.c.), a vigorous reaction occurring with deposition of an orange solid. The mixture was boiled under reflux for 1 hr., and then cooled and hydrolysed with water (100 c.c.). The insoluble product, now yellow, was collected, washed, and dried; it softened between *ca.* 80° and *ca.* 200°, becoming ultimately a viscous liquid. Its general properties are indicated above. When the solution of the lithiated amine was cooled in acetone–solid carbon dioxide before addition of the phosphine, the same product was obtained.

Tests kindly undertaken by Mr. O. D. Standen at the Wellcome Laboratories of Tropical Medicine have shown that 5 : 10-dihydro-10-hydroxyphenphosphazine has no apparent effect on schistosomiasis infection in mice.

We gratefully acknowledge a grant from the Medical Research Council (to E. R. H. J.).

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, September 15th*, 1955.]

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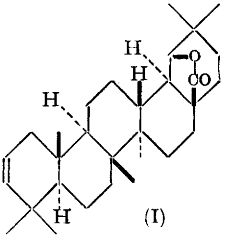
[9] Ullmann, *Annalen*, 1907, **355**, 352.

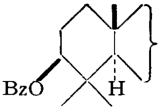
163. *Triterpenoids. Part XXI.* A Triterpenoid Lactone from Petroleum.*

By D. H. R. Barton, W. Carruthers, and K. H. Overton.

Recently Carruthers and Cook[1] reported some preliminary investigations on the constituents of high-boiling petroleum distillates. Amongst the compounds isolated was a high-melting crystalline substance of the approximate composition, $C_{30}H_{46}O_2$. With the kind permission of Dr. J. W. Cook, F.R.S., we have examined this substance and identified it as oxyallobetul-2-ene (I). An authentic specimen was prepared by the pyrolysis of oxyallobetulin benzoate (II).[2] The identification of this petroleum constituent as a derivative of the typical plant triterpenoid, betulin, shows that at least a small proportion of the petroleum must have been of vegetable rather than animal origin.[3]



(I)



(II)

Experimental.—Rotations were measured in chloroform solution. Ultraviolet absorption spectra were determined in ethanol with the Unicam S.P. 500 Spectrophotometer. The infrared spectra were taken in Nujol mulls, a Perkin-Elmer double-beam instrument Model 13 being used. All m. p.s were observed in evacuated capillaries.

Oxyallobetulin benzoate. Treatment of oxyallobetulin, m. p. *ca.* 330°, $[\alpha]_D$ +49° (*c*, 0·92), with pyridine–benzoyl chloride overnight at room temperature gave *oxyallobetulin benzoate*, m. p. (plates from chloroform–methanol) 345—348°, $[\alpha]_D$ +71° (*c*, 3·33), $\lambda_{max.}$ 230 mμ (ε, 13,500) (Found : C, 79·45; H, 9·3. $C_{37}H_{52}O_4$ requires C, 79·25; H, 9·35%).

Pyrolysis of oxyallobetulin benzoate. The benzoate (250 mg.) was pyrolysed at 550°/0·2 mm. in a stream of oxygen-free nitrogen (approx. ½ l. per hr. at room temperature and atmospheric pressure).[4] The product was refluxed with 5% ethanolic potassium hydroxide (20 ml.) for 1 hr. Most of the ethanol was removed *in vacuo*, and the residue acidified (5N-sulphuric acid) and extracted with ether. Removal of the ether *in vacuo* and chromatography of the residue in benzene solution on alumina gave *oxyallobetul*-2-*ene* (long plates from chloroform–methanol), sublimed below 345° after insertion at 310°, $[\alpha]_D$ +79° (*c*, 1·18) λ_{210} and λ_{206} mμ, ε = 750 and 1450, respectively) (Found : C, 82·2; H, 10·2. $C_{30}H_{46}O_2$ requires C, 82·15; H, 10·55%).

The compound isolated by Carruthers and Cook (*loc. cit.*) and for which they reported C, 81·8, 81·6; H, 10·7, 10·8 was repeatedly recrystallised from chloroform–methanol. It was identified as oxyallobetul-2-ene by crystal form, m. p. (sublimed by 345° after insertion at 310°; same behaviour on admixture with authentic material), rotation {$[\alpha]_D$ +75° (*c*, 0·68)}, ultraviolet absorption spectrum (λ_{210} and λ_{206} mμ, ε = 700 and 1350; similar identity at other wavelengths below 220 mμ), and infrared spectrum.

We thank the Government Grants Committee of the Royal Society and Imperial Chemical Industries Limited for financial assistance. One of us (W. C.) has been supported by the Medical Research Council. We acknowledge with gratitude the interest and encouragement of Dr. J. W. Cook, F.R.S. The infrared spectra were determined by Dr. G. Eglinton and the microanalyses were by Mr. J. M. L. Cameron.

The University, Glasgow, W.2. [*Received, September* 22*nd*, 1955.]

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* Part XX, *J.*, 1955, 2639.

[1] Carruthers and Cook, *J.*, 1954, 2047.

[2] See Davy, Halsall, Jones, and Meakins, *J.*, 1951, 2702.

[3] Cf. van Nes and van Westen, " Aspects of the Constitution of Mineral Oils," Elsevier Publishing Co., Amsterdam, 1951, p. 43.

[4] See Barton and de Mayo, *J.*, 1954, 887.

164. *Deoxy-sugars. Part XXX.** *Synthesis and Characterization of Derivatives of 2-Deoxy*aldehydo-*D-galactose and its 2-Deoxy-D-glucose Analogue.*

By J. L. Barclay, A. J. Cleaver, A. B. Foster, and W. G. Overend.

Considerable use has been made of derivatives of 2-deoxy*aldehydo*-D-galactose and of 2-deoxy*aldehydo*-D-glucose as model compounds in studies of the synthesis of 2-deoxy-sugar nucleotides.[1,2] We now describe improved methods for the preparation and characterization of 3 : 4 : 5 : 6-tetra-*O*-acetyl-2-deoxy*aldehydo*-D-galactose and its 2-deoxy*aldehydo*-D-glucose analogue.

