778. *Dealkylation and Hydrolysis of Alkyl Phosphites, Phosphates, and Phosphonates.*

By W. GERRARD, W. J. GREEN, and R. A. NUTKINS.

THE reaction of the butyl phosphates, tri-2-octyl phosphate, and di-2-octyl ethylphosphonate with hydrogen halides is comparable with that of the halides with *n*-butyl hydrogen phosphite, the much quicker rate of dealkylation (one group) of trialkyl phosphites (Gerrard and Whitbread, *J.*, 1952, 914) being brought into marked contrast. High predominance of inversion accompanied the formation of 2-halogeno-octane from the phosphate and phosphonate. From the degree of retention of configuration of the octan-2-ol formed, it appeared that acyl–oxygen fission occurred in alkaline and alkyl–oxygen fission in the acid hydrolysis of the phosphate and phosphonate, although under either condition the phosphite and hydrogen phosphite were hydrolysed to alcohol having a high degree of retention of configuration. In view of the slow hydrolysis of the phosphate and phosphonate, hydrogen bromide affords a ready means of removing alkyl groups, and especially is this of interest in the preparation of alkylphosphonic acids without incursion of water.

Blumenthal and Herbert (*Trans. Faraday Soc.*, 1945, **41**, 611) concluded that acyl–oxygen fission had occurred in the alkaline hydrolysis of trimethyl phosphate, because the methyl alcohol was not enriched in ^{18}O. Although it was realised that the results were not entirely unambiguous, it was believed that in acid hydrolysis alkyl–oxygen fission (70%) had occurred.

EXPERIMENTAL

Interaction of Hydrogen Halides and Tributyl Phosphates.—The esters were prepared in a pure condition by means of pyridine and phosphorus oxychloride (Gerrard, *J.*, 1940, 1464). Into the *n*-butyl ester (11·8 g.) dry hydrogen chloride was passed for 6 hours at 17°, the effluent gas being passed through a U-tube maintained at –80°, which was also employed to condense butyl chloride distilled from the final reaction mixture at 15°/1 mm. After the mixture had been at 17° for 12 hours, from it was obtained *n*-butyl chloride (0·43 mol.), b. p. 77° (Found : Cl, 38·1. Calc. for C_4H_9Cl : Cl, 38·3%). *n*-Butyl chloride (0·90 mol.), b. p. 77° (Found : Cl, 37·9%), was similarly obtained from the ester (4·2 g.) after the gas had been passed for 4·5 hours at 50—60° and the mixture kept at 16° for 12 hours. At evenly spaced intervals during 3 weeks the gas was passed into the ester (4·27 g.) for 10·6 hours at 50—60° and then for 34·5 hours at 90—100°, giving *n*-butyl chloride (2·75 mols.), b. p. 77° (Found : Cl, 38·0%). Tri*iso*butyl phosphate (15·0 g.), after being saturated with the gas (8 hours) at 25° (1·71 mols. absorbed) and kept at 25° for 75 days, afforded the chloride (0·55 mol.), b. p. 68—69° (Found : Cl, 38·0%). Tri-*sec.*-butyl phosphate (12·60 g.) under the same conditions gave the chloride (0·87 mol.), b. p. 68° (Found : Cl., 37·9%). Similarly the *iso*butyl ester (14·0 g.) and hydrogen bromide (2·07 mols. absorbed) afforded *iso*butyl bromide (1·27 mols.) b. p. 90—91° (Found: Br, 58·1. Calc. for C_4H_9Br : Br, 58·4%). The *sec.*-butyl ester (17·6 g.) gave *sec.*-butyl bromide (2·05 mols.), b. p. 91—92° (Found : Br, 57·6%), hydrogen bromide (2·21 mols.) being absorbed during the passage of the gas. Into the *n*-butyl ester (4·3 g.) at 20° hydrogen bromide was passed for 3 hours (2·02 mols. being absorbed) and *n*-butyl bromide (1·23 mols.), b. p. 100° (Found : Br, 58·2%), was obtained.

Hydrogen Bromide and (+)-*Tri-2-octyl Phosphate.*—Into the ester (2·0 g.) (from ROH, α_D^{20} +7·64°, l = 1 dm.) the gas was passed for 48 hours at 20°, and (–)-2-bromo-octane (2·48 g., 2·5 mols.), b. p. 61°/7 mm., α_D^{14} –27·8° (Found : Br, 41·4. Calc. for $C_8H_{17}Br$: Br, 41·4%), and a residue of phosphoric acid (0·46 g.) (Found : P, 30·2. Calc. : P, 31·6%) were obtained. The bromide (2·33 g., 2·4 mols.), b. p. 76°/15 mm., α_D^{14} –26·80° (Found : Br, 41·3%), and phosphoric acid (0·46 g.) were obtained after 9 hours at 45—50°; and after 6 hours at 95—100°, the bromide (2·48 g., 2·5 mols.), b. p. 63°/8 mm., α_D^{14} –24·3° (Found : Br, 41·4%), and phosphoric acid (0·46 g.) were obtained.

Hydrogen Halides and Di-2-octyl Ethylphosphonate.—Into the phosphonate (Gerrard and Green, *J.*, 1951, 2550) the gas was passed continuously for the time and at the temperature stated in Table 1. The calculated weights for $C_8H_{17}X$ are Cl 3·56 g. (Cl, 23·9%), Br 4·62 g. (Br, 41·4%), I 5·75 g. (I, 52·9%). In the chloride and bromide experiments, gas was removed from the mixture at 1 mm. before distillation; in the iodide experiments treatment with water was given.

TABLE 1. *Dealkylation of di-2-octyl ethylphosphonate* (4·0 *g*.) (*from* ROH, α_D^{18} −8·00°).

Time (hours)	Temp.	C_8H_{17}·Hal Yield (g.)	B. p./mm.	α_D (temp.)	Found : Hal, %
Hydrogen chloride.					
336	20—25°	0·62	59·5°/13	+27·6° (21°)	23·5
106	50—55	2·17	59°/12	+24·28 (16)	23·7
21·5	95—100	2·67	60°/14	+25·20 (24)	23·6
Hydrogen bromide.					
48	20—25	4·56	73°/14	+30·70 (20)	41·2
8	45—50	3·96	,,	+31·72 (20)	41·4
11	70—75	4·38	72·5°/13	+30·6 (23)	41·4
Hydrogen iodide.					
7·5	20—25	4·65	84·5°/11	+39·44 (20)	52·3
7	−15	2·18	87·5°/13	+47·72 (20)	52·7
14·5	50—55	4·54	90·5°/15	+23·70 (23)	52·0

