89. *Benzhydryl and 9-Fluorenyl Toluene-*p*-sulphonates.*

By A. Ledwith and D. G. Morris.

Benzhydryl toluene-*p*-sulphonate had not been reported in the literature until Cheeseman and Poller [1] showed that it could be obtained, in 59% yield, from the reaction between benzhydryl chloride and silver toluene-*p*-sulphonate in diethyl ether. Hoffman [2] showed that the same reaction in acetonitrile gave a product, thought to be benzhydryl toluene-*p*-sulphonate, but which was not isolated.*

Independently we have prepared this toluenesulphonate in quantitative yield by a totally different method involving the reaction between diazodiphenylmethane and toluene-*p*-sulphonic acid * in diethyl ether or tetrahydrofuran. The latter reaction appears to be much more convenient and to give better yields than that reported by previous workers. Similarly, 9-fluorenyl toluene-*p*-sulphonate, which has not been reported previously, can be obtained in greater than 90% yield by the reaction between 9-diazofluorene and toluene-*p*-sulphonic acid.

Preliminary kinetic studies of the rates of hydrolysis in 90% v/v aqueous tetrahydrofuran gave good first-order rate constants of $4{\cdot}50 \pm 0{\cdot}15 \times 10^{-3}$ sec.$^{-1}$ at 0° for the benzhydryl and $9{\cdot}66 \pm 0{\cdot}10 \times 10^{-5}$ sec.$^{-1}$ at 25° for the fluorenyl ester. The very great difference in reactivity between benzhydryl and 9-fluorenyl toluene-*p*-sulphonate agrees with that found [4] in the hydrolysis of the corresponding bromo-derivatives in 80% aqueous ethanol and a satisfactory explanation must await more detailed investigations.

Experimental.—Materials. Diazodiphenylmethane and 9-diazofluorene were prepared from the corresponding hydrazones by conventional oxidation with mercuric oxide.[5] Diethyl ether ("AnalaR"), tetrahydrofuran, and light petroleum (b. p. 30—40°) ("AnalaR") were distilled from calcium hydride before use. Toluene-*p*-sulphonic acid monohydrate (B.D.H. Micro-Analytical Reagent) was used without further purification.

*Benzhydryl toluene-*p*-sulphonate.* Addition of toluene-*p*-sulphonic acid (1 mol equiv.) to diazo diphenylmethane (*ca.* 1·5 g.) in diethyl ether (10 ml.) at room temperature, resulted in the immediate precipitation of a quantitative yield of the toluene-*p*-sulphonate. After three recrystallisations from 1 : 1 tetrahydrofuran–light petroleum the product had m. p. 61° (Found: C, 70·1; H, 5·4. Calc. for $C_{20}H_{18}O_3S$: C, 71·0; H, 5·3%). The i.r. spectrum showed strong absorptions at 1170 and 1358 cm.$^{-1}$, characteristic of sulphonate esters,[6] and was identical with the spectrum of the product obtained by Cheeseman and Poller.[1] Benzhydryl toluene-*p*-sulphonate slowly decomposes in air at room temperature but can be stored *in vacuo* below 0° without decomposition for long periods.

*9-Fluorenyl toluene-*p*-sulphonate.* Prepared as for the benzhydryl derivative, the *fluorenyl ester*, after three recrystallisations from 1 : 1 tetrahydrofuran–light petroleum, had m. p. 50·5—51·5° (decomp.) (Found: C, 71·5; H, 4·8. $C_{20}H_{16}O_3S$ requires C, 71·5; H, 4·8%). The i.r. spectrum showed strong absorption at 1176 and 1259 cm.$^{-1}$, characteristic of sulphonate esters.[6]

Kinetic experiments. Hydrolyses in 90% v/v aqueous tetrahydrofuran were followed by making up 0·02M-solutions of the toluene-*p*-sulphonates in dry tetrahydrofuran (45·0 ml.), and adding distilled water (5·0 ml.) to start the reaction. The solvents were allowed to equilibrate at the appropriate temperature before being mixed. At suitable intervals, samples

* From a detailed examination of the toluene-*p*-sulphonic acid-catalysed decomposition of diazodiphenylmethane in anhydrous acetonitrile, Bethell and Callister [3] have shown conclusively that although benzhydryl toluene-*p*-sulphonate is the initial product, it rapidly decomposes, the reaction having a first-order rate constant of approx. 2×10^{-2} sec.$^{-1}$ at 29·5°.

[1] Cheeseman and Poller, *J.*, 1962, 5277.
[2] Hoffman, *Chem. and Ind.*, 1963, 336.
[3] Bethell and Callister, *J.*, 1963, 3808; the authors are indebted to Dr. D. Bethell for permission to use his results before publication.
[4] Lovins, Andrews, and Keefer, *J. Amer. Chem. Soc.*, 1962, **84**, 3959.
[5] Gutsche and Johnson, *J. Amer. Chem. Soc.*, 1955, **77**, 5933.
[6] Tipson, *J. Amer. Chem. Soc.*, 1952, **74**, 1354.

(5·0 ml.) were withdrawn and quenched by running into a separating funnel containing light petroleum–water, essentially as described by Fainberg and Winstein.[7] The developing toluene-*p*-sulphonic acid was estimated by titration with 0·02M-methanolic sodium hydroxide, Bromocresol Green being used as indicator. Experimental infinity titres were never less than 95% of the theoretical values and the appropriate alcohol was recovered from the kinetic runs in virtually quantitative yield.

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[7] Fainberg and Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 2770.

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90. *The Configuration of Trinitrotriamminecobalt*(III).

By CHARMIAN O'CONNOR (*née* BISHOP).

THREE methods of preparation have been reported for trinitrotriamminecobalt(III), by Werner,[1] Jörgensen,[2] and Sueda,[3] severally. Previous attempts to assign configuration to these preparations resulted in the conclusions tabulated.

	Method of study		
Method of prepn.	*X*-Ray	U.v. spectrum	I.r. spectrum
Werner			*trans* [6]
Jörgensen	*trans* [4]	*trans* [5]	*cis* [6]
Sueda		*cis* [3]	

Beattie and Tyrrell [7] state that, although the infrared absorption spectra of nitroamminecobalt complexes depend to some extent on the stereochemistry of the complex, it is impossible to associate bands in this region with particular ligands.

Attempts were made to repeat the preparation by the three methods, but only those of Jörgensen [2] and Sueda [3] were successful in our hands. The main product isolated by Werner's method [1] was potassium tetranitrodiamminecobalt(III).

The ultraviolet spectra of our two samples agreed with that reported by Sueda [3,5] and the infrared spectrum of the Jörgensen preparation agreed (with only very minor differences) with those quoted by Beattie and Tyrrell [7] and by Majumdar *et al.*[6] The infrared spectrum of the Sueda preparation was very similar to that of the Werner compound,[6] having bands at 1634 (1626), 1418 (1420), 1399 (1398), 1361 (1360), 1316 (1321), 1280 (1285), and 825 (820) (those of the Werner compound are given in parentheses).

Since *X*-ray evidence has given the Jörgensen preparation unequivocally a *trans*-configuration, the Sueda preparation, which differs from it both in the infrared and in the ultraviolet absorption spectrum, can be assumed to have a *cis*-configuration. The infrared evidence indicates that a *cis*-configuration may also be assigned to the Werner preparation. Since the *cis*-configuration is much less stable than the *trans*-, this assignment might account for the difficulty experienced in the attempts to make the compound by Werner's method.

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[1] Werner, *Z. anorg. Chem.*, 1897, **15**, 166.
[2] Jörgensen, *Z. anorg. Chem.*, 1898, **17**, 463.
[3] Sueda, *Bull. Chem. Soc. Japan*, 1938, **13**, 450.
[4] Tanito, Saito, and Kuroya, *Bull. Chem. Soc. Japan*, 1952, **25**, 188.
[5] Sueda, *Bull. Chem. Soc. Japan*, 1937, **12**, 188.
[6] Majumdar, Duval, and Lecomte, *Compt. rend.*, 1958, **247**, 302.
[7] Beattie and Tyrrell, *J.*, 1956, 1849.

91. *Preparation of Triphenyl-lead Cyanide and Thiocyanate.*

By H. J. Emeléus and P. R. Evans.

Apart from a recent preparation of triphenyl-lead azide,[1] there is no publication about triphenyl-lead pseudohalides. We have prepared triphenyl-lead cyanide in 96% yield by the action of aqueous potassium cyanide on ethereal triphenyl-lead iodide. The product is a white solid, insoluble in ether and water, but soluble in ethanol. It was recrystallized from hot aqueous ethanol, and the purified compound decomposed at about 250°. As expected, no hydrolysis occurred during recrystallization; the ^-CN group in triphenyltin cyanide is also resistant to hydrolysis.[2] We were unable to prepare triphenyl-lead cyanide from silver cyanide and triphenyl-lead iodide in ether; in hot methanol the reaction was incomplete after one hour and the products could not be separated.

Triphenyl-lead thiocyanate has also been made, by refluxing triphenyl-lead chloride (but not iodide) with potassium thiocyanate in ethanol. It recrystallized from hot aqueous ethanol, and decomposed at about 230°. It could not be prepared by the action of aqueous potassium thiocyanate on ethereal triphenyl-lead iodide.

The infrared spectra of the products are recorded below.

In view of the poor hydrogen analysis obtained for triphenyl-lead cyanide, the lead content was determined. Existing methods of analysis of organolead compounds depend on conversion of the lead into an inorganic form, which is estimated gravimetrically or volumetrically. Removal of aryl groups has been achieved by oxidizing acids;[3] but liquid bromine has been found to be as efficient and much quicker. The lead bromide

Estimation of aryl organo-lead and -tin compounds by initial bromination.

Organolead compound	Pb (%) calc.	Pb (%), found	Organotin compound	Sn (%), calc.	Sn (%), found
Ph_4Pb	40·2	40·0, 40·1	Ph_3SnCl	30·8	30·65, 30·8
Ph_3PbI	36·65	36·7, 36·75	Ph_6Sn	33·8	33·5, 33·8
Ph_6Pb_2	47·25	47·1	Ph_3SnOH	32·4	32·3, 32·3
Ph_2PbCl_2.....	48·0	47·8			

formed was converted into chromate and estimated volumetrically. The method can be applied to many aryl-lead compounds (see Table). The same cleavage agent can also be used for aryltin compounds: the inorganic tin formed was determined by the method of Farnsworth and Pekola.[4] Some examples of tin estimations involving bromine oxidation are included in the Table.

Experimental.—Triphenyl-lead iodide and chloride were prepared from tetraphenyl-lead by standard methods.[5,6]

Triphenyl-lead cyanide. Triphenyl-lead iodide (1·41 g.) in ether (125 ml.) was shaken with potassium cyanide (0·33 g.) in water (50 ml.). The solid *product* (1·12 g., 96%) was filtered off and dried (Found: C, 49·3; H, 4·8; N, 3·0; Pb, 44·3. $C_{19}H_{15}NPb$ requires C, 49·1; H, 3·3; N, 3·0; Pb, 44·5%).

Triphenyl-lead thiocyanate. Triphenyl-lead chloride (1·00 g.) was refluxed with an excess of potassium thiocyanate in ethanol for 30 min. The solution was cooled and filtered. When water was added, a *thiocyanate* was precipitated which was recrystallized from aqueous ethanol (yield, 0·44 g., 42%) (Found: C, 46·2; H, 3·6; N, 3·0%. $C_{19}H_{15}NSPb$ requires C, 45·9; H, 3·0; N, 2·8%).

Infrared spectra. These were recorded by a Perkin-Elmer model 21 spectrometer, equipped with sodium chloride optics, for Nujol mulls. Frequencies below 2500 cm.$^{-1}$ were:

[1] Lieber and Keane, *Chem. and Ind.*, 1961, 747.
[2] Zimmer and Lubke, *Chem. Ber.*, 1952, **85**, 1119.
[3] Gilman and Robinson, *J. Amer. Chem. Soc.*, 1928, **50**, 1714.
[4] Farnsworth and Pekola, *Analyt. Chem.*, 1959, **31**, 410.
[5] Foster, Dix, and Gruntfest, *J. Amer. Chem. Soc.*, 1939, **61**, 1685.
[6] Gilman and Robinson, *J. Amer. Chem. Soc.*, 1929, **51**, 3112.