2-Deoxy-D-galactose [3] was readily converted into the diethyl dithioacetal which could also be obtained (but in lower yield) directly from D-galactal by treatment successively with ethanethiol and hydrochloric acid. Likewise 2-deoxy-D-galactose dibenzyl dithioacetal could be obtained from D-galactal. The diethyl dithioacetal was converted into a syrupy 3 : 4 : 5 : 6-tetra-acetate which on treatment with mercuric chloride and cadmium carbonate [1,4] afforded crystalline 3 : 4 : 5 : 6-tetra-*O*-acetyl-2-deoxy*aldehydo*-D-galactose. In a similar manner 3 : 4 : 5 : 6-tetra-*O*-acetyl-2-deoxy*aldehydo*-D-glucose was obtained from 2-deoxy-D-glucose.[5]

Very few derivatives have been reported of 2-deoxy*aldehydo*-sugars. 2-Deoxy-D-glucose dimethyl acetal has been described [6] and recently some phosphoric esters of 2-deoxy*aldehydo*hexoses were described by Barclay, Foster, and Overend.[1]

No crystalline product could be obtained by reaction of the 2-deoxy*aldehydo*-sugar derivatives with aniline under a variety of conditions but condensation with 2 : 4 : 1-xylidine or *o*-phenylenediamine afforded amorphous, pale yellow solids of ill-defined composition. A detailed study of the reaction of some *aldehydo*-sugars with primary aromatic amines has been published.[2]

The 2-deoxy*aldehydo*-D-glucose derivative was characterized as the semicarbazone.[7] Both the 2-deoxy*aldehydo*-D-glucose and -D-galactose derivatives gave crystalline 2 : 4-dinitrophenylhydrazones and the glucose derivative gave a bisdimedone.

Experimental.—*2-Deoxy-*D*-galactose diethyl dithioacetal.* Finely powdered 2-deoxy-D-galactose (5·0 g.) was dissolved in concentrated hydrochloric acid (5 ml.) at 0°, and ethanethiol (10 ml.) was added. After the mixture had been shaken for 12 hr. (at room temperature) the product was isolated in the usual fashion. After recrystallization from water the diethyl dithioacetal (5·5 g., 67%) was obtained as plates, m. p. 107—108°, $[\alpha]_D$ +18° (*c*, 1·0 in MeOH) (Overend, Shafizadeh, and Stacey [3] give m. p. 107—108°). The same product was prepared directly from D-galactal (1·0 g.) by successive treatment with ethanethiol (2 ml.) and concentrated hydrochloric acid (2 ml.). The reactants were cooled (ice–salt) before being mixed. Reaction was allowed to proceed at room temperature for 2 hr. before the product (0·6 g., 32%; m. p. 108°) was isolated.

3 : 4 : 5 : 6-*Tetra-*O*-acetyl-2-deoxy-*D*-galactose diethyl dithioacetal.* This *tetra-acetyl derivative,* prepared from 2-deoxy-D-galactose diethyl dithioacetal (2·0 g.) (yield; $Ac_2O-C_5H_5N$ method, 2·38 g., 73%; NaOAc–Ac_2O method, 2·70 g., 83%) formed a viscous syrup, b. p. 167—172° (bath)/0·016 mm., n^{19} 1·4852, $[\alpha]_D^{16}$ +31·5° (*c*, 1·65 in $CHCl_3$) (Found : C, 49·2; H, 6·9; S, 14·3. $C_{18}H_{30}O_8S_2$ requires C, 49·3; H, 6·9; S, 14·6%).

3 : 4 : 5 : 6-*Tetra-*O*-acetyl-2-deoxy*aldehydo-D*-galactose.* 3 : 4 : 5 : 6-Tetra-*O*-acetyl-2-deoxy-D-galactose diethyl dithioacetal (3·44 g.) in acetone (50 ml.) and water (25 ml.) was treated with a ten-fold excess of finely powdered cadmium carbonate (13·5 g.). The suspension was well stirred and a solution of mercuric chloride (9·0 g.) in acetone (25 ml.) was added dropwise

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* Part XXIX, *J.*, 1955, 2511.

[1] Barclay, Foster, and Overend, *J.*, 1955, 2505.
[2] *Idem, J.*, 1956, 476.
[3] Cf. Overend, Shafizadeh, and Stacey, *J.*, 1950, 671.
[4] Wolfrom, Konigsberg, and Weisblat, *J. Amer. Chem. Soc.*, 1939, **61**, 574.
[5] Cf. Overend, Stacey, and Staněk, *J.*, 1949, 2841.
[6] Bolliger and Schmid, *Helv. Chim. Acta*, 1951, **34**, 989, 1597, 1671.
[7] Wolfrom, *J. Amer. Chem. Soc.*, 1929, **51**, 2188.

during 1 hr. Stirring was continued for a further 24 hr. and then the mixture was filtered on to a small amount of cadmium carbonate. The filtrate was evaporated to dryness under diminished pressure in the presence of fresh cadmium carbonate (10 g.). The residue was extracted with hot chloroform (2 × 50 ml.), and the extract was washed with water (3 × 100 ml.), 5% potassium iodide solution (3 × 100 ml.), and water, and then dried (Na_2SO_4). Evaporation of the solvent and recrystallization of the residue from acetone–light petroleum (b. p. 60—80°) afforded 3 : 4 : 5 : 6-*tetra*-O-*acetyl*-2-*deoxy*aldehydo-D-*galactose* (1·42 g., 43%) as needles, m. p. 87—88°, $[\alpha]_D^{18}$ +52·0° (*c*, 1·12 in $CHCl_3$) (Found : C, 50·3; H, 5·9. $C_{14}H_{20}O_9$ requires C, 50·6; H, 6·0%). On storage slow decomposition occurred. This product (0·21 g.) readily gave a 2 : 4-dinitrophenylhydrazone (0·24 g.), m. p. 110° (sinter, 102—104°), $[\alpha]_D^{16}$ +21·6° (*c*, 1·48 in $CHCl_3$) (Found : C, 47·0; H, 4·8; N, 11·2. $C_{20}H_{24}O_{12}N_4$ requires C, 46·9; H, 4·7; N, 10·9%).

3 : 4 : 5 : 6-*Tetra*-O-*acetyl*-2-*deoxy*aldehydo-D-*glucose*. 2-Deoxy-D-glucose diethyl dithioacetal {m. p. 134°; $[\alpha]_D^{19}$ +10° (*c*, 1·0 in EtOH); 8 g.} was acetylated with acetic anhydride in pyridine (yield 12 g., 92%). The acetate {m. p. 77°, $[\alpha]_D^{18}$ +35° (*c*, 2·2 in $CHCl_3$); 6·9 g.} was dissolved in acetone (50 ml.) and water (20 ml.), and powdered cadmium carbonate (35 g.) was added, followed by mercuric chloride (30 g.) in acetone (40 ml.), added slowly. Reaction was allowed to proceed for 20 hr., and more cadmium carbonate was added at intervals. The product was isolated as described previously; 3 : 4 : 5 : 6-*tetra*-O-*acetyl*-2-*deoxy*aldehydo-D-*glucose* (5·2 g., 56%) was obtained as long needles, m. p. 100°, $[\alpha]_D^{14}$ +23° (*c*, 1·5 in $CHCl_3$) (Found : C, 50·7; H, 6·3. $C_{14}H_{20}O_9$ requires C, 50·6; H, 6·0%). The material slowly became discoloured, and acetic acid was liberated. The product was readily converted into a *semicarbazone*, m. p. 158°, $[\alpha]_D^{16}$ +50° (*c*, 1·0 in $CHCl_3$) (Found : C, 46·5; H, 6·1; N, 10·5. $C_{15}H_{23}O_9N_3$ requires C, 46·3; H, 5·9; N, 10·8%), and a 2 : 4-*dinitrophenylhydrazone*, m. p. 131°, $[\alpha]_D^{15}$ +45° (*c*, 0·4 in $CHCl_3$) (Found : C, 46·8; H, 4·6; N, 11·3. $C_{20}H_{24}O_{12}N_4$ requires C, 46·9; H, 4·7; N, 10·9%).