TABLE 2. *Hydrolysis of 2-octyl esters containing phosphorus.*

				Alcohol				
						α_D		
No.	Ester (g.)	Medium	Time of reflux (hours)	Weight (g.)	B. p./mm.	(Found)	(original)	n_D
1	$(RO)_3P$ (4·0)	N-HCl (aq.)	24	1·47	81·5°/17	−8·12° (16·5°)	−8·10° (24°)	1·4272 (16·5°)
2	,,	N-KOH (aq.)	,,	2·26	81°/16	−8·08 (16·5)	,,	1·4272 (16·5)
3	$(RO)_2P$·OH (4·0)	N-HCl (aq.)	28	1·56	75°/13	+6·92 (21)	+7·4 (23)	1·4268 (20)
4	,,	N-KOH (aq.)	28	1·37	74°/13	+7·24 (19)	,,	1·4265 (20)
5	$(RO)_3PO$ (2·0)	N-KOH (aq.)	24	0·26	81°/18	+6·12 (11)	+7·67 (19)	1·4299 (12)
6	,,	2N-KOH (EtOH)	37	0·32	68°/7	+6·56 (15)	,,	1·4275 (16)
7	,,	N-HCl (aq.)	24	0·28	75°/13	+4·48 (11)	,,	1·4299 (10)
8	Et·PO(OR)$_2$ (3·0)	N-KOH (aq.)	25	0·28	77°/15	−7·32 (15)	−8·0 (20)	1·4292 (15)
9	,,	N-HCl (aq.)	25	0·31	74°/13	−1·06 (15)	,,	1·4295 (15)
10	,,	N-KOH (aq. EtOH)	24	0·35	74°/12	−7·92 (15)	,,	1·4282 (15)
11	,,	2N-KOH (EtOH)	38	0·44	82°/18	−7·08 (15)	,,	1·4268 (17)
12	,,	N-HCl (aq. EtOH)	24	0·41	73°/11	−0·92 (15)	,,	1·4272 (15)

Weights of recovered esters were : (5) 0·7, (6) 0·5, (7) 0·64, (8) 1·21, (9) 1·69, (10) 1·77, (11) 1·1, and (12) 1·48 g.

Hydrolysis of 2-*Octyl Esters.*—The ester was heated under reflux with the medium (50 c.c.) for the time stated, the alcohol then being isolated from the dried ethereal extract of the steam-distillate. Data are recorded in Table 2 and in the following notes. (1—4) The esters were prepared as described by Gerrard (*J.*, 1944, 85). (5) The phosphate had b. p. 145°/0·05 mm., n_D^{15} 1·4412, α_D^{22} +20·68° (all rotatory powers are for $l = 1$ dm.) (from ROH, α_D^{19} +7·67°) (Found : C, 66·5; H, 11·6. Calc. for $C_{24}H_{51}O_4P$: C, 66·4 : H, 11·7%). Solvent termed aq. EtOH contained 25 c.c. of each liquid. When 2N-ethanolic hydrochloric acid was used the phosphate [see (5)] after 37 hours afforded 2-chloro-octane (0·66 g.), b. p. 50°/9 mm., α_D^{15} −14·65°, and the alcohol (0·2 g.), b. p. 68—69°/9 mm., α_D^{15} +1·60°, n_D^{16} 1·4265; and the phosphonate [see (8)] after 38 hours afforded 2-chloro-octane (1·12 g., b. p. 49°/8 mm., α_D^{10} +15·24°).

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779. *Trifluoromethylbenziminazoles.*

By A. SYKES and J. C. TATLOW.

FOR other studies, benziminazoles with trifluoromethyl substituents were required, and, since derivatives of this type have not yet been reported, the synthesis of two such compounds is herein described. 3-Amino-2- and -4-nitrobenzotrifluoride were prepared as described by Rouche (*Bull. Acad. roy. Belg., Classe Sci.*, 1927, **13**, 346) and Pouterman and Girardet (*Helv. Chim. Acta*, 1947, **30**, 107) by nitration of *m*-acetamidobenzotrifluoride with nitric acid–acetic anhydride, deacetylation of the product, and separation of the mixture. These nitro-amines, when reduced with stannous chloride in hydrochloric acid, yielded the corresponding phenylenediamines, 2 : 3- and 3 : 4-diaminobenzotrifluoride, respectively. The latter has been made by Whalley (*J.*, 1950, 2792), using hydrogen and palladium–charcoal. 2 : 3-Diaminobenzotrifluoride, when treated with formic acid according to Phillips (*J.*, 1928, 2393), gave 4-trifluoromethylbenziminazole; with benzil in methyl alcohol, 2 : 3-diphenyl-5-trifluoromethylquinoxaline was formed. These reactions confirm the structure assigned by the original authors to the parent nitro-amine. From the 3 : 4-diamine, 5-trifluoromethylbenziminazole was prepared in a similar manner.

EXPERIMENTAL

2 : 3-*Diaminobenzotrifluoride.*—Stannous chloride dihydrate (30 g.) in concentrated hydrochloric acid (60 c.c.) was added slowly to a warm solution of 3-amino-2-nitrobenzotrifluoride (5·0 g.) in ethyl alcohol (40 c.c.), and the mixture was refluxed for 30 minutes, before being poured into water. The solution was made strongly alkaline with aqueous sodium hydroxide and extracted with ether, and the extracts were washed with water, separated, dried ($MgSO_4$), filtered, and concentrated to leave a residue, which, on distillation under diminished pressure, gave 2 : 3-*diaminobenzotrifluoride* (2·8 g., 66%), b. p. 125°/14 mm., m. p. 41° (Found : C, 47·5; H, 3·8; F, 32·0. $C_7H_7N_2F_3$ requires C, 47·7; H, 4·0; F, 32·4%).

The diamine, with acetic anhydride and glacial acetic acid (30 minutes' refluxing), gave the *diacetyl* derivative, m. p. 228—229° (from ethyl alcohol) (Found : C, 50·9; H, 4·2. $C_{11}H_{11}O_2N_2F_3$ requires C, 50·8; H, 4·3%).

2 : 3-*Diphenyl*-5-*trifluoromethylquinoxaline.*—The 2 : 3-diamine (0·35 g.) and benzil (0·40 g.) were refluxed in methyl alcohol (10 c.c.) for 30 minutes, the solution was cooled, and the precipitate recrystallised from methyl alcohol to give the *quinoxaline* (0·38 g., 57%), m. p. 139° (Found : C, 72·1; H, 3·9. $C_{21}H_{13}N_2F_3$ requires C, 72·0; H, 3·7%).

4-*Trifluoromethylbenziminazole.*—2 : 3-Diaminobenzotrifluoride (4·40 g.), 90% formic acid (1·85 c.c.), and 4N-hydrochloric acid (25 c.c.) were refluxed together for 45 minutes, and the solution was then cooled and neutralised with ammonia solution, the resulting precipitate being recrystallised from water (charcoal), to give 4-*trifluoromethylbenziminazole* (2·06 g., 44%), m. p. 192·5° (Found : C, 51·6; H, 2·6; F, 31·0. $C_8H_5N_2F_3$ requires C, 51·6; H, 2·7; F, 30·6%).

3 : 4-*Diaminobenzotrifluoride.*—3-Amino-4-nitrobenzotrifluoride, reduced by the method described above, gave 3 : 4-diaminobenzotrifluoride (86%), m. p. 58°. Whalley (*loc. cit.*) recorded m. p. 58°.

5-*Trifluoromethylbenziminazole.*—The 3 : 4-diamine (5·20 g.), 90% formic acid (2·2 c.c.), and 4N-hydrochloric acid (30 c.c.), treated as before, afforded 5-*trifluoromethylbenziminazole* (1·90 g., 35%), m. p. 119° (Found : C, 51·3; H, 2·8; F, 30·8%).