$Ph_3Pb{\cdot}CN$: 2158w, 1574m, 1436s, 1058w, 1014m, 996s, 912w, 852w, 723vs, 716s shoulder, 686s.

$Ph_3Pb{\cdot}CNS$: 2103s, 1572w, 1437s, 1061w, 1015m, 994s, 724vs, 689s, 686s.

Determination of lead and tin in aryl compounds. The lead compound (~0·2 g.) was cautiously treated with a few ml. of bromine. After the vigorous reaction, water (20 ml.) was added and the excess of bromine was boiled off. The last trace of bromine was destroyed by adding 4N-ammonia until all the lead had been precipitated as hydroxide. This precipitate was just redissolved in 10% acetic acid, lead chromate was precipitated from the hot solution, and the lead was estimated volumetrically in the usual way.[7]

With aryltin compounds a sample (0·2 g.) was treated with bromine (~1 ml.), and the excess of bromine was removed as before. Hydrated stannic oxide was precipitated, redissolved in 18% hydrochloric acid, and reduced with aluminium foil, the estimation being completed by a standard method.

One of us (P. R. E.) thanks the Associated Octel Co. Ltd., for a grant.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, March 7th,* 1963.]

[7] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., Inc., New York, 1939, 5th edn., p. 512.

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92. *Reaction of Compounds Containing a Lead–Lead Bond with Hydrogen Chloride.*

By H. J. EMELÉUS and P. R. EVANS.

HEXAPHENYLETHANE and hydrogen chloride react with fission of the carbon–carbon bond. Tetramethyldistibine with hydrogen chloride gives dimethylchlorostibine and hydrogen,[1] the reaction presumably proceeding in two stages: addition with fission of the Sb–Sb bond, and reaction of the dimethylstibine so formed. Yet from a qualitative investigation of the behaviour of hexaethyldilead with hydrogen chloride, Midgley, Hochwalt, and Calingaert [2] suggested the reaction, $Et_6Pb_2 + 3HCl \longrightarrow Et_3PbCl + PbCl_2 + 3C_2H_6$, to explain the formation of a white precipitate and a colourless gas. This reaction implies that hydrogen chloride attacks the lead–carbon bond before the lead–lead bond, but there have been no proved examples of preferential lead–carbon bond cleavage in the literature. An alternative explanation is that the lead–lead bond was first broken ($Et_6Pb_2 + 2HCl \longrightarrow 2Et_3PbCl + H_2$), this being followed by the reaction, $2Et_3PbCl + 2HCl \longrightarrow 2Et_2PbCl_2 + 2C_2H_6$. Some decomposition of the rather unstable and insoluble dichloride to lead chloride may have occurred.

Other workers, using unmeasured quantities of gaseous hydrogen chloride with R_6Pb_2 compounds in chloroform, have obtained the results summarised in Table 1. From

TABLE 1.

			Products (%)			
No.	R	Reaction time	R_3PbCl	R_2PbCl_2	$PbCl_2$	Ref.
1	Ph	3 min.	—	16·5	82·6	3
2	*o*-C_6H_4Me	4 hr.	—	29	Yes	4
3	*p*-$C_6H_4{\cdot}OMe$	75 min.	—	42·7	52	5
4	*p*- ,,	25 min.	41·4 *	9·4	47	5

* Reported incorrectly as 51·4%.

reaction (4) we conclude that at least part of the lead chloride produced in the reaction is not formed from the monochloride R_3PbCl by way of the dichloride R_2PbCl_2. This is

[1] Burg and Grant, *J. Amer. Chem. Soc.*, 1959, **81**, 1.
[2] Midgley, Hochwalt, and Calingaert, *J. Amer. Chem. Soc.*, 1923, **45**, 1821.
[3] Gilman and Bailie, *J. Amer. Chem. Soc.*, 1939, **61**, 731.
[4] Austin, *J. Amer. Chem. Soc.*, 1931, **53**, 3514.
[5] Gilman and Towne, *J. Amer. Chem. Soc.*, 1939, **61**, 739.

supported by the formation only of an organo-bromide R_3PbBr and lead bromide in a reaction of hexa-*o*-tolyldilead with hydrobromic acid in chloroform.[6]

New results on the reaction of an excess of ethanolic and chloroform solutions of hydrogen chloride with a series of dilead compounds R_6Pb_2 are given in Table 2. They are based on the volumetric determination of unchanged hydrogen chloride.

TABLE 2.

Moles of HCl (0·1N) reacting per mole of R_6Ph_2 in 5 min. at 20° ± 2°.

R in R_6Pb_2	In 95% EtOH	In $CHCl_3$
Me	0·61, 0·605, 0·59	3·02, 2·94, 2·94, 2·97
Cyclohexyl	0·175, 0·175	1·76, 1·77
Ph	2·87, 2·90, 2·96	4·05, 3·95
m-C_6H_4Me	2·91	—
p-C_6H_4Me	3·03	3·82 in 2 min.
o-C_6H_4·OMe	2·90 (3·22 in 30 min.)	4·08, 3·92

Taken with the data in Table 1, our results show that in ethanol solution the overall equation is $R_6Pb_2 + 3HCl \longrightarrow R_3PbCl + PbCl_2 + 3RH$, as suggested by Midgley *et al.*[2] These therefore become the first proved reactions in which the lead–carbon bond is cleaved before the lead–lead bond. Reaction of the alkyl compounds with ethanolic hydrogen chloride was incomplete in the five-minute reaction period, but in chloroform hexamethyldilead reacted completely. The aryl derivatives, however, reacted with a further molecule of hydrogen chloride in chloroform; this converted the monochloride R_3PbCl into the dichloride R_2PbCl_2. As the identities of the products are well-established (Table 1), the materials were not isolated by us. Separate experiments showed that, under the reaction conditions, ethanolic hydrogen chloride was without action on triaryl-lead chlorides, whereas, in chloroform, precipitates of diaryl-lead dichlorides were obtained.

These results do not show the stage of the reaction at which lead chloride is formed. There are two possibilities: (*a*) $R_6Pb_2 + 2HCl \longrightarrow R_4Pb_2Cl_2 \longrightarrow R_4Pb + PbCl_2$, or (*b*) $R_6Pb_2 + 3HCl \longrightarrow R_3Pb_2Cl_3 \longrightarrow R_3PbCl + PbCl_2$. Reaction of a 0·01M-solution of hexamethyldilead in chloroform with one equivalent of ethanolic 0·1N-hydrogen chloride gave, after 50 hours, lead chloride corresponding to the whole of the hydrogen chloride added, indicating that, for this reaction at least, mechanism (*a*) is operative. Support for an intermediate $R_4Pb_2Cl_2$ comes from the reaction of anhydrous aluminium chloride with R_6Pb_2 compounds. Quantitative studies were made by Gilman and Apperson,[7] but they did not attempt to explain their results. We have used their data to calculate the figures in Table 3 (details of the organoaluminium reaction products have been omitted). These

TABLE 3.

No.	R in R_2Pb_6	Products (%)			
		R_4Pb	R_3PbCl	R_2PbCl_2	$PbCl_2$
1	Ph (deficiency)	30	6·6	5·8	45
2	Ph (excess)	44	—	—	47
3 *	*o*-C_6H_4Me (2 pts. of $AlCl_3$)	44	—	—	50
4	,, ,,	30·5	13·5	—	45

* 21% of starting material recovered; yields calculated on amount that reacted.

show that in each reaction the molar proportion of total organolead products is approximately equal to that of lead chloride formed. Only in reactions (1) and (4) (which involved an excess of aluminium chloride and went to completion) was an organolead chloride formed. We conclude that the first step in reaction is $R_6Pb_2 + AlCl_3 \longrightarrow R_4Pb_2Cl_2 \longrightarrow R_4Pb + PbCl_2$. As with the hydrogen chloride reaction, this must also proceed by initial cleavage of the lead–carbon bond.

[6] Austin, *J. Amer. Chem. Soc.*, 1931, **53**, 1548.
[7] Gilman and Apperson, *J. Org. Chem.*, 1939, **4**, 162.

Experimental.—Hexamethyldilead was prepared by Calingaert and Soroos's method [8] from methyl bromide; it was recrystallised from ether and stored in the dark under nitrogen. Any tetramethyl-lead was distilled off in a vacuum. The material was used within 2—3 hr. of its preparation (Found: C, 14·8; H, 3·5. Calc. for $C_6H_{18}Pb_2$: C, 14·2, H, 3·55%). Other hexa-organodilead compounds were prepared by recorded methods [3,9] and recrystallised from chloroform, and their m. p.s and analyses checked. Hexaphenyldilead was also prepared from triphenyl-lead iodide and sodium in liquid ammonia.[10]

Solutions of hydrogen chloride in 95% ethanol and in chloroform were prepared by passing the dried gas into the solvent and were standardised with 0·1N-aqueous sodium hydroxide (Methyl Orange). For the experiments summarised in Table 2 the compound R_6Pb_2 (0·2—0·5 g.) was treated with chloroform added to give an ~0·01M-solution. Hydrogen chloride solution (25 ml.) was added from a burette and, at the completion of the experiment, water (50 ml.) was added before titration with 0·1N-sodium hydroxide. Precipitation of lead hydroxide occurred only when all the hydrogen chloride had been neutralised. In some experiments the titration was done with a glass electrode in the aqueous layer: the results were identical by the two methods.

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[8] Calingaert and Soroos, *J. Org. Chem.*, 1938, **2**, 535.
[9] Krause, *Ber.*, 1921, **54**, 2060; Krause and Reissaus, *Ber.*, 1922, **55**, 888.
[10] Foster, Dix, and Gruntfest, *J. Amer. Chem. Soc.*, 1939, **61**, 1685.

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93. *Dialkyl Dihydrogen Methylenebisphosphonates and their Metal Salts.*

By H. GORIČAN and D. GRDENIĆ.

DISODIUM DIETHYL METHYLENEBISPHOSPHONATE, $CH_2[PO(OEt)\cdot ONa]_2$, was synthesized by Nylen,[1] and then by Arbuzov *et al.*,[2] and tetraethyl methylenebisphosphonate has been obtained from triethyl phosphite by the Arbuzov reaction.[3] Tetra-alkyl esters have also been obtained by the reaction between dialkyl chloromethylphosphonate and sodium dialkyl phosphites.[4,5]

Disodium dialkyl and tetra-alkyl methylenebisphosphonates (alkyl R = Me, Et, or Pr) are readily hydrolysed in hot aqueous acid. For this reason, only free methylenebisphosphonic acid has been examined,[4] while diacid dialkyl esters, the object of our investigation,[6] have not previously been considered. Owing to their insolubility in water, dialkyl esters with alkyl higher than butyl are not liable to hydrolysis and were therefore readily prepared from disodium dialkyl methylenebisphosphonate. The dibutyl and dioctyl esters have been obtained in 30% and 19% yield, respectively, by Nylen's method. The diethyl and dipropyl esters (the dimethyl ester has not been prepared) were obtained by treating the silver salts with equivalent amounts of hydrochloric acid (an excess of acid causes hydrolysis during evaporation of the solution).