3 : 4 : 5 : 6-Tetra-*O*-acetyl-2-deoxy*aldehydo*-D-glucose (120 mg.) and dimedone (130 mg.) were heated for 5 min. in 50% aqueous ethanol and the solution was then set aside overnight. Water was added until the solution became turbid, and the *bisdimedone* (95 mg.) which separated at 0° was crystallized from aqueous ethanol; it had m. p. 110°, $[\alpha]_D^{17}$ −30° (*c*, 1·0 in $CHCl_3$) (Found : C, 60·5; H, 7·0. $C_{30}H_{42}O_{12}$ requires C, 60·6; H, 7·1%).

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165. *The Synthesis and Reactions of* 3-iso*Hexyl*-3-*methyl*cyclo*hexanone.*

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By Kharasch and Tawney's method reaction between *iso*hexylmagnesium iodide and 3-methyl*cyclo*hex-2-enone in presence of cuprous chloride gave an excellent yield of a saturated ketone (semicarbazone and 2 : 4-dinitrophenylhydrazone) which was shown as follows to be the expected 3-*iso*hexyl-3-methyl*cyclo*hexanone. αα′-Dicyano-β-*iso*hexyl-β-methylglutarimide [2] was hydrolysed with 60% sulphuric acid to give β-*iso*hexyl-β-methylglutaric acid, the anhydride of which was converted into the half-ester and thence through the acid chloride and methylzinc iodide into ethyl 3-*iso*hexyl-3-methyl-5-oxohexanoate. The latter when heated with ethanolic sodium ethoxide afforded 5-*iso*hexyl-5-methyl*cyclo*hexane-1 : 3-dione, yielding on treatment with phosphorus trichloride,[3] followed by hydrogenation,[4] 3-*iso*hexyl-3-methyl*cyclo*hexanone, identical with the ketone described above. Alternatively, the substituted glutaric anhydride on reduction with sodium and ethanol [5] gave β-*iso*hexyl-β-methyl-δ-valerolactone, which was converted, by means of

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[1] Kharasch and Tawney, *J. Amer. Chem. Soc.*, 1941, **63**, 2308; Birch and Robinson, *J.*, 1943, 501; Büchi, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1948, **31**, 245.

[2] Guareschi, *Mem. Real. Acad. Sci. Torino*, 1901, **50**, 235.

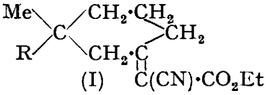
[3] Crossley and Le Sueur, *J.*, 1902, **81**, 675, 821; 1903, **83**, 117.

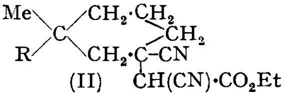
[4] France, Heilbron, and Hey, *J.*, 1939, 1290.

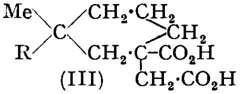
[5] Blanc, *Bull. Soc. chim. France*, 1905, **33**, 879.

phosphorus pentabromide and then ethanol, into ethyl δ-bromo-β-*iso*hexyl-β-methylvalerate; chain extension by use of malonic ester then gave β-*iso*hexyl-β-methylpimelic acid, which on ketonisation afforded the required *cyclo*hexanone.

The ketone was condensed with ethyl cyanoacetate [6] in presence of ammonium acetate and acetic acid to give α-cyano-α-(3-*iso*hexyl-3-methyl*cyclo*hexylidene)acetate (I), which formed an additive compound (II) with hydrogen cyanide.[7] The latter on hydrolysis yielded the corresponding dicarboxylic acid (III) as a viscous liquid.


(I)


(II)


(III)

R = $\cdot[CH_2]_3\cdot CHMe_2$

Experimental.—3-Methyl*cyclo*hex-2-enone [8] was prepared by condensation of paraformaldehyde (12 g.) with ethyl acetoacetate (104 g.) in presence of piperidine (4 ml.); it (23 g.) had b. p. 86—90°/13 mm.

3-iso*Hexyl*-3-*methyl*cyclo*hexanone.* A solution of *iso*hexylmagnesium iodide [activated magnesium (3·25 g.), *iso*hexyl iodide [9] (28 g.), dry ether (45 ml.)] was cooled in a freezing mixture and thoroughly mixed with dry powered cuprous chloride (0·2 g.), and then a solution of 3-methyl*cyclo*hex-2-enone (11 g.) in dry ether (15 ml.) was introduced with stirring, and the mixture set aside overnight. It was cooled in ice, mixed with a saturated solution of ammonium chloride (25 ml.), and acidified with dilute hydrochloric acid, and the liquid extracted with ether. The ethereal solution was washed with a solution of sodium thiosulphate and then with water, dried ($CaCl_2$), and distilled. 3-iso*Hexyl*-3-*methyl*cyclo*hexanone* formed a colourless liquid (11 g.), b. p. 135—140°/13 mm. (Found: C, 79·5; H, 12·1. $C_{13}H_{24}O$ requires C, 79·6; H, 12·2%). The *semicarbazone* separated from ethanol in plates, m. p. 169° (Found: C, 66·5; H, 10·6. $C_{14}H_{27}ON_3$ requires C, 66·4; H, 10·7%), and the 2 : 4-*dinitrophenylhydrazone* from light petroleum (b. p. 40—60°) or ethyl acetate in orange-red needles, m. p. 106° (Found: C, 60·5; H, 7·5. $C_{19}H_{28}O_4N_4$ requires C, 60·6; H, 7·4%).