The authors are indebted to the Imperial Smelting Corporation Ltd. for a gift of benzotrifluoride. One of them (A. S.) thanks the Department of Scientific and Industrial Research for the award of a maintenance grant.

THE CHEMISTRY DEPARTMENT, THE UNIVERSITY,
EDGBASTON, BIRMINGHAM, 15.

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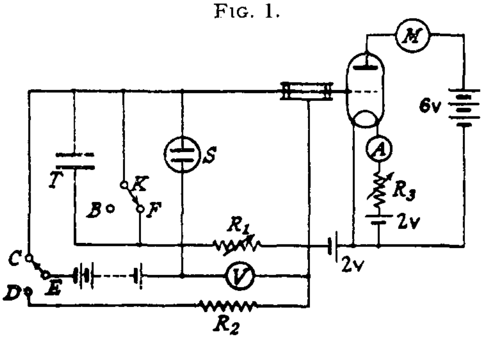
780. *The Electrical Conductivity of Liquid Dinitrogen Tetroxide.*

By C. C. ADDISON and J. LEWIS.

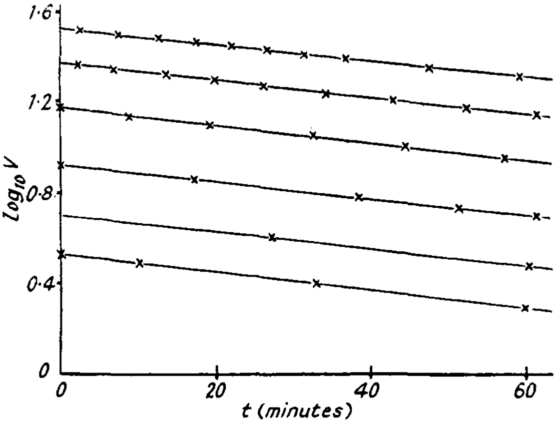
IN measurements of the electrical conductivity of liquid dinitrogen tetroxide, described by Addison, Allen, Bolton, and Lewis (*J.*, **1951**, 1289), the potential difference between the electrodes did not exceed 2 v. No evidence of a decomposition potential was obtained and no variation in the electrical resistance was observed, when this potential difference was varied within the 0—2 v range. Various mechanisms of electrical conduction were considered; one attractive possibility involved the passage of electric current through the liquid by the ionisation of the NO_2 molecule to the NO_2^+ ion, and the subsequent transfer of electrons along a chain of NO_2 groups. Since the ionisation potential for the NO_2 molecule in the gaseous phase is 12·3 v (Price and Simpson, *Trans. Faraday Soc.*, 1941, **37**, 106), it appeared possible that a different value for the conductivity might be obtained if a higher potential difference was applied across the electrodes. The conductivity has therefore been determined over the range 2—32 v. The results given below show that the conductivity has a constant value throughout the whole of this range. The values are of the same order as those obtained in the 0—2 v range and hence the mechanism referred to above is now considered to be unlikely.

FIG. 1.



R_1 = 50,000 *Ohms.*
R_2 = 50,000 *Ohms.*
R_3 = 20 *Ohms.*
S = *Conductivity cell.*
T = *Condenser, capacity* 0·01 μF.

FIG. 2.



The conductivity cell, the handling techniques, the precautions against surface conduction, the electrometer valve characteristics, and the method of preparation of pure liquid tetroxide were those already described by Addison *et al.* (*loc. cit.*). The electrical circuit employed is shown in Fig. 1. A potential of -2 v was applied to the valve grid by placing key K at F. The anode current (the " zero " reading) registered on the microammeter M was noted, and K was transferred to position B. A potential of -32 v was applied to the grid by switching the key E to position C; E was then moved to point D, and the resistance R_1 varied to restore the zero reading on M. Under these conditions, the extra negative potential applied was counterbalanced by the potential introduced by the potentiometer circuit. The voltage across R_1 required to do this was measured by a high-resistance voltmeter V. By varying R_1, the voltmeter reading was then decreased in steps of 1 v, and at each stage the time taken for the grid potential to decay to this voltage was noted.

If the resistance of the liquid remains constant over the voltage range employed, then a graph of log V against time t will be a straight line, since $V_t = V_0 e^{-t/CR}$. The experimental results in Fig. 2 show that this is the case. The lines in Fig. 2 represent sections of one continuous straight line extending over the range 2—32 v.

The table gives the electrical specific conductivities (κ in ohm.$^{-1}$ cm.$^{-1}$ $\times$ 10^{12}) of three separate preparations of liquid dinitrogen tetroxide, determined from the slope of the appropriate ($\log V$) $-$ t line. The second value in each case is a duplicate measurement taken several hours after the first.

Prep. no.	Temp.	κ	Prep. no.	Temp.	κ	Prep. no.	Temp.	κ
1	21°	5·20, 5·24	2	21°	4·31, 4·31	3	20°	1·14, 1·19

These conductivity values lie within the range (1·24—8·08 $\times$ 10^{-12}) of values obtained in measurements carried out between 0 and 2 v.

The authors are indebted to Dr. H. C. Bolton for valuable advice and discussion.

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781. *4-Chloro-2-iodophenoxyacetic Acid labelled with* ^{131}I.

By R. L. JONES.

4-CHLORO-2-IODOPHENOXYACETIC ACID labelled with ^{131}I was required for a radioautographic study of its translocation in plants, the results of which will be published elsewhere.

Because of the relatively short half life of ^{131}I and the dangers associated with its handling, it was desirable that this element should be introduced at the last stage of the synthesis. No suitable method is recorded in the literature.

4-Chlorophenoxyacetic acid, when boiled with aqueous mercuric acetate, yielded, on isolation as the chloride, 4-chloro-2-chloromercuriphenoxyacetic acid. When this was heated with chlorine, bromine, or iodine in acetic acid 2 : 4-dichloro-, 2-bromo-4-chloro-, or 4-chloro-2-iodophenoxyacetic acid, respectively, was obtained. The first of these was identified by comparison with an authentic sample, the others had m. p.s agreeing with those recorded in the literature. The process for the preparation of the labelled substance was based on this experiment.

EXPERIMENTAL

(a) *With Non-radioactive Material.*—*4-Chloro-2-chloromercuriphenoxyacetic acid.* 4-Chlorophenoxyacetic acid (20 g.), water (500 c.c.), and mercuric acetate (32 g.) were boiled under reflux for 2 hours. Aqueous sodium hydroxide (30%) was then added to the cooled mixture until all but a trace of solid was dissolved, the solution was treated with charcoal and filtered, and the filtrate acidified with hydrochloric acid. The flocculent precipitate was washed, dried at 80° (37 g.), and crystallised first from acetic acid (30 c.c.) and then from 35% aqueous ethanol. The *acid* had m. p. 189—190°, unchanged by further crystallisation (21·4 g.) (Found : Hg, 46·3; Cl, 15·0%. $C_8H_6O_3Cl_2Hg$ requires Hg, 47·5; Cl, 17·2%). This substance decomposes slowly on storage; material stored for 4 weeks was, however, satisfactory for the preparation of 4-chloro-2-iodophenoxyacetic acid.