Dialkyl methylenebisphosphonic acids are strong acids. Disodium diethyl, di-isopropyl, and di-n-butyl methylenebisphosphonate are readily soluble in water. The salts of other metals are insoluble and therefore accessible by precipitation. Various metal dioctyl methylenebisphosphonates were obtained by shaking an aqueous solution of a metal salt (in

[1] Nylen, " Studien über organische Phosphorverbindungen," Diss., Uppsala, 1930.
[2] Arbuzov and Kushikova, *Zhur. obshchei Khim.*, 1936, **6**, 283.
[3] Ford-Moore and Williams, *J.*, 1947, 1465.
[4] Schwarzenbach and Zurc, *Monatsh.*, 1950, **81**, 202.
[5] Petrov, Maklyayev, and Bliznyuk, *Zhur. obshchei Khim.*, 1960, **30**, 1602, 1608.
[6] Goričan and Grdenić, *Proc. Chem. Soc.*, 1960, 288.

excess) with a ligroin solution of the acid ester. In this way uranium(IV) dioctyl methylenebisphosphonate separated at the boundary between the phases. In the presence of an excess of dioctyl methylenebisphosphonic acid these metal salts dissolve, giving complexes soluble in ligroin or benzene and thus providing a method for extraction of the metal ions.[6] A ligroin solution of dioctyl dihydrogen pyrophosphate exhibits an analogous behaviour in contact with an aqueous solution of uranium(IV) sulphate.[7] The instructions for preparation of disodium di-isopropyl, di-n-butyl, and di-n-octyl methylenebisphosphonate described here, are based in principle upon the method used by Nylen [1] for the preparation of the ethyl ester. In our experience, these are the most favourable conditions and any deviation decreases the yield.

Experimental.—Disodium di-isopropyl methylenebisphosphonate. Sodium (10 g., 0·44 mole) was dispersed in xylene, the xylene removed by decantation, and the sodium washed and then covered with dry ether (200 ml.). Absolute ethanol (25·5 ml., 0·44 mole) was added dropwise with cooling and stirring until the sodium had dissolved (about 3 hr.). Di-isopropyl phosphite (73 g., 0·44 mole) was next added slowly with cooling, but when half of it had been added, the solution became clear and cooling was no longer necessary. Methylene iodide (17·6 ml., 0·22 mole) was then added with warming at the beginning, but then with cooling as the reaction proceeded. After being kept overnight, the solution was decanted from sodium iodide, ether was removed by distillation at atmospheric pressure and then other volatile components were distilled off at 0·4 mm. up to 150°. The residual vitreous mass was pulverized, covered with 1 : 1 ether–ethanol (300 ml.), and kept for several hours. The insoluble material was filtered off, washed with ether, and recrystallized from ethanol, giving needles of *sodium di-isopropyl methylenebisphosphonate* (21·5 g., 32% calc. on di-isopropyl phosphite), soluble in water, less soluble in ethanol, and insoluble in common organic solvents (Found: Na, 15·4; P, 20·2. $C_7H_{16}Na_2O_6P_2$ requires Na, 15·1; P, 20·4%).

Disodium di-n-butyl methylenebisphosphonate was prepared in the same way in 30% yield (calc. on dibutyl phosphite). It formed needles, soluble in water, less soluble in ethanol, and insoluble in common organic solvents (Found: Na, 13·4; P, 19·3. $C_9H_{20}Na_2O_6P_2$ requires Na, 13·85; P, 18·7%).

Disodium di-n-octyl methylenebisphosphonate was prepared similarly. However, the liquid by-products could not be removed by distillation alone but washing with ether–ethanol was necessary. The yield was 19% (calc. on di-n-octyl phosphite). On recrystallization from water the *salt* formed colourless crystals, insoluble in organic solvents (Found: Na, 10·45; P, 13·6. $C_{17}H_{36}Na_2O_6P_2$ requires Na, 10·95; P, 14·0%).

Diethyl dihydrogen methylenebisphoshonate was prepared from the silver salt that was precipitated on addition of a solution of silver nitrate to disodium diethyl methylenebisphosphonate in 50% ethanol. The precipitate (1·2 g.) was treated with 10% hydrochloric acid (50 ml.), the filtrate evaporated *in vacuo*, water added (10 ml.) to the residue, and this solution was filtered and evaporated to dryness. The viscous mass (0·41 g.) which remained did not distil without decomposition even *in vacuo*. This acid ester, n_D^{25} 1·4696, is readily soluble in water, ethanol, or chloroform, less soluble in ether or benzene (Found: P, 26·2. $C_5H_{14}O_6P_2$ requires P, 26·7%).

Di-isopropyl dihydrogen methylenebisphosphonate was similarly prepared and had similar properties (Found: P, 24·15. $C_7H_{18}O_6P_2$ requires P, 23·8%).

Di-n-butyl dihydrogen methylenebisphosphonate. To disodium di-n-butyl methylenebisphosphonate (3 g.) in water (25 ml.), 60% sulphuric acid (10 ml.) was added. The oily layer was extracted with 1 : 1 ether–chloroform and recovered by evaporation. The viscous mass (1·8 g.) was dried *in vacuo* over phosphoric pentoxide. It was soluble in ether, benzene, or ethanol, less soluble in light petroleum (Found: P, 21·2. $C_9H_{22}O_6P_2$ requires P, 21·5%).

Di-n-octyl dihydrogen methylenebisphosphonate was prepared as described for the dibutyl derivative. It formed crystals (from octane), m. p. 55°, insoluble in water or dilute acid, soluble in organic solvents (Found: P, 15·4. $C_{17}H_{38}O_6P_2$ requires P, 15·5%).

Thorium diethyl methylenebisphosphonate. To 0·4N-aqueous thorium chloride (5 ml.) a 0·4M-solution (10 ml.) of diethyl methylenebisphosphonate was added. The white precipitate

[7] Grdenić and Korpar, *J. Inorg. Nuclear Chem.*, 1961, **12**, 49.

was filtered off, washed with warm water, ethanol, and ether, and dried *in vacuo*. It is insoluble in all solvents except in a solution of the reagent itself with which it forms a complex (Found: Th, 33·8. $C_{10}H_{24}O_{12}P_4Th$ requires Th, 34·0%).

Thorium di-n-butyl methylenebisphosphonate, similarly prepared, is insoluble in water, dilute acids or organic solvents, but it is soluble in an ether or chloroform solution of the ester (Found: Th, 28·6. $C_{18}H_{40}O_{12}P_4Th$ requires Th, 28·8%).

Uranium(IV) *di-n-butyl methylenebisphosphonate* formed a pale green precipitate, insoluble in water or organic solvents but soluble in a solution of the reagent (Found: U, 29·4. $C_{18}H_{40}O_{12}P_4U$ requires U, 29·4%).

Cerium(IV) *di-n-butyl methylenebisphosphonate* formed a pale yellow precipitate, insoluble in water or organic solvents, but soluble in a solution of the reagent (Found: Ce, 19·6. $C_{18}H_{40}O_{12}P_4Ce$ requires Ce, 19·7%).

Iron(III) *di-n-butyl methylenebisphosphonate* was obtained as a white precipitate, insoluble in water and scarcely soluble in organic solvents (Found: Fe, 11·6. $C_{27}H_{60}Fe_2O_{18}P_6$ requires Fe, 11·5%).

Cobalt(II) *di-n-octyl methylenebisphosphonate*. 0·05M-Aqueous cobalt(II) chloride was extracted with a 0·025M solution of di-n-octyl dihydrogen methylenebisphosphonate in light petroleum. To the organic phase a five-fold amount of ethanol was added. The resulting blue precipitate of *cobalt*(II) *di-n-octyl methylenebisphosphonate* was insoluble in water or organic solvents, but soluble in a solution of the reagent (Found: Co, 12·5. $C_{17}H_{36}CoO_6P_2$ requires Co, 12·2%).

Uranium(IV) *di-n-octyl methylenebisphosphonate* was obtained in the same way as the cobalt salt, except that precipitation with alcohol was not necessary. It was a pale green powder, soluble only in a solution of the reagent (Found: U, 22·9. $C_{34}H_{72}O_{12}P_4U$ requires U, 23·0%).

Di-isopropyl and di-n-butyl phosphite were commercial products [Albright & Wilson (Mfg.) Ltd., London] and were distilled *in vacuo* before use. Di-n-octyl phosphite was prepared in this laboratory from octan-1-ol and phosphorus trichloride.

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94. *Fluorenylcysteines.*

By E. K. WEISBURGER and R. E. BOYD.

MERCAPTURIC ACIDS, $ArS{\cdot}CH_2{\cdot}CH(NHAc){\cdot}CO_2H$, have been identified as metabolites of certain aromatic hydrocarbons, *e.g.*, biphenyl [1] and phenanthrene.[2] In connection with a study of fluorene metabolism carried out in this laboratory,[3] the synthesis of mercapturic acid derivatives was undertaken.

Although the new compound, *S*-2-biphenylylcysteine, was easily prepared by the diazonium salt procedure [4] and acetylated, *S*-2-fluorenylcysteine could not be reproducibly synthesized by this method. In one instance only was the reaction successful. Generally, intractable tars, 2-fluorenol, and cystine were isolated. Boyland and Sims [2] reported somewhat similar difficulties in their syntheses of phenanthrylcysteines. Furthermore, acetylation of the fluorenylcysteine afforded only *S*-2-fluorenylthioacetate and not the desired mercapturic acid.

Two fluorenylcysteines, *S*-9-fluorenylcysteine and *S*-(4-methylenefluorenyl)cysteine, were prepared by Theodoropoulos's method.[5] This method, however, led to loss of optical activity in the products.

[1] West, Lawson, Miller, and Mathura, *Arch. Biochem. Biophys.*, 1956, **60**, 14.
[2] Boyland and Sims, *Biochem. J.*, 1962, **84**, 564.
[3] Grantham, *Biochemistry*, 1963, **2**, 610.
[4] du Vigneaud, Wood, and Binkley, *J. Biol. Chem.*, 1941, **138**, 369; West and Mathura, *ibid.*, 1954, **208**, 315.
[5] Theodoropoulos, *Acta Chem. Scand.*, 1959, **13**, 383.

Chromatographic studies showed that the various cysteines and mercapturic acids had similar R_F values on paper. However, solvent systems were developed which permitted separation of the two classes of compounds by thin-layer chromatography.

Experimental.—M. p.s were taken on a Kofler block. We are indebted to the staff of the N.I.H. Microanalytical Laboratory for analyses. Infrared spectra were determined as potassium bromide discs on a Perkin-Elmer model 21 spectrophotometer.

S-2-*Biphenylylcysteine.* From diazotization of 2-biphenylylamine (20 g.) and coupling with L-cysteine hydrochloride monohydrate (10 g.) according to previously published methods,[4] the crude *product* was obtained (3·5 g.; m. p. 177—180°). Two crystallizations from water (375 ml./g.) afforded white needles, m. p. 186—187° (Found: C, 66·3; H, 5·7. $C_{15}H_{15}NO_2S$ requires C, 65·9; H, 5·5%), $\nu_{max.}$ 3039—2967, 1669, 1557, 1492, 1394 cm.$^{-1}$.

S-2-*Biphenylylmercapturic acid.* Acetylation in cold 2N-sodium hydroxide with acetic anhydride gave almost quantitatively the *mercapturic acid* which melted at 155—157·5° after crystallization from acetone–water and had $\nu_{max.}$ 3401, 2898, 2500, 1712, 1626, 1526, and 1213 cm.$^{-1}$ (Found: C, 64·5; H, 5·5. $C_{17}H_{17}NO_3S$ requires C, 64·7; H, 5·4%).

S-2-*Fluorenylcysteine.* In one attempt, from diazotization of 2-fluorenylamine (5·4 g.) and coupling with L-cysteine hydrochloride monohydrate (2·5 g.), there was obtained, in addition to tars and 2-fluorenol, a material (25 mg.), m. p. 202—203° soluble in carbonate solution and insoluble in dilute ethanol. After crystallization from dilute acetic acid, the m. p. was 204·5—205° (taken rapidly). $\lambda_{max.}$ (in EtOH) 292 and 304 mμ (ε 17,200 and 13,700, respectively) (Found: C, 67·35; H, 5·4; N, 4·5. $C_{16}H_{15}NO_2S$ requires C, 67·3; H, 5·3; N, 4·9%).

Acetylation of this material in pyridine with acetic anhydride yielded *S*-2-fluorenyl thioacetate, m. p. 121·5—122·5°. The infrared spectrum was identical with that of a sample prepared by the method of Ray *et al.*[6] and the mixture m. p. showed no depression. It had $\nu_{max.}$ 1701, 1443, 1400, and 1109 cm.$^{-1}$ (Found: C, 75·3; H, 5·4. Calc. for $C_{15}H_{12}OS$: C, 75·0; H, 5·0%).