β-iso*Hexyl*-β-*methylglutaric acid.* *iso*Hexyl methyl ketone,[10] b. p. 40—41°/4 mm., 167—168°/760 mm., was prepared by hydrogenation of methylheptenone,[11] b. p. 54—55°/3 mm. The ketone (128 g.), ethyl cyanoacetate (226 ml.), and ethanol (400 ml.), saturated with ammonia at 0°, gave when kept in the cold for 2 days αα′-dicyano-β-*iso*hexyl-β-methylglutarimide (193 g.), which crystallised from ethanol in plates, m. p. 168° (lit.,[2] 166·5—168·5°) (Found: C, 64·5; H, 7·4. Calc. for $C_{14}H_{19}O_2N_3$: C, 64·4; H, 7·3%). When a mixture of the imide (110 g.), concentrated sulphuric acid (330 ml.), and water (275 ml.) was refluxed for 12 hr., β-*iso*hexyl-β-methylglutaric acid (90 g.) was obtained, which crystallised from aqueous acetic acid in short prisms, m. p. 80—81° (lit.,[12] 62—63°) (Found: C, 62·4; H, 9·6. Calc. for $C_{12}H_{22}O_4$: C, 62·6; H, 9·6%). The *diethyl ester* had b. p. 142°/7 mm. (Found: C, 67·1; H, 10·6. $C_{16}H_{30}O_4$ requires C, 67·1; H, 10·5%). The *anhydride*, prepared by heating the acid with acetic anhydride, had b. p. 160°/7 mm., m. p. 39—41° (Found: C, 67·6; H, 9·4. $C_{12}H_{20}O_3$ requires C, 67·9; H, 9·4%).

Ethyl 3-iso*hexyl*-3-*methyl*-5-*oxohexanoate* (3 : 7-*dimethyl*-3-2′-*oxopropyloctanoate*). The foregoing anhydride (43·5 g.) was heated with absolute ethanol (23 ml.) on the steam-bath for 3 hr. The half-ester (48 g.), b. p. 178—180°/6 mm., was mixed with thionyl chloride (15 ml.), and after 3 hr. the mixture was heated at 45° for 1 hr., and the excess of thionyl chloride removed; the crude ester chloride, dissolved in benzene, was allowed to react with an excess of methylzinc iodide [from methyl iodide (55 ml.), ethyl acetate (25 ml.), benzene (70 ml.), and zinc–copper couple [13] (70 g.)]. The *keto-ester* had b. p. 135—137°/5 mm. (Found: C, 69·9; H, 10·6. $C_{15}H_{28}O_3$ requires C, 70·3; H, 10·9%). A semicarbazone could not be prepared under the usual conditions.

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[6] Cope, Hofmann, Wyckoff, and Hardenbergh, *J. Amer. Chem. Soc.*, 1941, **63**, 3452.

[7] Hope and Sheldon, *J.*, 1922, **121**, 2223; Lapworth and McRea, *ibid.*, p. 2752.

[8] *Org. Synth.*, 1947, **27**, 24; Smith and Rouault, *J. Amer. Chem. Soc.*, 1943, **65**, 634; Knoevenagel and Klages, *Annalen*, 1894, **281**, 94; Rabe, *ibid.*, 1904, **332**, 1.

[9] Longinov, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1132.

[10] Wallach, *Annalen*, 1911, **381**, 86.

[11] Verley, *Bull. Soc. chim. France*, 1899, **17**, 176.

[12] Guareschi, *Gazzetta*, 1919, **49**, (i), 124.

[13] Gladstone and Tribe, *J.*, 1879, **35**, 567.

5-iso*Hexyl*-5-*methyl*cyclo*hexane*-1 : 3-*dione*. The preceding ester (36 g.) was refluxed with a solution from sodium (3·2 g.) in absolute ethanol (100 ml.) on the steam-bath for 20 hr. The *diketone* (32·5 g.), on purification from ethyl acetate–light petroleum (b. p. 40—60°), formed colourless prisms, m. p. 77—78° (Found : C, 74·3; H, 10·3. $C_{13}H_{22}O_2$ requires C, 74·3; H, 105%).

3-*Chloro*-5-iso*hexyl*-5-*methyl*cyclo*hex*-2-*enone*. The above diketone (18 g.), dry chloroform (36 ml.), and phosphorus trichloride (4 ml.) were heated on the steam-bath for 3 hr., and the product was worked up in the usual way, giving the *chloro-ketone* (10 g.), b. p. 165—168°/10 mm. (Found : C, 15·8. $C_{13}H_{21}OCl$ requires Cl, 15·5%). This on hydrogenation gave a liquid which readily yielded a semicarbazone, m. p. 169° (from ethanol) (Found : C, 66·3; H, 10·5%). This showed no depression of m. p. when mixed with the semicarbazone of 3-*iso*hexyl-3-methyl-*cyclo*hexanone described above. The regenerated ketone had b. p. 135—137°/13 mm. (Found : C, 79·4; H, 12·0%).

β-iso*Hexyl*-β-*methyl*-δ-*valerolactone* (*lactone of* 3-2′-*hydroxyethyl*-3 : 7-*dimethyloctanoic acid*). The anhydride of β-*iso*hexyl-β-methylglutaric acid (45 g.), in calcium-dried ethanol (183 ml.), was added as rapidly as possible to sodium (37 g.), heated at 80°. The temperature was slowly raised to 135°, and heating continued for 4—5 hr., absolute ethanol (68 ml.) being added from time to time to facilitate dissolution of sodium. The *lactone* (28 g.), isolated in the usual manner, formed an almost colourless liquid, b. p. 146°/8 mm., having a characteristic sweet smell (Found : C, 72·5; H, 11·3. $C_{12}H_{22}O_2$ requires C, 72·7; H, 11·1%).

Ethyl δ-*bromo*-β-iso*hexyl*-β-*methylvalerate* (3-2′-*bromoethyl*-3 : 7-*dimethyloctanoate*). A mixture of the above lactone (27 g.) and phosphorus tribromide (14 ml.) was cooled in a freezing mixture, bromine (8·4 ml.) was introduced gradually with shaking, and the whole left in the cold overnight. It was then heated at 60° for 1 hr., and on cooling, cautiously mixed with absolute ethanol (100 ml.). The *bromo-ester* (38 g.) had a sweet smell and b. p. 142°/5 mm. (Found : Br, 26·5. $C_{14}H_{27}O_2Br$ requires Br, 26·1%).

Triethyl 4-iso*hexyl*-4-*methylpentane*-1 : 1 : 5-*tricarboxylate* (*diethyl* 4-*ethoxycarbonylmethyl*-4 : 8-*dimethylnonane*-1 : 1-*dicarboxylate*). The bromo-ester (41·2 g.) was heated with ethyl sodiomalonate (ethyl malonate, 24 g.; sodium, 3·2 g.; absolute ethanol, 65 ml.) for 12 hr. The product was diluted with water and extracted with ether; the ethereal solution was washed with water, dried, and distilled, giving an *ester*, b. p. 180°/3 mm. (Found : C, 65·1; H, 9·8. $C_{21}H_{38}O_6$ requires C, 65·3; H, 9·8%).