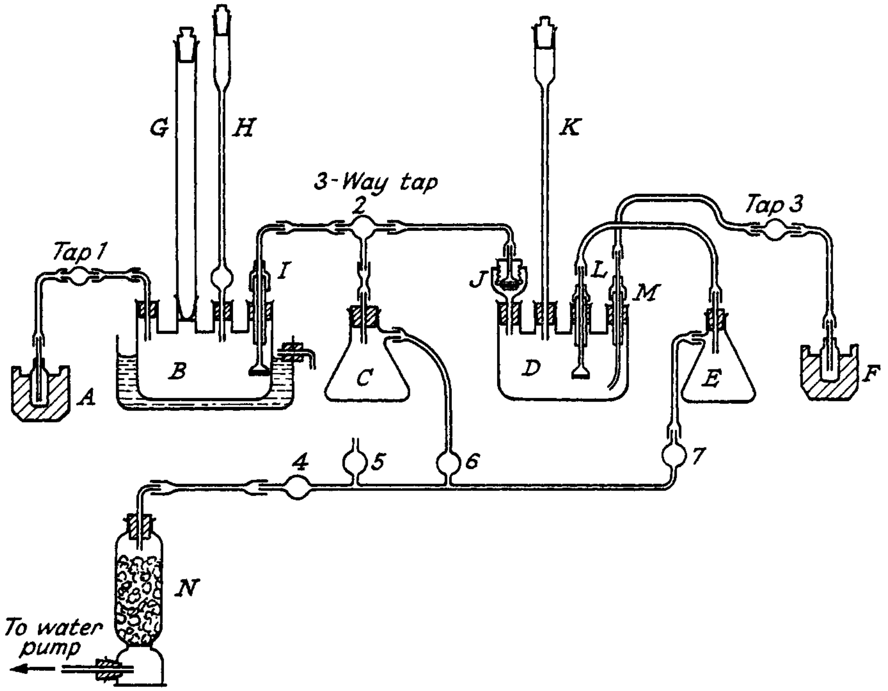
2 : *4-Dichlorophenoxyacetic acid.* 4-Chloro-2-chloromercuriphenoxyacetic acid (4·2 g.), m. p. 185—186°, was added to acetic acid (30 c.c.) containing chlorine (0·71 g.). After 1 hour the mixture was heated slowly to 90° (2 hours), then poured into water and filtered, the insoluble material was extracted with warm dilute sodium hydroxide and filtered, and the filtrates were acidified with hydrochloric acid. The precipitate was crystallised from water and then had m. p. 137—138°, undepressed on admixture with an authentic sample of 2 : 4-dichlorophenoxyacetic acid.

2-Bromo-4-chlorophenoxyacetic acid, m. p. 138–139°, was similarly obtained from bromine (1·6 g.) and the mercurial (4·2 g.) in glacial acetic acid (37 c.c.). 4-Chloro-2-iodophenoxyacetic acid, m. p. 140° (Newman, Fones, and Renoll, *J. Amer. Chem. Soc.*, 1947, **69**, 718, give m. p. 136—140°) (Found : C, 30·4; H, 2·1; Cl, 11·3; I, 40·2. Calc. for $C_8H_6O_3ClI$: C, 30·7; H, 1·9; Cl, 11·4; I, 40·6%), was obtained similarly.

(b) *With Radioactive Material.*—The apparatus, shown in the diagram, was mounted on a sheet of lead ½″ × 8″ × 36″, behind a permanent lead screen, ½″ × 20″ × 36″, in a fume cupboard fitted with ¾″ thick sliding lead doors. *G*, *H*, and *K* (see below) extended above the screen.

I and *L* were 9-mm. diameter sintered-glass disc filters of grade 3 porosity, which could be raised and lowered, vacuum being maintained by rubber sleeves. The tube *M* could be similarly handled. *J* was an auxilliary filter made of Perspex, taking four 1-cm. filter circles of Whatmans No. 42 grade filter paper. The scrubbing tower *N* was packed with pumice stone soaked in a solution of glycerine, water, and potassium iodide.

The sample, from the Atomic Energy Research Establishment, Harwell, contained 500 millicuries of ^{131}I and consisted of a trace of sodium iodide in 20 c.c. of water together with 10—20 mg. of sodium sulphite and small amounts of sulphate. It was sucked from its container in the lead safe *A* into the 100-c.c. four-necked round-bottomed flask *B*, by applying suction *via I* (in the raised position) and the 100-c.c. Buchner flask *C*. The sample was washed in with water (5 c.c.). The vacuum was released and an aqueous solution (5 c.c.) of potassium iodide (10·2 g. made up to 250 c.c.) and sulphuric acid (5 c.c.; 150 c.c. of 98% sulphuric acid diluted with 100 c.c. water) added *via H* which was jointed to *B* with a rubber bung and had a bubble blown in it about 1″ above *B* to avoid the rise, by capillarity, of bubbles containing radioactive material. The mixture was shaken and aqueous potassium dichromate (8 c.c.; 3·02 g. in 250 c.c.) added *via H*. The mixture was again shaken and set aside overnight at room temperature. The liquors were then sucked through *I* (lowered) into *C* and the residual iodine was washed with water (2 × 5 c.c.) (collected in *C*). Meanwhile, 4-chloro-2-chloromercuriphenoxyacetic acid (0·20 g.), m. p. 189—190°, was ground to a coarse powder, wetted with glacial acetic acid (0·5 c.c.), and moulded by being frozen (ethanol–solid carbon dioxide) in a glass tube. The frozen pellet was transferred to *G* (a ½″ diameter glass tube, jointed to *B* with a B.14 ground-glass joint) and thence by gravity into *B*. Acetic acid (2·5 c.c.) was added *via H*, and the contents of *B* heated (bath-temp. 90°) for 1 hour and then cooled. After 20 minutes, water (20 c.c.) was added, the mixture well shaken, and set aside for 15 minutes. Tube *I* was then lowered and the liquors were filtered into *C*. The residue of mercuric iodide and 4-chloro-2-iodophenoxyacetic acid was washed with water (2 × 5 c.c.) (collected in *C*), and then extracted with a solution of (5 c.c.) of triethanolamine (20 g. made up to 250 c.c. with water) with intermittently shaking for 5 minutes; the liquors were sucked into the second 100 c.c. four-neck flask *D via I* (lowered) and *J*. The residue in *B* was washed with water (2 × 5 c.c.), which was added to the solution already in *D*. Hydrochloric acid (5 c.c.) (30 c.c. of acid, *d* 1·16, made up to 250 c.c. with water) was added *via K*; the mixture was shaken, and, after 10 minutes, the liquors were filtered into the 100-c.c. Buchner flask *E via L* (lowered). The



white solid remaining was washed with water (2 × 5 c.c.), and ethanol (3 c.c.; 98%) was added. *D* was shaken until dissolution was complete; any solid sticking to *L* was washed off by gently blowing air through it in the lowered position. The solvents were then removed by drawing a stream of dry air ($CaCl_2$), through *K* and *L* (raised), over the ethanolic solution for 16 hours. Ethanol (1 c.c.; 98%) was added, and *D* was shaken until dissolution of the contents was complete. Olive oil (40 c.c.) was then added and shaking continued until a homogeneous solution was obtained; this was blown into the container in the lead safe *F*.