Fluorene-2-thiol. Reduction of fluorene-2-sulphonyl chloride [6] (10·0 g.) with lithium aluminum hydride (7·3 g.) gave yellow crystals (3·42 g.), m. p. 83—85°. After six recrystallizations from dilute ethanol, a sample melted at 127—128° (lit.,[6] 127—129°) (mixed m. p. 127—129°), and had $\nu_{max.}$ identical with that of fluorene-2-thiol prepared by the method of Ray *et al.*[6] (2557, 1608, 1449, 1300, and 1066 cm.$^{-1}$).

Further attempted syntheses of 2-fluorenylcysteine. (*A*) A mixture of fluorene-2-thiol (300 mg.) in 5% alcoholic potassium hydroxide (100 ml.) was refluxed with 3-chloroalanine methyl ester (250 mg.) for 1 hr., filtered, and acidified. The white precipitate had an infrared spectrum quite similar to that of authentic arylcysteine [7] but decomposed during efforts to remove inorganic salts. During this work, Iwamoto *et al.*[8] reported successful syntheses of aromatic " nitrogen mustards " by a similar method.

(*B*) Silver 2-fluorenyl sulphide (500 mg.) (from fluorene-2-thiol and silver nitrate) in water–ethanol suspension, or in diethylene glycol or dimethyl sulphoxide solution, on treatment with 3-chloroalanine (920 mg.) apparently formed the desired *S*-2-fluorenylcysteine as shown by colour tests and ultraviolet spectrum of the syrupy product. However, the reaction mixtures were not amenable to the actual isolation of the products.

(*C*) Reaction of acetamidoacrylic acid [9] with fluorene-2-thiol was also unsuccessful in affording isolable amounts of fluorenylmercapturic acid, although the infrared spectrum indicated the presence of the desired compound.

S-9-*Fluorenylcysteine.* L-Cysteine hydrochloride monohydrate (1·75 g.) in absolute ethanol (30 ml.) was treated with metallic sodium (0·92 g.) and 9-bromofluorene (2·45 g.). The mixture was stirred for 5 min., poured into water (50 ml.), and filtered. Adjustment to pH 5 with glacial acetic acid yielded a white precipitate (2·95 g.), m. p. 185—189°. Recrystallization of the *amino-acid* from dimethylformamide–water raised the m. p. to 199—201° (2·50 g., 88%), $\nu_{max.}$ 2976, 1626, 1375, and 1348 cm.$^{-1}$ (Found: C, 67·9; H, 5·7. $C_{16}H_{15}NO_2S$ requires C, 67·3; H, 5·3%). 2-Bromofluorene and 3-bromo-2-nitrofluorenone, a compound containing an activated halogen atom,[10] failed to react under these conditions.

[6] Ray, Argus, and Barth, *J. Org. Chem.*, 1947, **12**, 794.
[7] Fuson, Josien, and Powell, *J. Amer. Chem. Soc.*, 1952, **74**, 1.
[8] Iwamoto, Acton, Ross, Baker, and Goodman, *J. Med. Chem.*, 1963, **6**, 43.
[9] Eiger and Greenstein, *Arch. Biochem.*, 1948, **19**, 467.
[10] Suzuki, Weisburger, and Weisburger, *J. Org. Chem.*, 1961, **26**, 2236.

S-9-*Fluorenylmercapturic acid.* *S*-9-Fluorenylcysteine (500 mg.) in 2N-sodium hydroxide (20 ml.) was chilled to 5° and acetylated with acetic anhydride (0·6 ml.). The mixture was stirred in the cold for 10 min. and neutralized with glacial acetic acid. The yield was 200 mg., the m. p. 193—195° after recrystallization from acetone–cyclohexane, and $\nu_{max.}$ 3300, 1709, 1613, 1543, 1274, and 1239 cm.$^{-1}$ (Found: C, 66·45; H, 5·25. $C_{18}H_{17}NO_3S$ requires C, 66·0; H, 5·2%).

4-*Fluorenylmethanol.* Fluorene-4-carboxylic acid (8·0 g.) was reduced by lithium aluminum hydride (8·0 g.) in the usual manner. The yield, after recrystallization from acetone–water (1 : 1), was 3·29 g. and the m. p. 129—130° (lit.,[11] 129—130°).

S-(4-*Methylenefluorenyl*)*cysteine.* To a boiling solution of 4-fluorenylmethanol (3·24 g.) in acetic acid (200 ml.), 48% hydrobromic acid (33 ml.) was added during 30 min. After 1 hour's refluxing, the cooled mixture was poured into 1 l. of water. The brown precipitate was recrystallized from acetone–water, to yield 1·64 g. of white crystals, m. p. 116—128°. Further recrystallization lowered this range. The crude 4-fluorenylmethyl bromide proved to be of sufficient purity for the next step in the reaction sequence. *S*-(4-Methylenefluorenyl)cysteine was prepared from 4-fluorenylmethyl bromide (1·18 g.) in the manner described for *S*-9-fluorenylcysteine. After recrystallization from dimethylformamide–water (1 : 1) the yield was 404 mg.

TABLE 1.

Paper chromatography.

Compound	R_F in solvent systems * 1	2	3
S-9-Fluorenylcysteine	0·62—0·73	0·82—0·88	0·80—0·87
S-(4-Methylenefluorenyl)cysteine	0·61—0·72	0·82—0·84	0·87—0·90
S-2-Biphenylylcysteine		0·84—0·89	0·88—0·93
S-9-Fluorenylmercapturic acid	0·64—0·79	0·83—0·92	0·90—0·92
S-(4-Methylenefluorenyl)mercapturic acid	0·64—0·80	0·81—0·92	0·85—0·92
S-2-Biphenylylmercapturic acid		0·83—0·91	0·90—0·94

* Solvent systems: (1) butan-2-ol–3% aq. NH_3 (3 : 1); (2) butan-1-ol–acetic acid–water (4 : 1 : 5); (3) propan-1-ol–2N-aqueous NH_3 (1 : 9). Whatman 3M paper was used. Mobilities are listed from back to front of spot. The compounds were detected by spraying the chromatograms with ninhydrin, which revealed the cysteines, and the dichromate–silver nitrate reagent [12] which reacted with both the cysteines and the mercapturic acids.

TABLE 2.

Thin-layer chromatography.

Compound	R_F in solvent systems * 1	2	3
S-9-Fluorenylcysteine	0—0·10	0	0
S-(4-Methylenefluorenyl)cysteine	0—0·10	0	0
S-2-Biphenylylcysteine	0—0·10	0	0
S-9-Fluorenylmercapturic acid	0·14—0·37	0—0·08	0·11—0·19
S-(4-Methylenefluorenyl)mercapturic acid	0·14—0·37	0—0·08	0·10—0·18
S-2-Biphenylylmercapturic acid	0·14—0·37	0—0·08	0·10—0·16

* Solvent systems: (1) *m*-cresol saturated with 0·1M-borate buffer at pH 8·2; (2) chloroform–butan-2-ol–0·05M-sodium benzoate (60 : 36 : 4); (3) propan-1-ol–light petroleum (b. p. 30—60°) (1 : 1) saturated with 0·3M-acetate buffer (pH 6). The support used was silica gel G (Brinkmann Instruments, Inc., Great Neck, L.I., New York). R_F values were not reproducible from one run to another, but the compounds showed the same movement relative to each other.

and the m. p. 152—153°; the ninhydrin and sulphur tests were positive.[12] Infrared bands were at 3400, 3100, 1640, and 1390 cm.$^{-1}$ (Found: C, 68·6; H, 6·4; N, 4·2. $C_{17}H_{17}NO_2S$ requires C, 68·2; H, 5·7; N, 4·7%).

Crystallization from dilute aqueous ammonia afforded the pure *ammonium salt*, m. p. 181—183° (Found: C, 64·7; H, 6·2. $C_{17}H_{20}N_2O_2S$ requires C, 64·5; H, 6·4%).

[11] Quelet and Barge, *Compt. rend.*, 1960, **251**, 1019.
[12] Boyland and Sims, *Biochem. J.*, 1955, **77**, 176.

S-(4-*Methylenefluorenyl*)*mercapturic acid.* Acetylation of the cysteine with acetic anhydride in 2N-sodium hydroxide gave the corresponding mercapturic acid, m. p. 167—169°, $\nu_{max.}$ 3390, 2898, 2513, 1724, 1626, 1534, 1209, and 1179 cm.$^{-1}$ (Found: C, 64·0; H, 6·5; N, 4·35. $C_{19}H_{19}NO_3S,H_2O$ requires C, 63·5; H, 5·9; N, 3·9%).

Chromatography. The cysteine derivatives were chromatographed as described in Tables 1 and 2.

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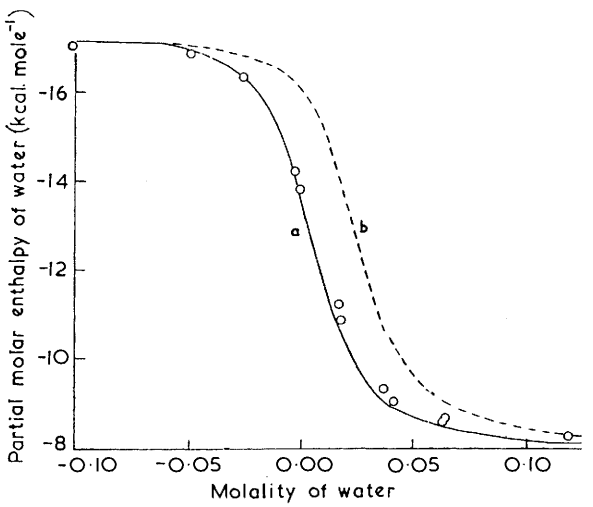
95. *The Partial Enthalpy of Water in the Immediate Vicinity of Pure Sulphuric Acid.*

By G. A. MOUNTFORD and P. A. H. WYATT.

IN an earlier study of the partial enthalpies of solutes in sulphuric acid,[1] we derived some confidence in our experimental results from the good agreement with those of Kunzler and Giauque [2] for water as solute. Since then, however, Giauque and his co-workers have published the final version of their important and extensive results for the sulphuric



(a) Results of Kirkbride and Wyatt.[1]
(b) Recommended values of Giauque *et al.*[3]

○, New experimental points.

acid–water system [3] and have smoothed out apparent inconsistencies in their separate runs in the neighbourhood of the pure acid, favouring a composition shift of as much as 0·02 molal in the water direction. Whilst this appears only a minor detail on the scale of their comprehensive study, the change, if justified, would have serious effects on our former calculations on the equilibria in the pure acid. One cannot treat lightly a disagreement with such experienced investigators, but we found it difficult to believe that our values, based on extensive measurements with compositions cryoscopically related to the pure acid, could be so much in error. An opportunity has now arisen to check the matter.

To provide data for a full comparison of the self-dissociation of the normal and the dideutero-acid, we have adapted the thermal method so that much smaller samples can be used (50 g. in place of 1500 g.). The new apparatus is much simpler and owes much

[1] Kirkbride and Wyatt, *Trans. Faraday Soc.*, 1958, **54**, 483.
[2] Kunzler and Giauque, *J. Amer. Chem. Soc.*, 1952, **74**, 3472.
[3] Giauque, Hornung, Kunzler, and Rubin, *J. Amer. Chem. Soc.*, 1960, **82**, 62.

in design to experience acquired in developing a thermal kinetic method.[4] A small glass vessel has conductance electrodes sealed into the sides near the base, and ground-glass entries in the cap for the thermocouple, heater, and addition devices. The contents are stirred by a rotating magnet and the whole is enclosed in polystyrene foam. Since the composition is checked conductimetrically in the calorimeter itself during a set of measurements, errors due to transfer or storage of stock solutions are completely eliminated.