β-iso*Hexyl*-β-*methylpimelic acid*. The preceding ester (38 g.) was hydrolysed by boiling with alcoholic potassium hydroxide for 1 hr. The excess of ethanol was removed on the water-bath, and the residual solution acidified and extracted with ether. On removal of the solvent an oil remained which was heated at 180° until evolution of carbon dioxide ceased (3 hr.). On distillation, the required *acid* formed an almost colourless viscous liquid (18 g.), b. p. 213—215°/3 mm. (Found : C, 64·8; H, 10·1. $C_{14}H_{26}O_4$ requires C, 65·1; H, 10·1%). Its *diethyl ester* had b. p. 147—148°/6 mm. (Found : C, 68·5; H, 10·9. $C_{18}H_{34}O_4$ requires C, 68·7; H, 10·8%). The acid (10 g.) was mixed with barium hydroxide (1 g.) and distilled slowly from an air-bath heated to 305—310°. The resulting ketone (5·5 g.), isolated in the usual way, had b. p. 135—136°/12 mm. (Found : C, 79·8; H, 12·3%) (semicarbazone, m. p. and mixed m. p. 169°). The same ketone (11 g.; b. p. 141—142°/15 mm.; semicarbazone, m. p. 169°) was obtained when the substituted pimelic acid (25 g.) was heated with acetic anhydride (65 ml.) for 3 hr. Dieckmann cyclisation of the above diethyl ester (10 g.) with sodium (0·8 g.) in benzene (25 ml.) and hydrolysis of the resultant product with acetic acid (48 ml.) and hydrochloric acid (24 ml.) gave an oil (3·2 g.), b. p. 140—145°/15 mm. (semicarbazone, m. p. 169°).

Ethyl α-*cyano*-α-(3-iso*hexyl*-3-*methyl*cyclo*hexylidene*)*acetate* (I). A mixture of the ketone (37·3 g.), ethyl cyanoacetate (22·5 ml.), ammonium acetate (3·8 g.), acetic acid (10 ml.), and dry benzene (50 ml.) was heated at 130—140° in an oil-bath until no more water[6] was formed (3 hr.). On cooling, water was added, and the benzene solution separated, washed with a little water, dried, and distilled. The unsaturated *cyano-ester* (I) (46 g.) had b. p. 165—167°/5 mm. (Found : C, 74·0; H, 10·1. $C_{18}H_{29}O_2N$ requires C, 74·2; H, 9·9%).

Ethyl α-*cyano*-α-(1-*cyano*-3-iso*hexyl*-3-*methyl*cyclo*hexyl*)*acetate* (II). The above ester (12 g.) was dissolved in ethanol (24 ml.), and a solution of sodium cyanide (4 g.) in water (8 ml.) added. The solution was cooled in ice and treated dropwise with 20% hydrochloric acid (12 ml.). After 1 hr. it was poured into water (100 ml.) containing concentrated hydrochloric acid (4 ml.). The oil which separated was collected in ether, and the ethereal solution washed with water, dried, and distilled. The *dicyano-ester* (II) (11·2 g.) had b. p. 176—178°/3 mm. (Found : C, 71·4; H, 9·6. $C_{19}H_{30}O_2N_2$ requires C, 71·7; H, 9·4%).

*Ethyl 1-ethoxycarbonyl-3-*iso*hexyl-3-methyl*cyclo*hexylacetate* (as III). The foregoing ester (40 g.), sulphuric acid (100 ml.), acetic acid (70 ml.) and water (30 ml.) were gently refluxed on the sand-bath for 10 hr. On cooling, the solution was saturated with ammonium sulphate and extracted with ether, and on removal of solvent a viscous oil (35 g.) was obtained which was esterified with ethanol (70 ml.), sulphuric acid (7 ml.), and benzene (130 ml.), affording the *diethyl ester* (34 g.), b. p. 178—179°/7 mm. (Found: C, 70·6; H, 10·7. $C_{20}H_{36}O_4$ requires C, 70·5; H, 10·5%). The corresponding acid formed an amorphous mass, and when boiled with acetic anhydride gave the *anhydride*, b. p. 182—183°/5 mm. (Found: C, 72·0; H, 9·6. $C_{16}H_{26}O_3$ requires C, 72·2; H, 9·8%), which slowly crystallised. The *anilic acid* separated from ethanol in prisms, m. p. 177° (Found: C, 73·3; H, 9·2. $C_{22}H_{33}O_3N$ requires C, 73·5; H, 9·2%). The *anil*, obtained on heating the anilic acid, crystallised from aqueous ethanol in needles, m. p. 96° (Found: C, 77·6; H, 9·0. $C_{22}H_{31}O_2N$ requires C, 77·4; H, 9·1%).

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166. *Bis-2 : 4-diaminophenyl Sulphone, and a New Synthesis of 2 : 8-Diaminophenothiazine 5 : 5-Dioxide.*

By Helena Bradbury and F. J. Smith.

In view of the well-known pharmacological action of bis-*p*-aminophenyl sulphone, it appeared desirable to prepare the closely related tetra-amino-compound from bis-2 : 4-dinitrophenyl sulphone.[1] Tin or stannous chloride with concentrated hydrochloric acid, iron with dilute hydrochloric acid, and titanous sulphate in hot acid solution or in a cold citrate buffer did not give the desired tetra-amine.

However, use of alcoholic stannous chloride, with subsequent addition of concentrated hydrochloric acid, gave an excellent yield—this method was employed by Ullmann and Pasdermajian [2] for the reduction of 2 : 4-dinitrophenyl phenyl sulphone to the diamine.

2 : 8-Diaminophenothiazine 5 : 5-dioxide was obtained in approximately 40% yield from the tetra-amine by prolonged refluxing with zinc chloride and dilute hydrochloric acid. Michels and Amstutz [3] obtained the same substance by a seven-stage synthesis from phenothiazine, but their final yield was very low. They established the orientation by an alternative synthesis, but in our case, the formula appears to be beyond doubt from the method of synthesis and from the fact that the compound resists oxidation with aqueous ferric chloride. 3 : 7-Diaminophenothiazine 5 : 5-dioxide [4] is readily oxidised by aqueous ferric chloride to a coloured quinonoid compound, and an isomer is similarly oxidised; the orientation of the amino-groups in our compound precludes the formation of a quinonoid structure.