Yield and Quality of Product.—It was not possible to estimate the purity of the radioactive product because of the hazard involved in the isolation of the undiluted solid material; monitoring indicated 150 millicuries. In the many practice runs carried out with non-radioactive material, however, the yield was 0·1 ± 0·01 g. (from 4-chloro-2-chloromercuriphenoxyacetic acid, 0·20 g.), melting sharply at 139—140°: and the radio-active solution produced the expected biological response when applied to plants.

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Research Laboratories, Imperial Chemical Industries Limited,
Dyestuffs Division, Blackley, Manchester. [*Received, May* 21*st*, 1952.]

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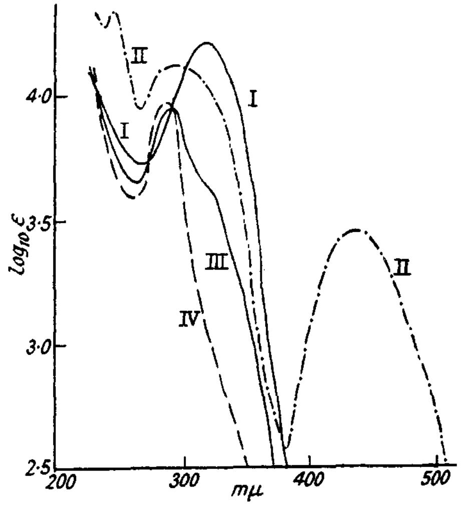
782. *The Absorption Spectrum of an Equimolecular Mixture of Azoxybenzene and Hydrazobenzene.*

By R. J. W. Le Fèvre and (Miss) J. Northcott.

Following recent work involving the absorption spectrum of *trans*-azoxybenzene (*J.*, 1952, 3384) we recorded also the spectra of hydrazobenzene and of an equimolecular mixture of azoxybenzene and hydrazobenzene. The figure displays our results (obtained with a Beckman Photoelectric Spectrophotometer, model D.U. on M/1000-solutions in alcohol); for hydrazobenzene they are reconcilable with the earlier, cruder graphs published by Purvis and McCleland (*J.*, 1912, **101**, 1519) and Kato and Someno (*Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1937, **33**, 209).



I. trans-*Azoxybenzene.*
II. cis-*Azobenzene.*
III. *Equimolecular mixture of* trans-*azoxybenzene and hydrazobenzene.*
IV. *Hydrazobenzene.*

The improbability that the equimolecular mixture just mentioned has been previously wrongly identified as *cis*-azobenzene (cf. Hodgson's suggestion to this effect, *J.*, 1948, 1097, and subsequent comment on it by Le Fèvre and Souter, *J.*, 1949, 1595) is further strengthened by the present spectral evidence. If the extinction coefficients for the mixture are calculated on the molecular weight basis of $(Ph{\cdot}N_2O{\cdot}Ph + PhNH{\cdot}NHPh)/2$, its absorption curve is seen to be nearly the mean of those of its constituents. Most pertinent, however, is the fact that the mixture, when fresh, lacks the visible colour characteristic of *cis*-azobenzene :

Substance	$\lambda_{max.}$	$\log_{10} \varepsilon_{max.}$	$\lambda_{max.}$	$\log_{10} \varepsilon_{max.}$
cis-Azobenzene *	280—315	4·1	440	3·45
trans-Azobenzene *	315	4·7	440—450	2·9
trans-Azoxybenzene	320	4·2	—	—
Hydrazobenzene	285	4·0	—	—

* Data relating to absorption in ethanol from Hausser (*Z. Naturforsch.*, 1950, **5***a*, 56).

Of course, on storage a yellow-orange tint develops in both the mixture and the hydrazobenzene ; this is irreversible and is presumably due to oxidation by air.

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783. *αβ-Unsaturated Aldehydes and Related Compounds. Part II.* The Reaction of αβ-Unsaturated Aldehydes with Unsaturated Alcohols in the presence of Alkali.*

By R. H. HALL and E. S. STERN.

A PATENT (Whetstone, Smith, Norton, and Shell Development Co., U.S.P. 2,561,254/1951), describing the reactions of αβ-unsaturated aldehydes with unsaturated alcohols, has prompted publication of the present note which reports somewhat similar work (the subject of B.P. Appln. 6681/50).

The alkali-catalysed reaction of aliphatic αβ-unsaturated aldehydes with aliphatic alcohols to give β-alkoxy-aldehydes has been known for some time (Heyse and I.G. Farbenind., G.P. 554,949) but unsaturated alcohols had hitherto not been employed in this reaction, although the likely products, containing an aldehyde group and an ethylenic linkage, seem of possible interest as reactive intermediates for further syntheses. Such aldehydes, containing terminal methylene groups, were required for another investigation, and the preparation of a few of these compounds was therefore undertaken.

$$CH_2{:}CR''{\cdot}CH_2{\cdot}OH + CHR{:}CR'{\cdot}CHO \xrightarrow{\text{Alkali}} CH_2{:}CR''{\cdot}CH_2{\cdot}O{\cdot}CHR{\cdot}CHR'{\cdot}CHO$$

No difficulty was experienced in the condensation of acraldehyde with allyl and 2-methylallyl alcohols under the usual alkaline conditions and the desired alkenyloxy-aldehydes were isolated in about 50% yields and characterised as 2 : 4-dinitrophenylhydrazones and semicarbazones. The reaction was subsequently extended to crotonaldehyde and α-methylacraldehyde, each of which reacted with allyl alcohol.

Hydrogenation of the alkenyloxy-aldehydes over Adams's catalyst or over palladium–charcoal readily saturated the ethylenic linkage without affecting the aldehyde grouping and gave the corresponding saturated aldehydes, two of which were also prepared by condensing *n*-propanol with acraldehyde and crotonaldehyde, respectively. The two specimens of β-propoxypropaldehyde gave the same 2 : 4-dinitrophenylhydrazone and semicarbazone (mixed melting points) ; similar results were also obtained in the case of the two specimens of β-propoxybutaldehyde.

Experimental.—M. p.s and b. p.s are uncorrected. Microanalyses are by Drs. Weiler and Strauss of Oxford.

β-*Allyloxypropaldehyde.* In a typical experiment, acraldehyde (170 ml. ; equivalent to 126 g. of pure aldehyde) was added dropwise during about 2 hours to stirred allyl alcohol (500 ml.) containing 50% wt./vol. aqueous sodium hydroxide (3 g.) at −10° to −5°, the cold mixture was acidified with acetic acid (5 ml.) and phosphoric acid (1·5 g.), and then rapidly distilled under reduced pressure. The distillate, on careful fractionation, gave first allyl alcohol and then β-allyloxypropaldehyde (140 g., 55%), b. p. 55°/14 mm., n_D^{20} 1·4291 (Found : C, 62·85;

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* *J.*, 1950, 490, is regarded as Part I.