To test the apparatus before beginning the deuterium work, we have carried out some runs with the hydrogen acid, making additions of pure water beneath the surface of the acid in the cell, following Kunzler and Giauque.[2] Despite the differences in technique, the diagram shows that our new results are much closer to those of Kirkbride and Wyatt than to the revised values of Giauque *et al.*, and we therefore conclude that the older values [1,2] are more reliable. In using Table 1 of the later work,[3] a correction of −0·002 to A should therefore be applied.

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[*Received, May 24th,* 1963.]

[4] Wyatt, *J.*, 1960, 2299; Surfleet, Ph.D. Thesis, Sheffield, 1962.

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96. *The Reaction of Tetramethylsilane with Sulphuric Acid: Dangers in its Use as an Internal Reference Standard in Nuclear Magnetic Resonance Spectroscopy.*

By R. E. REAVILL.

UNTIL the use of the tetramethylammonium ion [1] and methanesulphonic acid [2] as internal reference standards for nuclear magnetic resonance (n.m.r.) spectroscopy in concentrated sulphuric acid were generally accepted, the author used tetramethylsilane [3] which appeared to be slightly soluble. Bubbles of gas formed in the solution were attributed to air or tetramethylsilane vapour. It is now shown that tetramethylsilane is immiscible with sulphuric acid, but shaking at room temperature forms methane and trimethylsilyl sulphate.

The n.m.r. spectrum of a mixture of tetramethylsilane, tetramethylammonium sulphate, and an excess of sulphuric acid, immediately after sealing and shaking, consisted of the tetramethylammonium singlet, a small singlet with τ 9·75 p.p.m. and a medium sized singlet with τ 9·44 p.p.m. The size of the latter increased rapidly on shaking and slowly on storage, that of the small peak remaining constant. After 70 hours all the tetramethylsilane had reacted. Opening the tube and storage at room temperature caused fresh bubbles of gas to appear, these being due to dissolved methane, which was removed by applying a vacuum. Remeasurement of the n.m.r. spectrum then showed no change in the size of the large peak but the small peak had disappeared completely and was thus due to methane (τ 9·87 p.p.m.[4]).

The other product, isolated by extraction with n-pentane, showed chemical shifts in both chloroform and sulphuric acid as for authentic trimethylsolyl sulphate,[5] τ being 9·59 and 9·44 p.p.m., respectively.

Methyl groups are cleaved from silicon as methane by the use of electrophilic reagents.

[1] Personal communication from G. van D. Tiers to H. Hart.
[2] Hart and Law, *J. Amer. Chem. Soc.*, 1962, **84**, 2462.
[3] Katritzky and Reavill, *J.*, 1963, 753.
[4] Schneider, Bernstein, and Pople, *J. Chem. Phys.*, 1958, **28**, 601; Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 52.
[5] Sommer, Pietrusza, Kerr, and Whitmore, *J. Amer. Chem. Soc.*, 1946, **68**, 156.

The earliest reported case was the formation of methane from sulphuric acid and benzylethylmethylpropylsilane,[6] the other product on hydrolysis of the reaction mixture being 1,3-diethyl-1,3-dipropyl-1,3-bis-sulphobenzyldisiloxane, $O(SiEtPr^{n}\cdot CH_2\cdot C_6H_4\cdot SO_3H)_2$. Sulphuric acid often cleaves one methyl group as methane from silyl compounds, forming products which are hydrolysed to the corresponding disiloxane.[7] Eaborn [8] suggested that the low boiling point and low solubility of tetramethylsilane in sulphuric acid prevents this reaction from being observed for tetramethylsilane. Cleavage of the allyl group from allyltrimethylsilane [9] gives propene and a product affording hexamethyldisiloxane on hydrolysis. Tetramethyl-lead gives methane and a trimethyl-lead salt [10] with perchloric or acetic acids.

Chemical shifts previously [3] measured in sulphuric acid should be reduced by 0·56 p.p.m.

Experimental.—Trimethylsilyl sulphate. "AnalaR" sulphuric acid (5·36 g.) and tetramethylsilane (1·22 g.) were shaken together in a sealed tube at 20° for 1½ hr., after which the two layers became one. The sulphate was extracted with dry (P_4O_{10}) pentane. The pentane was evaporated under reduced pressure; the residue solidified at −10° and was purified by sublimation at 30°/0·1 mm., to give square plates which fumed in air.[5]

Spectra were measured at 40 Mc./sec. on a Perkin-Elmer spectrometer with sample spinning. Concentrations were ~10% w/v. Tetramethylammonium sulphate was used as an internal reference (τ 6·80 p.p.m.[1]).

I thank Professor H. Hart and Dr. A. R. Katritzky for helpful discussions, and the D.S.I.R. for a studentship.

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[6] Kipping, *J.*, 1907, 717.
[7] Sommer *et al.*, *J. Amer. Chem. Soc.*, 1951, **73**, 882; 1953, **75**, 2932, 3765.
[8] Eaborn, "Organosilicon Compounds," Butterworths Scientific Publns., London, 1960, p. 129.
[9] Sommer, Tyler, and Whitmore, *J. Amer. Chem. Soc.*, 1948, **70**, 2872.
[10] Robinson, *J. Org. Chem.*, 1963, **28**, 843.

97. *The Direct Oxidation of Aliphatic Iodides to Carbonyl Compounds.*

By A. P. JOHNSON and A. PELTER.

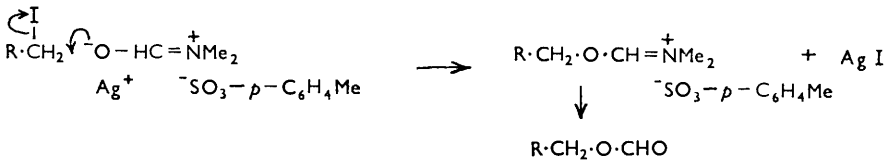
OXIDATION of α-halogeno-ketones,[1] α-halogeno-esters,[2] and benzyl halides [3,4] to the corresponding carbonyl compounds by dimethyl sulphoxide has been acccomplished under a variety of conditions. We now report the direct oxidation of aliphatic iodides by this reagent.

Kornblum and his co-workers stated [4] that halides less reactive than benzyl halides must be converted into toluene-*p*-sulphonates before oxidation. The conversion was carried out by reaction of the iodide with silver toluene-*p*-sulphonate in acetonitrile.

In certain cases, difficulty was found in the latter reaction. For instance, 8-chloro-oct-1-ene after being kept overnight and then refluxed for two hours with a solution of silver toluene-*p*-sulphonate in acetonitrile was still only partially converted into the sulphonate. With 8-iodo-oct-1-yne the conversion was not possible, even at room temperature, owing to fast coupling reactions. Other solvents did not speed up the reaction;

[1] Kornblum, Powers, Anderson, Jones, Larsen, Levand, and Weaver, *J. Amer. Chem. Soc.*, 1957, **79**, 6562.
[2] Hunsberger and Tien, *Chem. and Ind.*, 1959, 88.
[3] Nace and Monagle, *J. Org. Chem.*, 1959, **24**, 1792; U.S.P. 2,888,488.
[4] Kornblum, Jones, and Anderson, *J. Amer. Chem. Soc.*, 1959, **81**, 4133.

use of dimethylformamide led to large quantities of formate esters, presumably by nucleophilic attack on the iodide by the silver toluene-*p*-sulphonate complex of dimethylformamide:[5,6]



We therefore re-examined the direct oxidation of the halides themselves. In 4 minutes at 150° with dimethyl sulphoxide, octyl chloride gave only 2% of the aldehyde, but octyl iodide yielded 74% of aldehyde. This proved to be a general reaction and makes conversion into the sulphonate unnecessary whilst broadening the scope of the reaction. Results are presented in the Table. The yields are calculated from the iodides. At least 97% yields of iodide were always obtained (analysis by vapour-phase chromatography) when a refluxing solution of the chloride in acetone was stirred with an excess of *solid* sodium iodide, reactions being complete after 18 hours.

Oxidation of 8-iodo-octan-2-one was unsatisfactory owing to rapid aldol condensation. Dodecyl iodide was immiscible with dimethyl sulphoxide and at first gave a low yield of aldehyde, but use of 1,2-dimethoxyethane as co-solvent proved satisfactory.

Formation of aldehydes from iodides.

Iodide	Reaction time (min.)	Temp.	Yield (%)	Isolated as
$Me\cdot[CH_2]_5$	3	150°	86	DNP *
$Me\cdot[CH_2]_7$	4	148	74	,,
$Me\cdot[CH_2]_{11}$	3	150	44	,,
	4	150	64	,, †
$CH_2{=}CH\cdot[CH_2]_6$	4	145	83	,,
$CH{\equiv}C\cdot[CH_2]_6$	4	150	70	Aldehyde
$CH_3\cdot CO\cdot[CH_2]_6$	4	145	25	,,

* 2,4-Dinitrophenylhydrazone. † $(CH_2\cdot OMe)_2$ used as co-solvent.

6-Iodohexan-1-ol was also oxidised to give 62% yield of the aldehyde 2,4-dinitrophenylhydrazone that was eluted in a pure state from a Bentonite–kieselguhr column; analysis of this product was not totally satisfactory but a mass spectrum showed it to be the required compound. All the products denoted in the Table have been identified by analysis or by comparison of the infrared spectrum and melting point (also mixed melting point) with authentic specimens.

An attempt to combine the conversion into the iodide with the oxidation, by addition of the chloride to a mixture of sodium iodide and sodium hydrogen carbonate in dimethyl sulphoxide, did not succeed, the exchange being much slower than the oxidation. If the mixture was left for a longer time aldols were obtained and the best yield of aldehyde was only 20%.

Use of pyridine as proton acceptor was unsatisfactory: 1-iodoheptane with pyridine and dimethyl sulphoxide gave no aldehyde in 4 hour at 100°.

We next tried to extend the reaction to secondary iodides. 2-Iodo-octane was oxidised by dimethyl sulphoxide in the presence of magnesium oxide at 150° for 1 hour to give octan-2-one (identified as dinitrophenylhydrazone) in 32% yield. Cyclohexyl iodide did not react under these conditions, presumably owing to the fixed conformation such that S_N2 attack is not favoured. Heating cyclohexyl chloride with dimethyl sulphoxide in the presence of silver acetate gave 9·7% of cyclohexanone.

[5] Chang and Blickenstaff, *J. Amer. Chem. Soc.*, 1958, **80**, 2906.
[6] Kuhn and Schretzmann, *Angew. Chem.*, 1955, **67**, 785.

The mechanism of the oxidation has been formulated [2,3] as an S_N2 displacement followed by concerted elimination of a proton and dimethyl sulphide:

$$R\cdot CH_2X + \bar{O}-\overset{+}{S}Me_2 \longrightarrow R\cdot \underset{H}{CH}-O-\overset{+}{S}Me_2 \; {}^{+X^-} \longrightarrow R\cdot CHO + SMe_2 + H^+ + X^-$$

The ease of oxidation of certain benzyl halides suggests, however, that a different mechanism may be possible. Thus, diphenylmethyl chloride gave benzophenone in 44% yield under normal oxidation conditions.[3] In view of the lack of reactivity of even primary aliphatic chlorides this may be formulated as follows:

$$Ph_2CHCl \longrightarrow Ph_2\overset{+}{H}C\ \overset{-}{Cl} \longrightarrow Ph_2CH\cdot O\cdot\overset{+}{S}Me_2 \longrightarrow Ph_2CO + SMe_2 + H^+$$

The reaction of cyclohexyl chloride in dimethyl sulphoxide in the presence of a silver salt may proceed similarly.

Experimental.—The following experiments are typical.

8-Iodo-oct-1-yne. 8-Chloro-oct-1-yne (5·05 g., 34·9 mmoles) was added to a stirred refluxing mixture of sodium iodide (12 g., 80 mmoles) and dry acetone (40 ml.) and the stirred mixture was allowed to reflux for 18 hr., poured into water, and extracted into ether. The combined ether extracts were dried ($MgSO_4$) and filtered, and the ether was removed by distillation through a Dufton column to give the iodide (8·12 g., 99·6%). This was shown to contain at least 99% of iodide by analysis on a 6-ft. silicone–Celite column at 170°. The *iodide* had b. p. 64·0—64·5°/1 mm., n_D^{19} 1·5058 (Found: C, 41·3; H, 5·75; I, 53·2. $C_8H_{13}I$ requires C, 40·7; H, 5·55; I, 53·6%).