Experimental.—Bis-2 : 4-diaminophenyl sulphone. Pure crystalline stannous chloride (17 g., 0·12 mole) was dissolved in ethanol (30 ml.) with gentle warming and finely powdered bis-2 : 4-dinitrophenyl sulphone (4·0 g., 0·01 mole) was added with constant swirling at such a rate that the liquid was kept just boiling by the heat of reaction. Hydrochloric acid (*d* 1·19; 30 ml.) was added to the resulting orange-coloured solution and *ca.* 25 ml. of liquid distilled off. The solution was then poured into 10% sodium hydroxide solution (400 ml.). The almost white *tetra-amine*, washed free from inorganic matter, dried at 100°, and crystallised from pure redistilled aniline, formed very pale buff rhombic plates, m. p. 236° (yield, *ca.* 90%) (Found: N, 20·0; S, 11·5. $C_{12}H_{14}O_2N_4S$ requires N, 20·15; S, 11·5%).

From a solution of the substance in hot hydrochloric acid (*d* 1·19), colourless rosettes of a *trihydrochloride* separated slowly on cooling. It was filtered off, washed three times with dry ether, and rapidly dried between absorbent paper (Found: equiv., 130·5. $C_{12}H_{14}O_2N_4S,3HCl$ requires equiv., 129·2). After 4 weeks' exposure to the atmosphere this became a buff-coloured *dihydrochloride* (Found: equiv., 175. $C_{12}H_{14}O_2N_4S,2HCl$ requires equiv., 175·5).

The tetra-amine (3 g.) was added to acetic anhydride (10 ml.) containing one drop of

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[1] Bradbury, Smith, and Talman, *J.*, 1953, 1184.

[2] Ullmann and Pasdermajian, *Ber.*, 1901, **34**, 1152.

[3] Michels and Amstutz, *J. Amer. Chem. Soc.*, 1950, **72**, 888.

[4] Ciocca and Canonica, *Boll. Ist. Sierioterap. Milanese*, 1944, **23**, 81.

sulphuric acid (*d* 1·84). On gentle warming the substance dissolved to give a brown solution which rapidly became almost solid. Water was added, and after filtration the residue was treated with 2N-sodium hydroxide, in which the tetra-acetyl derivative, but not the tetra-amine, is soluble. The filtered alkaline solution was made just acid with hydrochloric acid (*d* 1·19) and after cooling in ice the *tetra-acetyl derivative* was separated and crystallised from water as needles, m. p. 254—256° (bath preheated at 230°), 268° (slow heating) (Found: N, 12·6; Ac, 38·4. $C_{20}H_{22}O_6N_4S$ requires N, 12·6; Ac, 38·6%).

The tetra-amine (2 g.), 2N-sodium hydroxide (100 ml.), acetone (5 ml.), and benzoyl chloride (2 ml.) gave the *tetrabenzoyl derivative*, m. p. 235° (after shrinking) (from acetic acid) (Found: N, 8·0, 8·0. $C_{40}H_{30}O_6N_4S$ requires N, 8·1%).

2 : 8-*Diaminophenothiazine* 5 : 5-*dioxide.* The tetra-amino-sulphone (5 g.) was heated in a saturated solution of zinc chloride in 2N-hydrochloric acid (20 ml.) at $\ngtr 120^\circ$ for 72 hr., then poured into 2N-ammonia, and the precipitated impure cyclic base collected and washed with water. It was then boiled with hydrochloric acid (*d* 1·19) and charcoal, then filtered. The insoluble material consisted of the dihydrochloride of 2 : 8-diaminophenothiazine 5 : 5-dioxide, which was dissolved in dilute hydrochloric acid; this solution was boiled with charcoal, filtered, and made alkaline with ammonia, and the liberated diaminophenothiazine dioxide collected, dried, and crystallised from aqueous acetone. It had m. p. 339—342° (decomp.)[3] (Found: N, 16·1, 16·0. Calc. for $C_{12}H_{11}O_2N_3S$: N, 16·1%). From a solution of the above in dilute hydrochloric acid, the dihydrochloride was precipitated in colourless rosettes by the addition of hydrochloric acid (*d* 1·19) (Found: equiv., 167·7. Calc. for $C_{12}H_{11}O_2N_3S,2HCl$: equiv., 167).

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167. *Some Derivatives of* cis-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydrophenazine.*

By PATRICIA J. EARLE and MURIEL L. TOMLINSON.

HOPING to obtain an unknown hexahydrophenazine we condensed *o*-phenylenediamine with 2-hydroxy*cyclo*hexanone, but we obtained equimolecular proportions of 1 : 2 : 3 : 4-tetrahydro- and *cis*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-phenazine. These compounds have been described by Clemo and McIlwain,[1, 2] who give reasons for believing that this octahydro-compound, m. p. 147°, is the *cis*-isomer. Mono- and di-acetyl derivatives of this octahydrophenazine have now been prepared, and bromination of them has produced two dibromo-compounds which contain the bromine atoms in different positions, because the 9-acetyldibromo-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenazine obtained can be acetylated to give a 9 : 10-diacetyl compound different from that obtained by direct bromination of 9 : 10-diacetyl-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenazine.

Experimental.—Condensation of o-*phenylenediamine with* 2-*hydroxy*cyclo*hexanone.* *o*-Phenylenediamine (4·65 g.) and 2-hydroxy*cyclo*hexanone (4·5 g.) were powdered together and heated at 125—145° until evolution of water vapour ceased (10 min.). The mass solidified when cooled, and was recrystallised from ethanol (13 c.c.). *cis*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-Octahydrophenazine separated and a further quantity was obtained by careful dilution of the filtrate with water (10 c.c.). It was recrystallised again from alcohol and formed plates, m. p. 147° (2·4 g.) (Found: C, 76·9; H, 8·6; N, 14·9. Calc. for $C_{12}H_{16}N_2$: C, 76·6; H, 8·5; N, 14·9%). When water was added to the original mother-liquor crude 1 : 2 : 3 : 4-tetrahydrophenazine separated. It was extracted with light petroleum (b. p. 60—80°) and purified chromatographically on alumina. 1 : 2 : 3 : 4-Tetrahydrophenazine was obtained as waxy prisms, m. p. 93°, raised to 94° on admixture with authentic 1 : 2 : 3 : 4-tetrahydrophenazine, m. p. 95°, made from *o*-phenylenediamine and 1 : 2-dioxo*cyclo*hexane.[1]

9 : 10-*Diacetyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenazine.* Octahydrophenazine (15 g.) and acetic anhydride (40 c.c.) were boiled (5 min.). Dilution with water afforded 9 : 10-*diacetyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenazine* (14 g.), which crystallised from alcohol as prisms, m. p. 148° (Found: C, 70·8; H, 7·1. $C_{16}H_{20}O_2N_2$ requires C, 70·6; H, 7·3%). It was hydrolysed to the original octahydrophenazine by boiling hydrochloric acid ($\frac{1}{2}$ hr.).