H, 9·0. Calc. for $C_6H_{10}O_2$: C, 63·15; H, 8·85%). The *semicarbazone* crystallised from ethyl acetate–light petroleum (b. p. 40—60°) in fine needles, m. p. 109° (Found : C, 49·5; H, 7·8; N, 24·4. $C_7H_{13}O_2N_3$ requires C, 49·1; H, 7·65; N, 24·55%); the 2 : 4-dinitrophenylhydrazone crystallised from 95% ethanol in long, matted needles, m. p. 78·5° (Found : C, 49·5; H, 4·95; N, 18·9. Calc. for $C_{12}H_{14}O_5N_4$: C, 49·0; H, 4·8; N, 19·05%). Whetstone *et al.* (*loc. cit.*) record b. p. 71—73°/30 mm., n_D^{20} 1·4362, for the aldehyde and m. p. 73—73·5° for its 2 : 4-dinitrophenylhydrazone.

The aldehyde (57 g.) dissolved in ethanol (250 ml.) containing concentrated sulphuric acid (1 ml.) with spontaneous warming. The mixture was kept for 24 hours, then neutralised with sodium ethoxide in ethanol, and rapidly distilled under reduced pressure. The distillate on fractional distillation gave the *diethyl acetal* (73·5 g., 78%), b. p. 86°/13 mm., n_D^{20} 1·4219 (Found : C, 68·85; H, 10·5. $C_{10}H_{20}O_3$ requires C, 63·8; H, 10·7%).

On hydrogenation over Adams's catalyst (0·1 g.) in ethanol (50 ml.) at 16° and 740 mm., β-allyloxypropaldehyde (5 g.) rapidly absorbed hydrogen (1093 ml., *i.e.*, 1·01 mol.); absorption then slowed down considerably. Interruption of the reaction, filtration of the mixture, and fractional distillation of the filtrate gave β-*propoxypropaldehyde* (4·1 g.), b. p. 88°/90 mm., n_D^{20} 1·4100 (Found : C, 62·15; H, 10·4. $C_6H_{12}O_2$ requires C, 62·05; H, 10·4%), which was also obtained, in 23% yield, by the alkali-catalysed condensation of acraldehyde and propanol under the usual conditions. The aldehyde (prepared by either route) gave a 2 : 4-*dinitrophenylhydrazone*, which separated from ethanol in a felted mass of needles, m. p. 100·5° (Found : C, 49·05; H, 5·25; N, 19·1. $C_{12}H_{16}O_5N_4$ requires C, 48·65; H, 5·45; N, 18·9%), and a *semicarbazone*, which crystallised from ethyl acetate in fine needles, m. p. 130° (Found : C, 48·85; H, 8·8; N, 24·1. $C_7H_{15}O_2N_3$ requires C, 48·55; H, 8·75; N, 24·25%).

β-*Allyloxy*iso*butaldehyde.* Freshly distilled α-methylacraldehyde (70 g.) was added slowly at −5° to stirred allyl alcohol (230 g.) containing 40% aqueous sodium hydroxide solution (2·5 g.), the mixture was acidified with acetic acid and phosphoric acid, and rapidly distilled at about 120 mm. Fractionation of the distillate separated methylacraldehyde (28 g.), b. p. 31°/110 mm., n_D^{20} 1·4150, and allyl alcohol (202 g.), b. p. 51°/110 mm., n_D^{20} 1·4130, from the product, β-allyloxy*iso*butaldehyde (34 g., 50%), b. p. 63°/16 mm., n_D^{20} 1·4288 (Found : C, 65·7; H, 9·5. Calc. for $C_7H_{12}O_2$: C, 65·6; H, 9·45%). The *semicarbazone*, which crystallised from ethyl acetate–light petroleum in needles, had m. p. 88° (Found : N, 22·6. $C_8H_{15}O_2N_3$ requires N, 22·7%), and the 2 : 4-dinitrophenylhydrazone, which crystallised from 95% ethanol in flat needles, m. p. 72° (Found : C, 50·5; H, 5·3; N, 18·0. Calc. for $C_{13}H_{16}O_5N_4$: C, 50·65; H, 5·25; N, 18·2%). Whetstone *et al.* (*loc. cit.*) record b. p. 52—53°/10 mm., n_D^{20} 1·4320, for the aldehyde and m. p. 71·8—72·3° for its 2 : 4-dinitrophenylhydrazone.

Hydrogenation of the aldehyde (10 g.) in ethanol (100 ml.) over 5% palladium–charcoal catalyst (0·8 g.) resulted in the absorption of 1·00 mol. of hydrogen; gas absorption then ceased, and distillation of the filtered mixture gave β-*propoxy*iso*butaldehyde* (6·5 g.), b. p. 65°/28 mm., n_D^{20} 1·4100 (Found : C, 64·35; H, 10·9. $C_7H_{14}O_2$ requires C, 64·6; H, 10·9%). The aldehyde readily gave a 2 : 4-*dinitrophenylhydrazone*, which crystallised from methanol in flat needles, m. p. 71° (Found : C, 50·6; H, 6·0; N, 17·9. $C_{13}H_{18}O_5N_4$ requires C, 50·3; H, 5·85; N, 18·05%), and a *semicarbazone*, crystallising from ethyl acetate–light petroleum (1 : 3) in fine needles, m. p. 108—108·5° (Found : C, 51·45; H, 9·0; N, 22·2. $C_8H_{17}O_2N_3$ requires C, 51·35; H, 9·15; N, 22·45%).

β-*Allyloxybutaldehyde.* Slow addition, as above, of crotonaldehyde (105 g., 1·5 moles) to allyl alcohol (540 ml., 8 moles) containing 40% aqueous sodium hydroxide (5·8 g.), acidification of the solution with acetic acid and phosphoric acid, and fractional distillation of the product gave β-*allyloxybutaldehyde* (115·6 g., 60%), b. p. 77°/30 mm., n_D^{20} 1·4279 (Found : C, 65·9; H, 9·7. $C_7H_{12}O_2$ requires C, 65·6; H, 9·45%), the *semicarbazone* of which crystallised from ethyl acetate as fine clusters of needles, m. p. 109—109·5° (Found : C, 52·05; H, 8·25; N, 22·7. $C_8H_{15}O_2N_3$ requires C, 51·85; H, 8·15; N, 22·7%). The 2 : 4-*dinitrophenylhydrazone* crystallised from 95% ethanol in plates, m. p. 70—71° (Found : C, 50·9; H, 5·5; N, 18·0. $C_{13}H_{16}O_5N_4$ requires C, 50·65; H, 5·25; N, 18·2%).