Oct-7-ynal. To a stirred mixture of dimethyl sulphoxide (30 ml.) and sodium hydrogen carbonate (4 g.), at 150° under dry nitrogen was added 8-iodo-oct-1-yne (1·64 g., 6·95 mmoles). After 4 min. the mixture was rapidly cooled and then poured into water. The aqueous solution was extracted with ether (4 × 50 ml.). The combined extracts were washed with water, dried ($MgSO_4$), and filtered. The ether was removed by distillation through a Dufton column to give the crude aldehyde (0·862 g.).

To this material (0·291 g.), an excess of Brady's reagent was added. The product was chromatographed on kieselguhr–bentonite (1 : 3), to give the pure *2,4-dinitrophenylhydrazone*, m. p. 99—100° (0·5 g., 70%) (Found: C, 55·25; H, 5·7. $C_{14}H_{16}N_4O_4$ requires C, 55·25; H, 5·3.

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98. *Polyphosphoric Acid-catalyzed Reactions. Part II.* The Synthesis of 3-Nitroquinolines.*

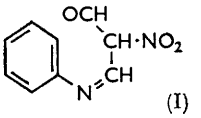
BY FRANK D. POPP and PETER SCHUYLER.

UHLE and JACOBS [1] reported attempts to prepare 3-nitroquinoline (II) from *N*-(2-nitro-3-oxopropylidene)aniline (I). They found that acetic anhydride, concentrated sulphuric acid, potassium hydrogen sulphate, and sodium ethoxide all failed to cause cyclization. However, with anhydrous zinc chloride at 200° 3-nitroquinoline was obtained in 21% yield. Morley and Simpson [2] obtained a 41% yield of 3-nitroquinoline by refluxing a solution of aniline hydrochloride and the Schiffs base (I) in acetic acid for 17 hours, and in a similar manner prepared a number of substituted 3-nitroquinolines. This intramolecular acylation would seem to be ideally suited to catalysis by polyphosphoric acid.[3]

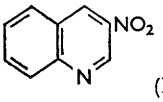
* Part I, Popp, *J. Org. Chem.*, 1962, **27**, 2658.

[1] Uhle and Jacobs, *J. Org. Chem.*, 1945, **10**, 76.
[2] Morley and Simpson, *J.*, 1948, 2024.
[3] Popp and McEwen, *Chem. Rev.*, 1958, **58**, 321.

We have found that when *N*-(2-nitro-3-oxopropylidene)aniline is heated at 140° for 10 minutes with polyphosphoric acid a 29% yield of 3-nitroquinoline is obtained. Varying the reaction time from 15 to 110 minutes and the temperature from 120° to 170° had little effect on the yield. In a similar manner *N*-(2-nitro-3-oxopropylidene)-β-naphthylamine



(I)



(II)

with polyphosphoric acid at 140° (10 minutes) gave a 78% yield of 3-nitro-5,6-benzoquinoline. In this case an increase in temperature to 200° decreased the yield to 50% while at 85° (50 minutes) no quinoline was obtained. A number of other *N*-(2-nitro-3-oxopropylidene)anilines were subjected to this cyclization at 140° for 10 minutes (without an attempt to find the ideal conditions for each case): the results (see Table) show that both in yield and in ease of reaction conditions the polyphosphoric acid-catalyzed reaction is

Cyclization of 2-nitro-3-oxopropylidenaniline.

Quinoline obtained	Yield * (%)	M. p. Obsd.	M. p. Lit.	Reported yields $ZnCl_2$, 200°	Reported yields Ar·NH_3Cl, 17 hr.
3-Nitro-	29	125—126°	127—128° †	21 †	41 §
3-Nitro-5,6-benzo-	78	152—154	155—156 †	77 †	—
6,7-Dimethoxy-3-nitro-	58	213—214	213 ‡	—	—
6-Methyl-3-nitro-	58	183—185	185—186 §	17 §	77 §
8-Methyl-3-nitro-	17	118—121	122—123 §	—	6 §
3,6-Dinitro-	0 ¶	—	—	—	0 §

* For conditions see text. † See ref. 1. ‡ Clemo and Swan, *J.*, 1952, 867. § See ref. 2. ¶ Substantial amounts of *p*-nitroaniline were isolated.

superior to the zinc chloride method. While the amine hydrochloride method may have something to offer in the way of yields in a few cases, the polyphosphoric acid reaction is much more convenient with a reaction time of only 10 minutes compared with 16 hours and does not require the formation of the hydrochloride of the amine. In view of the ready availability of starting materials [4] it seems that the ease and convenience of our method makes it the method of choice for this cyclization.

Experimental.—*3,4-Dimethoxy*-N-(*2-nitro-3-oxopropylidene*)*aniline.* A solution of sodium nitromalonaldehyde (5·2 g.) in water (35 ml.) was added to 4-aminoveratrole (5·0 g.) in 2% hydrochloric acid (175 ml.). Filtration gave an orange solid which recrystallized from ethanol to give 3·6 g. of solid, m. p. 150° (Found: C, 52·7; H, 4·9; N, 10·9. Calc. for $C_{11}H_{12}N_2O_5$: C, 52·4; H, 4·8; N, 11·1%).

The remaining propylidenanilines were prepared in 77—92% yield by a similar sequence.[1,2]

Cyclization. The *N*-(2-nitro-3-oxopropylidene)aniline (1 g.) and commercial polyphosphoric acid (100 g.) were heated with stirring while the temperature was brought to 140° (10—20 min.). The mixture was then stirred at 140° for 10 min., poured on ice, and filtered. The filtrate was neutralized with aqueous sodium hydroxide and extracted with chloroform. Concentration of the chloroform extract and recrystallization of the residue from ethanol, when necessary, gave the 3-nitroquinolines described in the Table.

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[4] Fanta and Stein, *Chem. Rev.*, 1960, **60**, 261.

99. *Infrared and Proton Resonance Measurements of some Stannanes and Germane.*

By P. E. Potter, L. Pratt, and G. Wilkinson.

Proton resonance lines of hydrogen bound to transition metals in complexes lie at characteristically high values,[1] *ca.* 5—25 p.p.m. on the high-field side of tetramethylsilane. Protons bonded to a few non-transition metal atoms (*e.g.*, in hydrogen iodide) also occur above tetramethylsilane. For comparison, we now report proton resonance and infrared spectra of some hydrides of tin and germanium; our results are in substantial agreement with those of Flitcroft and Kaesz.[2]

Proton Resonance Spectra.—Chemical shifts and metal–hydrogen coupling constants for the hydridic protons of n-butylstannanes, tri-n-propylstannane, stannane, and germane are listed in Table 1. The resonances of protons in the Sn–H and Ge–H bonds lie on the low-field side of tetramethylsilane, showing that a proton bonded to a heavy-metal atom does not always have a large diamagnetic shielding. Also, the shielding in the hydrides

Table 1.

Chemical shifts and coupling constants.

Compound	τ (±0·02)	J(H–^{117}Sn) (c./sec.) (±2)	J(H–^{119}Sn) (c./sec.) (±2)	J_{119}/J_{117}
SnH_4	6·11	1842	1933	1·049
Bu^nSnH_3	5·98	1720	1800	1·047
$Bu^n_2SnH_2$	5·23	2119	2219	1·047
Bu^n_3SnH	7·93	1650	1722	1·044
Pr^n_3SnH	—	1530	1600	1·046
GeH_4	6·83	—	—	—

Table 2.

Chemical shifts and electronegativites of the central atoms, in group IVB hydrides.

Compound	CH_4	SiH_4	GeH_4	SnH_4
τ	9·96	6·96	6·83	6·11
Electronegativity *	2·60	1·90	2·00	1·93

* Allred and Rochow, *J. Inorg. Nuclear Chem.*, 1958, **5**, 269.

Table 3.

Infrared spectra of tin hydrides (ν in cm.$^{-1}$).

Compound	SnH_4	Bu^nSnH_3	$EtSnH_3$	$MeSnH_3$	$Bu^n_2SnH_2$	Me_2SnH_2	Bu^n_3SnH	Pr_3SnH
ν(Sn–H)	1906	1865	1869	1876	1842, 1835	1856	1808, 1820	1795, 1820
Ref.	*a*	*b*	*c*	*c*	*b* 7	*d*	*b* 7	*b* 7

a, G. R. Wilkinson, personal communication. *b*, This work. *c*, Emeléus and Kettle, *J.*, 1958, 2444. *d*, Kettle, *J.*, 1959, 2936.

MH_4 does not correlate with the electronegativity of the metal M (Table 2). The position of the SnH proton resonance varies with the number of alkyl groups on the tin atom, but there is no simple relation between the relative shifts and the number of groups. An inductive contribution to the shifts might be expected to increase regularly with the number of alkyl groups, but it is possible that contributions to the shielding due to magnetic anisotropy of the tin atom, which would arise if these alkyl hydrides do not have regular tetrahedral structures, would not vary regularly with increasing substitution. In those molecules containing the isotopes ^{117}Sn ($I = \frac{1}{2}$, $\mu = 0{\cdot}9949$, abundance = 7·67%) and ^{119}Sn ($I = \frac{1}{2}$, $\mu = 1{\cdot}0409$, abundance = 8·68%) the hydride line is split into a doublet

[1] See Wilkinson, "Advances in the Chemistry of the Coordination Compounds," Macmillan Co., New York, 1961, p. 50.

[2] Flitcroft and Kaesz, *J. Amer. Chem. Soc.*, 1963, **85**, 1377.

by coupling between the proton and the spin of the tin nucleus. This gives rise to two pairs of satellite hydride lines for the natural isotopic mixture. The ratios of the splittings for the two isotopes are constant and equal to the ratio of the nuclear magnetic moments of the two tin isotopes within the limits of experimental error. As with the shifts, the values of the splittings do not vary smoothly with the number of alkyl groups (Table 1). In contrast, the Sn–H couplings in methyltin chlorides show a smooth increase with increasing number of chlorine atoms bonded to the tin.[3] This was attributed to an increase in the amount of *s*-character in the hybrid orbitals used by the tin in the Sn–C bonds, the major part of the coupling being by the " contact " interaction. In the hydrides, changes in the amount of *s*-character in the Sn–H bonds could also result from departures from a regular tetrahedral structure.

In absolute terms, the Sn–H splittings are much larger than those of protons bonded to lighter atoms whose nuclei have magnetic moments about the same as those of tin. Thus the ^{13}C–H splitting in CH_4 is 125 c./sec.[4] (^{13}C has $\mu = 0{\cdot}702$) and the ^{29}Si–H splitting in SiH_4 is 202·5 c./sec.[5] (^{29}Si has $\mu = -0{\cdot}555$). It has been shown by Schneider and Buckingham [6] that the nuclei of heavy atoms might be expected to give such large coupling constants, since the value of the $|\psi^2|$ term, which determines the magnitude of the contact interaction, is large for large values of the effective nuclear charge.

Infrared Spectra.—Comparison of the spectra of tri-n-butylstannane and deuterostannane shows that the Sn–H and Sn–D stretching frequencies can be assigned as *ca.* 1808 and 1300 cm.$^{-1}$, respectively. Lesbre *et. al.*[7] had given the former frequency as *ca.* 1820 cm.$^{-1}$ for trialkylstannanes. The values found in the present work are given in Table 3; the bands were all very broad and were no better resolved when calcium fluoride optics were used. No solvent effect was observed; most of the spectra were measured in the presence of dibutyl ether. The decrease in the Sn–H stretching frequency with increasing number of alkyl groups may be the result of increasing repulsions between these groups and the hydridic proton. A similar effect was observed [8] for alkylsilanes.

Experimental.—Germane was prepared by reducing a solution of germanium tetrabromide in dilute hydrobromic acid with sodium borohydride, as described by Piper and Wilson.[9] The gaseous product was condensed and then distilled into a small-diameter tube containing cyclohexane used as the internal reference for the nuclear magnetic resonance spectrum. The tube was sealed before measurement of the spectrum.