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[1] Clemo and McIlwain, *J.*, 1934, 1991.

[2] *Idem, J.*, 1936, 259.

*9-Acetyl-*1 : 2 : 3 : 4 : 9 : 10 : 11 : 12*-octahydrophenazine.* (i) Diacetyloctahydrophenazine (5 g.) in alcohol containing potassium hydroxide (5 g.) was boiled for ½ hr. Dilution with water precipitated *9-acetyl-*1 : 2 : 3 : 4 : 9 : 10 : 11 : 12*-octahydrophenazine,* which crystallised from alcohol as prisms, m. p. 155° (Found : C, 73·5; H, 7·9. $C_{14}H_{18}ON_2$ requires C, 73·0; H, 7·9%). (ii) Octahydrophenazine (15 g.) was added to acetic anhydride (40 c.c.). It dissolved with evolution of heat, and on cooling 9-acetyl-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenazine (8 g.; m. p. 153°) separated. Dilution of the filtrate, and hydrolysis with alcoholic alkali of the mixture of mono- and di-acetyl compounds so produced, afforded more monoacetyloctahydrophenazine (8 g.).

9 : 10*-Dibenzoyl-*1 : 2 : 3 : 4 : 9 : 10 : 11 : 12*-octahydrophenazine,* prepared by the Schotten–Baumann method, crystallised from alcohol as prisms, m. p. 203° (Found : C, 78·8; H, 6·1. $C_{26}H_{24}O_2N_2$ requires C, 78·8; H, 6·0%).

Bromination of 9 : 10*-diacetyl-*1 : 2 : 3 : 4 : 9 : 10 : 11 : 12*-octahydrophenazine.* (i) Bromine (1·79 g.) in acetic acid (20 c.c.) was added to the octahydrophenazine (3 g.) in acetic acid (20 c.c.). A yellow *addition compound* separated at once. It had m. p. 99° (decomp.) and could not be recrystallised. It liberated iodine from potassium iodide in the presence of acid and was itself converted into the original diacetyl compound (Found, by titration : Br, 38·6. $C_{16}H_{20}O_2N_2Br_2$ requires Br, 37·0%). (ii) Diacetyloctahydrophenazine (4·2 g.) was treated with bromine (6·1 g.) in acetic acid (total volume 60 c.c.). The addition compound (8 g.) was collected, and dilution of the filtrate with water gave colourless needles, m. p. 160—170° (2 g.). Recrystallisation from alcohol then afforded a 9 : 10*-diacetyldibromo-*1 : 2 : 3 : 4 : 9 : 10 : 11 : 12*-octahydrophenazine,* m. p. 202—204° (Found : C, 44·9; H, 4·0; N, 7·0. $C_{16}H_{18}O_2N_2Br_2$ requires C, 44·7; H, 4·2; N, 6·5%).

Bromination of 9*-acetyl-*1 : 2 : 3 : 4 : 9 : 10 : 11 : 12*-octahydrophenazine.* Bromine (5·56 g.) in acetic acid (20 c.c.) was slowly stirred into a solution of 9-acetyloctahydrophenazine (4 g.) in acetic acid (40 c.c.). A yellow precipitate separated but redissolved, and addition of water precipitated a solid (6·9 g.). Recrystallisation from alcohol gave a 9*-acetyldibromo-*1 : 2 : 3 : 4 : 9 : 10 : 11 : 12*-octahydrophenazine,* as needles, m. p. 118—120° (Found : C, 43·6; H, 4·4. $C_{14}H_{16}ON_2Br_2$ requires C, 43·3; H, 4·2%). Boiling this dibromo-compound with acetic anhydride containing a trace of sulphuric acid (20 min.) afforded a second 9 : 10*-diacetyldibromo-*1 : 2 : 3 : 4 : 9 : 10 : 11 : 12*-octahydrophenazine,* m. p. 164—165°, different from the above (Found : C, 45·2; H, 4·2%).

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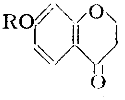
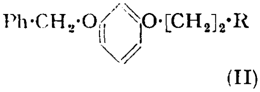
168. *Some Derivatives of Chroman-4-one.*

By RITA A. GREGORY and MURIEL L. TOMLINSON.

7-HYDROXYCHROMAN-4-ONE (I; R = H) is not easily obtained in quantity by either of the methods recorded in the literature for its preparation.[1,2] Requiring this substance as a starting material, we decided to investigate the possibility of preparing it from 7-benzyloxychroman-4-one (I; R = CH_2Ph). *m*-Benzyloxyphenol was condensed with acrylonitrile to give β-3-benzyloxyphenoxypropionitrile (II; R = CN) which was hydrolysed to the corresponding acid (II; R = CO_2H). The most effective method of cyclising the acid (II; R = CO_2H) was by boiling it with phosphoric oxide in benzene,



(I)



(II)

but the yields were not good, and so far it has not proved possible to debenzylate the 7-benzyloxychroman-4-one so produced, neither could hydrogenolysis of β-3-benzyloxyphenoxypropionic acid be effected.

m-Di-2-cyanoethoxybenzene has been converted into 7-2′-carboxyethoxychroman-4-one (I; R = $CH_2{\cdot}CH_2{\cdot}CO_2H$). Simpson, Taylor, and Tomlinson[3] found that some

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[1] Pfeiffer, Oberlin, and Konermann, *Ber.*, 1925, **58**, 1947.

[2] Pfeiffer, Breith, and Hoyer, *J. prakt. Chem.*, 1931, **129**, 31.

[3] Simpson, Taylor, and Tomlinson, *J.*, 1951, 2239.

β-2- and -4-aroylphenoxypropionic acids readily lose acrylic acid and give the corresponding phenols, in the presence of aqueous alkali, but the acid (I; $R = CH_2{\cdot}CH_2{\cdot}CO_2H$), which might have been expected to behave similarly, failed to give the chromanone (I; $R = H$) by this means. Under mild conditions it was unaffected, and more vigorous treatment with alkali caused changes which are probably due to polymerisation.[4]

Experimental.—m-*Benzyloxyphenol.* The method of Klarmann *et al.*[5] was used with the following modification which greatly facilitated purification and gave a 25% yield. The mixture, obtained by boiling benzyl chloride and resorcinol in xylene and pouring on ice, separated into three layers when kept overnight. The lowest layer was dissolved in benzene and washed free from resorcinol with water. After the resulting solution had been dried and evaporated *m*-benzyloxyphenol was purified as described by the original authors.