On hydrogenation in ethanol over 5%-palladium–charcoal (1·0 g.) at 25° and 750 mm. the aldehyde (15·8 g.) rapidly absorbed hydrogen (3210 ml., 1·01 mol.); absorption then slowed down. Interruption of the reaction, filtration of the mixture, and fractional distillation of the filtrate gave β-*propoxybutaldehyde* (10·6 g.), b. p. 54°/16 mm., n_D^{20} 1·4110 (Found : C, 64·1; H, 11·15. $C_7H_{14}O_2$ requires C, 64·6; H, 10·85%), which was also obtained in 45% yield by the alkali-catalysed reaction, in the usual manner, of crotonaldehyde with propanol. The aldehyde (prepared by either route) gave a 2 : 4-*dinitrophenylhydrazone*, crystallising from methanol at

−15° in rosettes of needles, m. p. 54—55° (Found : C, 49·95; H, 5·5; N, 18·1. $C_{13}H_{18}O_5N_4$ requires C, 50·3; H, 5·85; N, 18·05%), and a *semicarbazone*, which crystallised from ethyl acetate–light petroleum (b. p. 40—60°) (1 : 6, by vol.) in needles, m. p. 88° (Found : C, 51·3; H, 8·95; N, 22·5. $C_8H_{17}O_2N_3$ requires C, 51·35; H, 9·15; N, 22·45%).

β-2-*Methylallyloxypropaldehyde.* Reaction, in the usual manner, of acraldehyde (75 ml.) and 2-methylallyl alcohol (256 g.) containing a solution of sodium hydroxide (1·06 g.) in water (2 ml.) gave β-2-*methylallyloxypropaldehyde* (51 g., 40%), b. p. 62°/9 mm., n_D^{20} 1·4352 (Found : C, 65·25; H, 9·7. $C_7H_{12}O_2$ requires C, 65·6; H, 9·45%). The 2 : 4-*dinitrophenylhydrazone* crystallised from 95% ethanol in long matted needles, m. p. 77—78° (Found : C, 50·25; H, 5·2; N, 18·2. $C_{13}H_{16}O_5N_4$ requires C, 50·65; H, 5·25; N, 18·2%); the *semicarbazone* crystallised from ethyl acetate–light petroleum (b. p. 40—60°) in fine needles, m. p. 110° (Found : C, 51·55; H, 7·95; N, 22·4. $C_8H_{15}O_2N_3$ requires C, 51·85; H, 8·15; N, 22·7%).

On hydrogenation in ethanol (100 ml.) over 5% palladium–charcoal (0·75 g.) at 20° and 750 mm. the aldehyde (12·2 g.) rapidly absorbed hydrogen (2420 ml., 1·01 mols.); absorption then ceased, and distillation of the filtered product gave β-iso*butoxypropaldehyde*, b. p. 65°/26 mm., n_D^{20} 1·4118 (Found : C, 64·5; H, 10·8. $C_7H_{14}O_2$ requires C, 64·6; H, 10·85%). The 2 : 4-*dinitrophenylhydrazone* crystallised from aqueous methanol in fine needles, m. p. 80° (Found : C, 50·8; H, 5·85; N, 17·8. $C_{13}H_{18}O_5N_4$ requires C, 50·3; H, 5·85; N, 18·05%), and the *semicarbazone* from ethyl acetate–light petroleum (b. p. 40—60°) (1 : 1, by vol.) in long fine needles, m. p. 118° (Found : C, 51·7; H, 9·0; N, 22·8. $C_8H_{17}O_2N_3$ requires C, 51·35; H, 9·15; N, 22·45%).

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GREAT BURGH, EPSOM, SURREY. [*Received, June 17th,* 1952.]

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784. *Dihalogeno-substituted Terephthalaldehydes and* p-*Tolualdehydes.*

By J. R. NAYLOR.

2 : 5-DIBROMO- AND 2 : 5-DICHLORO-TEREPHTHALALDEHYDES have been prepared by side-chain halogenation of the corresponding nuclear dihalogenated *p*-xylene, followed by hydrolysis of the product with concentrated sulphuric acid (Ruggli and Brandt, *Helv. Chim. Acta*, 1944, **27**, 274). The yields were not good, particularly that of the dichloro-compound. It is now shown that these compounds may be conveniently prepared, but not in good yield, by oxidation of the dihalogeno-substituted *p*-xylene, by means of chromium trioxide and sulphuric acid in the presence of acetic acid and acetic anhydride, to the corresponding terephthalaldehyde tetra-acetates (Thiele and Winter, *Annalen*, 1900, **311**, 359), from which the free aldehydes may be obtained in almost quantitative yield by hydrolysis with dilute sulphuric acid.

The previously unreported 2 : 5-dibromo- and 2 : 5-dichloro-4-methylbenzaldehyde diacetate are obtained as by-products of the oxidation. Hydrolysis of these compounds with dilute sulphuric acid gives the corresponding hitherto unknown benzaldehydes.

EXPERIMENTAL

M. p.s are uncorrected. Micro-analyses were carried out by Drs. Weiler and Strauss of Oxford.

2 : 5-*Dichloroterephthalaldehyde Tetra-acetate.*—2 : 5-Dichloro-*p*-xylene (32·7 g.) was dissolved in a stirred mixture of acetic acid (300 g.), acetic anhydride (600 g.), and sulphuric acid (90 g.) and cooled to 5°. Chromium trioxide (60 g.) was added at such a rate (2½ hours) as to keep the temperature of the cooled mixture between 5° and 12°. The mixture was stirred for a further 4 hours (10—15°), poured on crushed ice (5 kg.), and stirred overnight. The product (45·1 g.) was filtered off, and after recrystallisation from ethanol (1100 c.c.) gave 2 : 5-dichloroterephthalaldehyde tetra-acetate (25·2 g.), m. p. 199·5—200° (37%) (Found : C, 47·6; H, 4·2; Cl, 17·25. Calc. for $C_{16}H_{16}O_8Cl_2$: C, 47·2; H, 3·9; Cl, 17·4%).

2 : 5-*Dichloroterephthalaldehyde.*—The foregoing tetra-acetate (43 g.) was added to a mixture of ethanol (250 c.c.), water (250 c.c.), and sulphuric acid (25 g.), heated under reflux for 1½ hours, and cooled. Filtration and recrystallisation of the product from aqueous ethanol gave 2 : 5-di-

chloroterephthaldehyde (18·4 g.), m. p. 157° (86%) (Found: C, 47·8; H, 2·2; Cl, 34·6. Calc. for $C_8H_4O_2Cl_2$: C, 47·3; H, 2·0; Cl, 35·0%).

2 : 5-*Dichloro*-4-*methylbenzaldehyde Diacetate.*—Concentration to 100 c.c. of the mother-liquor from the tetra-acetate gave 2 : 5-*dichloro*-4-*methylbenzaldehyde diacetate* (10·8 g.), m. p. 108° (20%) (Found: C, 49·9; H, 3·9; Cl, 23·9. $C_{12}H_{12}O_4Cl_2$ requires C, 49·5; H, 4·1; Cl, 24·4%).

2 : 5-*Dichloro*-4-*methylbenzaldehyde.*—The foregoing diacetate (8·7 g.) was treated as for the previous tetra-acetate but on a one-fifth scale and with 45 minutes' refluxing, giving the *aldehyde* (5·2 g.), m. p. 110·5—111° (91%) (Found: C, 51·1; H, 3·25; Cl, 37·2. $C_8H_6OCl_2$ requires C, 50·8; H, 3·2; Cl, 37·6%). Its 2 : 4-*dinitrophenylhydrazone* had m. p. 257° (Found: N, 15·5. $C_{14}H_{10}O_4N_4Cl_2$ requires N, 15·2%).