Stannane was prepared by similar reduction of stannous chloride in dilute hydrochloric acid.[10] This gas was condensed in a small-diameter tube containing carbon disulphide, and also tetramethylsilane as an internal reference for the nuclear magnetic resonance spectrum.

n-Butylstannanes and tri-n-propylstannane. Tri-n-butyl-, di-n-butyl-, and tri-n-propylstannane were prepared by reduction of the corresponding alkyltin chloride (from Pure Chemicals Ltd.) by lithium aluminium hydride in diethyl ether.

Trichloro-n-butyltin was prepared by refluxing tin tetrachloride with an excess of tetra-n-butylstannane and distilling the product under reduced pressure. A similar method was used to prepare chlorotri-n-propyltin. These chlorides were reduced with lithium aluminium hydride to obtain the corresponding stannanes.

Tri-n-butyl deuteriostannane was obtained by reducing the chloride in diethyl ether with lithium aluminium deuteride (Metal Hydrides Inc., Beverly, Mass.).

The nuclear magnetic resonance spectra were measured at 56·45 Mc./sec. on a Varian Associates spectrometer. The spectra of stannane and germane were measured under pressure

[3] Holmes and Kaesz, *J. Amer. Chem. Soc.*, 1961, **83**, 3903.
[4] Muller and Pritchard, *J. Chem. Phys.*, 1959, **31**, 768.
[5] Ebsworth and Turner, *J. Chem. Phys.*, 1962, **36**, 2628.
[6] Schneider and Buckingham, *Discuss. Faraday Soc.*, 1962, **34**, 154.
[7] Lesbre, Mathis-Noël, and de Roche, *Compt. rend.*, 1956, **243**, 257.
[8] Westermark, *Acta Chem. Scand.*, 1955, **9**, 947.
[9] Piper and Wilson, *J. Inorg. Nuclear Chem.*, 1957, **4**, 22.
[10] Schaeffer and Emilius, *J. Amer. Chem. Soc.*, 1954, **76**, 1204.

in CCl_4 at *ca.* −20°. The infrared spectra were measured on a Perkin-Elmer model 21 double-beam spectrophotometer with calcium fluoride and sodium chloride optics.

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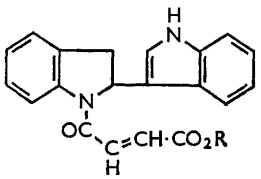
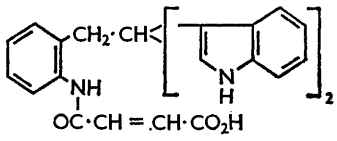
100. *Addition Reactions of Heterocyclic Compounds. Part XVII.* Products from Indole and Maleic Anhydride.*

By R. M. ACHESON, R. S. FEINBERG, and A. R. HANDS.

INDOLE and maleic anhydride in ethyl acetate in the cold yield a 2 : 1 molar adduct,[1] but at room temperature or at the b. p. a 3 : 1 molar adduct has now been obtained. The first adduct must have structure (I). The methyl ester was different from the *trans*-ester (II) which was synthesised from indole dimer [2] and *trans*-3-methoxycarbonylacryloyl chloride; this acid chloride was obtained, surprisingly, from *cis*-3-methoxycarbonylacrylic acid and thionyl chloride. Hydrogenation of the methyl ester (II) gave the same dihydro-ester as was obtained from the acid (I) by hydrogenation and esterification; the corresponding

(I) *cis*; R = H
(II) *trans*; R = Me





(III)

dihydro-acids were also identical. Compounds (I) and (II) with concentrated potassium hydroxide gave indole and indol-3-ylsuccinic acid. Presumably the alkali removes the 1-hydrogen atom of the indole ring giving the resonance stabilised anion and a Michael addition from the 3-position of this ring to the side-chain leads to a 6-membered cyclic intermediate which disintegrates to the products isolated. At this stage the independant studies of Noland and Hammer [3] on this interesting reaction were discovered and our investigation was discontinued.

The long-wavelength absorption band possessed by the *trans*-ester (II), but not by the *cis*-acid (I), closely resembles those of the two minor products [3] from maleic anhydride and 2-methyl- and 1,2-dimethyl-3-(2-indolinyl)indole, and supports the suggestion [3] that these products are fumaric acid derivatives.

The structure of the 3 : 1 molar adduct (III) follows from its hydrolysis to tri-indole [4] and its synthesis from tri-indole and maleic anhydride. There is a remarkable correspondence of weak absorption maxima in the 4·2—5·5 μ region for the *cis*-compounds (I) and (III).

Experimental.—Ultraviolet absorption spectra are for solutions in methanol and are given in mμ ($10^{-4}\varepsilon$ in parentheses). Infrared absorption spectra are for Nujol mulls, and the major peaks for the 2·5—7 μ region are listed. Inflexions are marked with an asterisk.

4-[2-(*Indol*-3-*yl*)*indolin*-1-*yl*]-4-*oxobut*-cis-2-*enoic acid* (I). Indole (24 g.) and maleic anhydride (20 g.), dissolved in ethyl acetate (150 ml.) at room temperature, were left at about 0° for 9 weeks. The *cis*-butenoic acid (16·1 g.) was slowly precipitated; it recrystallised from methanol as yellow prisms, m. p. 162° (decomp.) [lit., 157°,[1] 162—163·5° (decomp.) [3]] (Found: C, 72·4; H, 4·9; N, 8·5; active H, 0·56. Calc. for $C_{20}H_{16}N_2O_3$; C, 72·3; H, 4·8; N, 8·4;

* Part XVI, *J.*, 1963, 3888.

[1] Diels, Alder, and Lübbert, *Annalen*, 1931, **490**, 277.
[2] Hodgson and Smith, *J.*, 1957, 3544.
[3] Noland and Hammer, *J. Org. Chem.*, 1960, **25**, 1536, 1525; 1958, **23**, 320.
[4] Erlenmeyer and Schoemauer, *Helv. Chim. Acta*, 1937, **20**, 1008.

active H, 0·60%), $\lambda_{max.}$ 289·5 (1·09), 280 (1·23), and 257 (1·31), $\nu_{max.}$ 3·05, 4·23w, 4·43w, 4·73w, 5·32w, 5·86, 6·19, 6·26, 6·50, 6·65, 6·90, and 6·96 μ. Treatment with diazomethane in ether–methanol gave the ester as a glass which crystallised on trituration with acetone after many unsuccessful attempts. It had m. p. 151—152° (lit.,[1] 151°), $\lambda_{max.}$ 289 (1·15), 281 (1·32), and 262 (1·40), $\nu_{max.}$ 3·15, 3·29w, 5·80, 6·16, 6·28, 6·45w, 6·75, 6·85, and 6·99 μ.

Hydrogenation of the acid (I) (5·0 g.) in methanol (150 ml.) over 5% palladised charcoal (2·0 g.) for 2 hr. at 5 atm. gave the corresponding butanoic acid (4·7 g.) which separated from ether or acetonitrile as prisms, m. p. 170—171° (decomp.) (lit.,[1] 169—170°) (Found: C, 71·6; H, 5·4; N, 8·2; active H, 0·83. Calc. for $C_{20}H_{18}N_2O_3$: C, 71·8; H, 5·4; N, 8·4; active H, 0·60%), $\lambda_{max.}$ 289 (0·93), 279 (1·13), and 254 (1·79), $\nu_{max.}$ 2·99, 3·25, 3·75w, 5·86, 6·10, 6·28, 6·47w, 6·78, and 6·90 μ. The methyl ester of this butanoic acid, obtained with diazomethane, was a glass which in our hands failed to crystallise (lit.,[1] m. p. 132—133°). The solid obtained on refluxing the crude ester (1·0 g.) with benzylamine (3 ml.) and ammonium chloride (0·1 g.) for 0·5 hr., followed by cooling, was washed with acetone, and crystallisation from methanol gave *NN'*-dibenzylsuccinamide as colourless plates, m. p. 209—210° (Found: C, 73·3; H, 7·1; N, 9·4. $C_{18}H_{20}N_2O_2$ requires C, 73·0; N, 6·8; N, 9·5%). An authentic specimen obtained similarly from dimethyl succinate had the same m. p., undepressed mixed m. p., and $\nu_{max.}$ 3·03, 3·25w, 6·13, 6·45, 6·72w, 6·90, and 7·00 μ.

Methyl 3-*chloroformyl*-trans-*acrylate*. Maleic anhydride (68 g.) and methanol (29 ml.) were heated on a steam-bath for 1 hr. and, after it had cooled, freshly distilled thionyl chloride (50 ml.) was added slowly and the mixture refluxed for 1·5 hr. Next day the colourless precipitate was collected, and recrystallisation from water gave methyl hydrogen fumarate (0·62 g.), m. p. 144—145° (lit.,[4] 143°) (Found: C, 46·1; H, 4·7; OMe, 23·7. Calc. for $C_5H_6O_4$: C, 46·2; H, 4·6; OMe, 23·8%). Distillation of the filtrate gave methyl 3-chloroformyl-*trans*-acrylate (55·6 g.), b. p. 72—76°/10 mm., n_D^{16} 1·4708 (lit.,[4] b. p. 70—71°/14 mm.) (Found: C, 40·6; H, 3·3; Cl, 23·6. Calc. for $C_5H_5ClO_3$: C, 40·5; H, 3·4; Cl, 23·6%).

The acid chloride (1·0 g.) was shaken with 10% aqueous sodium hydroxide (25 ml.) at room temperature for 1 hr. Subsequent acidification precipitated fumaric acid (0·63 g., 80%), m. p. and mixed m. p. 283° (sealed tube). The acid chloride with an excess of methanol gave dimethyl fumarate (85% yield), identified by its m. p. and mixed m. p. 103—104°, and infrared absorption spectrum.

Methyl 4-[2-*indol*-3-*yl*)*indolin*-1-*yl*]-4-*oxobut*-trans-2-*enoate* (II). A blood-red solution of methyl 3-chloroformyl-*trans*-acrylate (7·8 g.) in dimethylaniline (50 ml.) was added to indole dimer (12·4 g.) in dimethylaniline (125 ml.) at 0°, and the mixture allowed to attain room temperature. After 2 hr. chloroform (500 ml.) was added, and the solution was washed with 5N-hydrochloric acid, dried ($MgSO_4$), and evaporated to about 60 ml. After 3 days a yellow powder (3·0 g.), which was precipitated slowly, was collected and the filtrate evaporated *in vacuo*. The residual oil in benzene–ether (9 : 1 v/v) was chromatographed on deactivated alumina [5] (500 g.). The fast-moving, yellow compound was eluted and obtained as an oil which solidified after 3 weeks. Crystallisation from methanol now gave the *methyl butenoate* (4·6 g.) as yellow needles, m. p. 144—145° (Found: C, 72·8; H, 5·3; N, 8·0. $C_{21}H_{18}N_2O_3$ requires C, 72·8; H, 5·2; N, 8·1%), $\lambda_{max.}$ 323 (0·81), 288 (1·02), and 280 (1·06), $\nu_{max.}$ 2·98, 5·80, 6·02, 6·18, 6·28, 6·42w, 6·78, 6·88, and 7·00 μ.

Hydrogenation of this ester (1·0 g.) in methanol (100 ml.) over Adams catalyst (0·3 g.) at 5 atm. for 2 hr. and evaporation *in vacuo* gave a viscous oil with an infrared absorption spectrum identical with that of the methyl ester prepared from the reduced *cis*-acid. The viscous oil with aqueous-ethanolic alkali at room temperature was hydrolysed and, after acidification, the resulting acid was collected with chloroform, crystallised from acetonitrile, and was identical in m. p., mixed m. p., and infrared absorption spectrum with the hydrogenation product of the adduct (I).