β-3-*Benzyloxyphenoxypropionitrile.* *m*-Benzyloxyphenol (5 g.), acrylonitrile (10 g.), and a trace of sodium were heated at 95—105° for 30 hr. The resulting solution was poured into sodium hydroxide (10 g.) in water (100 c.c.) and β-3-*benzyloxyphenoxypropionitrile* (6 g.) was obtained as a pink solid. It was recrystallised from benzene–light petroleum (b. p. 80—100°) and formed needles, m. p. 89—90° (Found: C, 75·7; H, 6·1. $C_{16}H_{15}O_2N$ requires C, 75·9; H, 5·9%).

β-3-*Benzyloxyphenoxypropionic acid.* The propionitrile (10 g.) was boiled with hydrochloric acid (100 c.c.) for 3 hr.; a further equal volume of hydrochloric acid was then added, and boiling continued for 2 hr. The solid was collected when cold, and extracted with sodium carbonate solution. Slow acidification of this extract liberated β-3-*benzyloxyphenoxypropionic acid* in a form which could be recrystallised from acetic acid. It separated as prisms, m. p. 166—168°, containing solvent of crystallisation which could be removed by melting (Found: C, 67·5; H, 5·9. $C_{16}H_{16}O_4,\frac{1}{2}C_2H_4O_2$ requires C, 67·5; H, 6·0%).

7-*Benzyloxychroman*-4-*one.* Phosphoric oxide (20 g.) was added during 4 hr. to a solution of pure, dry β-3-benzyloxyphenoxypropionic acid (8 g.) in benzene (200 c.c.) heated under reflux. When the mixture was cold the benzene was decanted and the phosphorus compounds were then decomposed with water, which was extracted with ether. The combined ether–benzene solution was washed with sodium carbonate solution and dried ($MgSO_4$). 7-*Benzyloxychroman*-4-*one* remained when solvents were distilled off, and was recrystallised from light petroleum (b. p. 100—120°), separating as prisms, m. p. 153—155° (Found: C, 75·3; H, 5·5. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%). The original acid (2·7 g.) was recovered. The benzyloxychromanone resisted hydrogenolysis at atmospheric pressure in the presence of palladium–charcoal, palladium-black, and platinum oxide in methanol and ethanol, with or without traces of perchloric acid, and in acetic acid: at 3 atm., only traces of the phenol were formed after hydrogenation for many hours. It was also recovered after boiling in alcohol with Raney nickel, and after long boiling with hydrochloric acid or a mixture of hydrochloric and acetic acids.

7-2′-*Carboxyethoxychroman*-4-*one* (with V. GRENVILLE). *m*-Di-2-cyanoethoxybenzene (5·5 g.) and powdered anhydrous zinc chloride (5·0 g.) were suspended in dry ether (200 c.c.) at 0°, and hydrogen chloride was bubbled in for 4 hr. The product was digested with sodium carbonate solution, starting material (1·8 g.) was removed by filtration, and addition of hydrochloric acid then precipitated 7-2′-*carboxyethoxychroman*-4-*one* (1·6 g.). It crystallised from alcohol as needles, m. p. 173—175° (Found: C, 61·4; H, 5·1. $C_{12}H_{14}O_5$ requires C, 61·0; H, 5·1%).

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[4] Padfield and Tomlinson, *J.*, 1950, 2272.

[5] Klarmann, Gatyas, and Shternov, *J. Amer. Chem. Soc.*, 1931, **53**, 3404.

169. *Triphenylene and 2-Methyltriphenylene.*

By J. W. BARTON and J. F. W. MCOMIE.

AN unsuccessful attempt to prepare diphenylene by the action of phenyl-lithium on 2 : 2′-dibromodiphenyl gave triphenylene (8%) and diphenyl. The production of a hydrocarbon from an aryl-lithium has been noted by Gilman and Brannen[1] who obtained small yields of perylene from 1-naphthyl-lithium. It was improbable that the triphenylene was derived solely from the phenyl-lithium, and in order to establish this the action of *p*-tolyl-lithium

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[1] Gilman and Brannen, *J. Amer. Chem. Soc.*, 1949, **71**, 657.

on 2 : 2′-dibromodiphenyl was examined. The products of the reaction included 2-methyltriphenylene (5%), but no trimethyltriphenylene, hence these reactions probably proceed *via* a 2-aryl-2′-bromodiphenyl. No reaction occurred between *p*-methoxyphenyl-lithium and 2 : 2′-dibromodiphenyl.

Experimental.—*Triphenylene.* To a stirred solution of phenyl-lithium, from bromobenzene (16 g.), lithium (1·5 g.), and ether (25 ml.), was added during 15 min. a solution of 2 : 2′-dibromodiphenyl (8 g.) in ether (50 ml.), and the dull red solution was stirred for 4 hr. Next day dilute hydrochloric acid was added and the products were collected in ether. The ethereal extracts were washed with 10% aqueous sodium hydroxide, dried, and distilled, giving fractions: (1) b. p. 50—60°/12 mm., bromobenzene; (2) b. p. 120—130°/12 mm., which after crystallisation from ethanol gave diphenyl (1·3 g.); (3) b. p. 100—150°/0·5 mm., a yellow halogen-containing oil, probably 2-bromodiphenyl (recorded[2] b. p. 296—298°); (4) b. p. 150—190°/0·5 mm., which when crystallised from ethanol gave triphenylene, m. p. and mixed m. p. 194—195° (0·54 g., 8%).

2-*Methyltriphenylene.* A similar reaction, with *p*-bromotoluene (17·1 g.) instead of bromobenzene, gave fractions: b. p. 60—70°/12 mm., *p*-bromotoluene; b. p. 120—130°/12 mm., 4 : 4′-dimethyldiphenyl (1·0 g.); b. p. 145—155°/12 mm., 4 : 4′-dimethyldiphenyl (trace) and a halogen-containing yellow oil; and a residue which yielded the picrate of 2-methyltriphenylene. This derivative was twice crystallised from ethanol, giving yellow needles, m. p. 191—192° (0·65 g., 5%) (recorded[3] m. p. 192·4—193°). A portion of the picrate in ethanol was passed through an alumina column, and the regenerated hydrocarbon sublimed at 130—140°/0·5 mm. (bath-temperature). After crystallisation from ethanol the 2-methyltriphenylene had m. p. 102—103° (recorded[3] m. p. 102·6—103·6°).

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[2] Schultze, *Annalen*, 1881, **207**, 353.

[3] Fieser and Joshel, *J. Amer. Chem. Soc.*, 1939, **61**, 2960.