2 : 5-*Dibromoterephthalaldehyde Tetra-acetate.*—2 : 5-Dibromo-*p*-xylene (59 g.) was treated exactly as for the dichloro-analogue, but with 1·2-fold quantities. The product (56·5 g.) was filtered off and after recrystallisation from ethanol (4 l.) gave 2 : 5-dibromoterephthaldehyde tetra-acetate (33·6 g.), m. p. 218·5—219° (30·5%) (Found: C, 38·55; H, 3·05; Br, 32·5. Calc. for $C_{16}H_{16}O_8Br_2$: C, 38·7; H, 3·2; Br, 32·3%).

2 : 5-*Dibromoterephthalaldehyde.*—The tetra-acetate (4·9 g.) was treated as for its chloro-analogue, but on a one-fifth scale, giving 2 : 5-dibromoterephthaldehyde (2·7 g.), m. p. 189° (92%) (Found: C, 32·8; H, 1·9; Br, 54·35. Calc. for $C_8H_4O_2Br_2$: C, 32·9; H, 1·4; Br, 54·8%).

2 : 5-*Dibromo*-4-*methylbenzaldehyde Diacetate.*—Concentration to 100 c.c. of the mother-liquor from the tetra-acetate gave 2 : 5-*dibromo*-4-*methylbenzaldehyde diacetate* (13·5 g.), m. p. 117—117·5° (16%) (Found: C, 38·3; H, 3·3; Br, 41·6. $C_{12}H_{12}O_4Br_2$ requires C, 37·9; H, 3·2; Br, 42·05%).

2 : 5-*Dibromo*-4-*methylbenzaldehyde.*—The above diacetate (7·5 g.) was treated as for the dichloro-analogue (1 hour's refluxing), affording 2 : 5-*dibromo*-4-*methylbenzaldehyde* (5·2 g.), m. p. 142° (94%) (Found: C, 34·6; H, 2·3; Br, 58·5. $C_8H_6OBr_2$ requires C, 34·5; H, 2·2; Br, 57·6%). Its 2 : 4-*dinitrophenylhydrazone* had m. p. 265° (Found: N, 12·2. $C_{14}H_{10}O_4N_4Br_2$ requires N, 12·23%).

RESEARCH DEPARTMENT, THE CALICO PRINTERS' ASSOCIATION LTD.,
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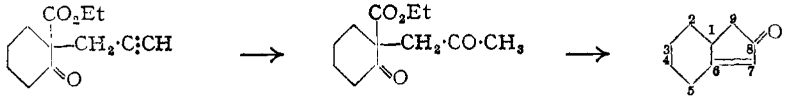
785. bicyclo[4 : 3 : 0]*Non*-6-*en*-8-*one*.

By A. M. ISLAM and R. A. RAPHAEL.

THE hitherto unknown *bicyclo*[4 : 3 : 0]non-6-en-8-one (III) has been synthesised in the following manner.



(I) (II) (III)

Reaction of the sodio-derivative of ethyl 2-keto*cyclo*hexane-1-carboxylate with propargyl bromide gave a good yield of the expected product (I), which with methanolic boron trifluoride in the presence of mercuric oxide (cf. Hamlet, Henbest, and Jones, *J.*, 1951, 2652) yielded the hydration product (II). Attempts to prepare (II) directly from ethyl 2-keto*cyclo*hexane-1-carboxylate and chloroacetone were unsuccessful under a variety of conditions, very small yields of impure products being obtained. When (II) was heated with dilute potassium hydroxide solution an intramolecular aldol-type condensation took place with concomitant hydrolysis and decarboxylation to furnish finally the required ketone (III).

EXPERIMENTAL

Ethyl 2-*Keto*-1-*propargyl*cyclo*hexane*-1-*carboxylate* (I).—A mixture of sodium ethoxide solution (from sodium, 1·7 g., and alcohol, 300 c.c.) and ethyl 2-keto*cyclo*hexane-1-carboxylate (12·5 g.) was heated under reflux for 30 minutes. Propargyl bromide (10 g.) was then added to the boiling solution during 1 hour and heating continued for a further 2 hours. Most of the alcohol was removed, water (200 c.c.) was added, and the product isolated with benzene. Evaporation and distillation gave ethyl 2-keto-1-propargyl*cyclo*hexane-1-carboxylate as a colourless oil (12 g., 83%), b. p. 154°/12 mm., n_D^{19} 1·4590. In spite of the sharp b. p. a satisfactory carbon analysis for either this compound or its hydration product (II) could not be obtained. The *semicarbazone* crystallised from aqueous alcohol in colourless needles, m. p. 144° (Found : N, 15·7. $C_{13}H_{19}O_3N_3$ requires N, 15·8%).

Ethyl 1-*Acetonyl*-2-*keto*cyclo*hexane*-1-*carboxylate* (II).—A solution of the foregoing ester (7·3 g.) in methanol (15 c.c.) was added slowly to a catalyst solution prepared by warming together red mercuric oxide (0·5 g.), boron trifluoride–ether complex (0·2 c.c.), trichloroacetic acid (10 mg.), and methanol (1 c.c.). After the initial exothermic reaction was over, the mixture was shaken at room temperature for 2 hours and then poured into dilute sulphuric acid. Isolation by means of ether, evaporation, and distillation gave the required diketone (II) as a pale yellow oil (6 g., 75%), b. p. 144°/1 mm., n_D^{19} 1·4504. The *disemicarbazone* crystallised in plates, m. p. 214°, from aqueous alcohol (Found : N, 24·9. $C_{14}H_{24}O_4N_6$ requires N, 24·8%).

bicyclo[4 : 3 : 0]*Non*-6-*en*-8-*one* (III).—The 2-acetonyl compound (3 g.) and aqueous potassium hydroxide solution (5%; 150 c.c.) were heated under reflux for 6 hours under nitrogen. After being cooled, the mixture was acidified with dilute sulphuric acid and the product isolated with ether. Evaporation and distillation gave bicyclo[4 : 3 : 0]*non*-6-*en*-8-*one* (1·3 g., 73%) as a colourless oil, b. p. 88°/4 mm., n_D^{19} 1·5190 (Found : C, 79·1; H, 8·9. $C_9H_{12}O$ requires C, 79·4; H, 8·8%). Light absorption in ethanol : $\lambda_{max.}$ 2280 (ε = 16,500) and 2860 Å (ε = 140) [Acheson and Robinson, *J.*, 1952, 1131, record $\lambda_{max.}$ 2250 Å (ε = 18,150) for 3-methyl-*cyclo*pent-2-enone]. The 2 : 4-*dinitrophenylhydrazone* formed red needles, m. p. 200°, from alcohol (Found : C, 57·0; H, 4·9; N, 18·1. $C_{15}H_{16}O_4N_4$ requires C, 56·9; H, 5·1; N, 17·7%). Light absorption in ethanol : $\lambda_{max.}$ 2580 (ε = 19,000) and 3900 Å (ε = 26,500). The *semicarbazone* crystallised from alcohol in leaflets, m. p. 224° (Found : N, 21·5. $C_{10}H_{15}ON_3$ requires N, 21·7%).

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