The yellow powder, which was virtually insoluble in all solvents examined, recrystallised from formamide as needles, m. p. 313° (hot stage) (Found: C, 73·2; H, 5·4; N, 8·6; OMe, 7·9; S, 0·9. $C_{21}H_{18}N_2O_3$ requires C, 72·8; H, 5·2; N, 8·1; OMe, 9·0%), $\nu_{max.}$ 2·93, 5·75, 5·93, 6·28, 6·69, and 6·88 μ. This *substance* gave an Ehrlich reaction and was not examined further.

Reaction of 4-[2-(*indol*-3-*yl*)*indolin*-1-*yl*]-4-*oxobut*-cis-2-*enoic acid with alkali*. The acid (5·0 g.) was refluxed with 30% aqueous potassium hydroxide (50 ml.) for 4 hr., then the mixture

[5] Jackson and Manske, *Canad. J. Res.*, 1935, **17***b*, 170; Perron and Minor, *J. Org. Chem.*, 1959, **24**, 1165.

was cooled and extracted with ether (3 × 100 ml.). Evaporation of the dried ($MgSO_4$) extract gave indole (1·7 g.) which, after steam-distillation and recrystallisation from water, was identified by m. p. and mixed m. p. 50—52°, and infrared absorption spectrum comparison. Ether-extraction of the acidified aqueous layer, followed by evaporation and crystallisation of the residue from water, gave indol-3-ylsuccinic acid as needles, m. p. 200° (decomp.) [lit.,[5] 197°, 204—205° (decomp.)] (Found: C, 62·0; H, 4·8; N, 6·3; active H, 1·28. Calc. for $C_{12}H_{11}NO_4$: C, 61·8; H, 4·7; N, 6·3; active 3H, 1·42%), $\lambda_{max.}$ 289 (0·61), 280·5 (0·72), 274* (0·67), and after acidification 288·5 (0·67), 2·78·5 (0·77), and 273 (0·74).

Hydrolysis of methyl 4-[2-(*indol*-3-*yl*)*indolin*-1-*yl*]-4-*oxobut*-trans-2-*enoate*. The ester (1·0 g.), methanol (10 ml.), potassium hydroxide (7·5 g.), and water (15 ml.) were refluxed for 3·5 hr., then diluted with water (50 ml.), and the methanol was removed *in vacuo*. The precipitated indole, combined with that obtained on ether-extraction (total 0·27 g.), was identified as in the previous experiment. Acidification of the basic solution gave indol-3-yl-succinic acid (0·6 g.) which after crystallisation was identical in m. p., mixed m. p., and infrared absorption spectrum with the specimen described before.

3-{o-[2,2-*Di*(*indol*-3-*yl*)*ethyl*]*phenylcarbamoyl*}-cis-*acrylic acid* (III). (i) Saturated hot solutions of indole (25 g.) and maleic anhydride (20 g.) in the minimum of ethyl acetate (about 25 ml. for each) were mixed and refluxed for about 3·5 hr. The solvent was then removed *in vacuo* and the residual red oil, on trituration with methanol at 0°, solidified to the *acid* (7·88 g.), m. p. 188° (decomp.), which decomposed slowly on storage and more rapidly in hot solvents. For analysis the compound was recrystallised from nitromethane, powdered in an agate mortar, and extracted rapidly with a little boiling ethyl acetate; it then had m. p. 191° (decomp.) (Found: C, 74·7; H, 4·8; N, 9·4; active H, 0·80. $C_{28}H_{23}N_3O_3$ requires C, 74·8; H, 5·1; N, 9·4; active 4H, 0·89%), $\lambda_{max.}$ 291 (1·43), 282 (1·62), 276* (1·42), and after acidification 289 (2·31), 281 (2·65), and 274* (2·37), $\nu_{max.}$ 2·92, 3·02, 3·20w, 3·25w, 4·23w, 4·46w, 4·71w, 5·30w, 5·84, 6·16, 6·38, 6·54, 6·80, and 6·91 μ. It gave a positive Ehrlich reaction, a tar on attempted methylation, and no reaction with 2,4-dinitrophenylhydrazine.

(ii) Tri-indole (1·0 g.) in methylene chloride–acetonitrile–methanol (36 ml.; 1 : 1 : 1 v/v) was heated with maleic anhydride (0·35 g.) for 1 hr. on a steam-bath. The residual solid, obtained on evaporation, crystallised from methanol, yielding the acid (III) as yellow needles (0·85 g.), m. p. 186—187°, identical in mixed m. p. and infrared absorption spectrum with a sample prepared by method (i).

The acid (III) (2·0 g.), sodium hydroxide (45 g.), methanol (100 ml.), and water (50 ml.) were refluxed for 3·5 hr., more water (100 ml.) was added, and the methanol distilled off. On cooling, a solid (1·43 g.) separated. Crystallisation from carbon tetrachloride followed by Soxhlet extraction with light petroleum (b. p. 60—80°) gave tri-indole, m. p. 167—170° (lit.,[4] m. p. 169—170·5°), identical in infrared absorption spectrum with an authentic sample.

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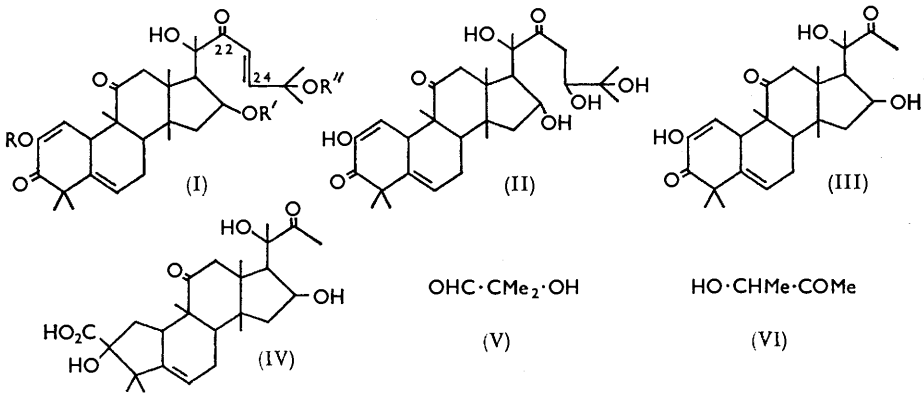
101. *Bitter Principles of the Cucurbitaceae. Part XIII.*[1] *The Constitutions of Cucurbitacins J, K, and L.*

By P. R. Enslin and K. B. Norton.

The root of *Citrullus ecirrhosus* contains a mixture of bitter principle glycosides which on enzymic hydrolysis afforded cucurbitacins E, I, J, K, and L.[2] Constitutions for cucurbitacins E and I have recently been proposed.[3] This paper deals with the constitutions of cucurbitacins J, K, and L.

Gmelin [4] recently isolated cucurbitacins J and K from *Iberis amara*, of the Cruciferae family, and found that they were also formed on treatment of cucurbitacin I (I; R = R′ = R″ = H) with alkali. This prompted us to reinvestigate the action of alkali on cucurbitacin E (I; R = R′ = H, R″ = Ac). Previous work [5,6] has shown that, on treatment of cucurbitacin E with cold alkali, hydrolysis of the acetate group and hydration of the conjugated double bond in the side chain occur, to give the β-ketol elateridin, $C_{30}H_{44}O_8$. On treatment of elateridin with hot alkali, ecballic acid (IV) and acetoin (VI) are formed. The first step in this reaction is probably a retro-aldolisation to give a tetranorcucurbitacin I (III) and α-hydroxy-α-methylpropionaldehyde (V). Under the influence of alkali, the latter is converted into acetoin,[6–8] and the tetranorcucurbitacin I undergoes a benzilic acid rearrangement to the α-hydroxy-acid, ecballic acid.[5]



Treatment of cucurbitacin E with cold alkali gave in our hands, under a variety of conditions, an amorphous product shown by paper chromatography to be a mixture of substances which was separated into a polar and a less-polar fraction (see Experimental section). Chromatography of the more-polar fraction on cellulose powder impregnated with formamide gave cucurbitacins I, J, and K.

Cucurbitacin J, $C_{30}H_{44}O_8$, and cucurbitacin K, $C_{30}H_{44}O_8,\frac{1}{2}H_2O$ both contain a diosphenol grouping but no αβ-unsaturated keto-group. The close relation between the two compounds is evident from their almost identical infrared spectra. In dilute alcoholic sodium hydroxide or hydrochloric acid solution, either of cucurbitacins J or K gave a mixture containing approximately equal quantities of both (paper chromatography).

[1] Part XII, van der Merwe, Enslin, and Pachler, *J.*, 1963, 4275.
[2] Enslin, Rehm, and Rivett, *J. Sci. Food Agric.*, 1957, **8**, 673.
[3] de Kock, Enslin, Norton, Barton, Sklarz, and Bothner-By, *J.*, 1963, 3828.
[4] Gmelin, 1963, personal communication.
[5] Lavie and Szinai, *J. Amer. Chem. Soc.*, 1958, **80**, 707.
[6] Lavie, Shvo, and Willner, *J. Amer. Chem. Soc.*, 1959, **81**, 3062.
[7] Rivett and Herbstein, *Chem. and Ind.*, 1957, 393.
[8] Rivett and Enslin, *Proc. Chem. Soc.*, 1958, 301.

On treatment with hot aqueous alkali, both gave ecballic acid and acetoin (isolated as biacetyl bis-2,4-dinitrophenylhydrazone). Acetylation gave in each case cucurbitacin I diacetate (I; R = R′ = Ac, R″ = H). These reactions show that cucurbitacins J and K must both contain a hydroxy-group at position 24, β to the keto-group at position 22. Their constitutions are therefore as given in (II) and they differ from each other only in the configuration of the hydroxy-group at position 24.

The less-polar fraction (see above) from the reaction of cucurbitacin E with cold alkali contained a mixture of several substances from which the postulated tetranorcucurbitacin I intermediate (III) could not be isolated.

Cucurbitacin L is identical with 23,24-dihydrocucurbitacin I.

Experimental.—Unless specified to the contrary, $[\alpha]_D$ refer to chloroform, ultraviolet absorption spectra to ethanol, and infrared absorption spectra to chloroform solutions. Infrared spectra were determined on a Perkin-Elmer model 21 and ultraviolet absorption spectra on a Unicam model 500 spectrometer. The descending method of paper chromatography on Whatman No. 1 paper impregnated with a 50% solution of formamide in ethanol was used. Oven-dried chromatograms were sprayed with a solution of vanillin (10 g.) in a mixture of ethanol (150 ml.) and 85% phosphoric acid (50 ml.). Spots were revealed by heating at 90° for *ca.* 2 min.

Treatment of cucurbitacin E with alkali. Finely ground cucurbitacin E (10 g.) was treated under nitrogen with N-sodium hydroxide in 10% aqueous ethanol (2·5 l.). After the mixture had been shaken at 20° for 5½ hr., practically all the cucurbitacin E had dissolved. Extraction of the acidified solution with chloroform gave an amorphous foam which showed on paper chromatograms (solvent, 1 : 1 benzene–ethyl acetate) spots at R_F 0·17, 0·27, 0·46, and 0·75—0·92. A similar mixture was obtained when the reaction was carried out in 0·1N-sodium hydroxide at 0° for 68 hr. The crude product was dissolved in formamide (250 ml.), and the solution diluted with water (250 ml.). Extraction with benzene (10 × 100 ml.) and washing with water gave, on evaporation, a foam (4·5 g.) containing substances of R_F 0·75—0·92. Chromatography on cellulose powder impregnated with formamide [2] gave unchanged cucurbitacin E (960 mg.) and small amounts of crystalline products which could not be obtained pure.

Further extraction of the above aqueous-formamide solution with chloroform gave a fraction (3·49 g.) containing mainly substances of R_F 0·17, 0·27, and 0·46. The mixture was separated by chromatography on formamide-impregnated cellulose powder (500 g.). Elution with 4 : 1 benzene–ethyl acetate (1·4 l.) gave a gum (393 mg.), and elution with 2 : 1 benzene–ethyl acetate (0·8 l.) gave crystalline fractions (R_F 0·46) which were crystallised from ethyl acetate to afford cucurbitacin I (107 mg.), m. p. 145—148°, identified by mixed m. p. and infrared spectrum. Further elution of the column with 2 : 1 benzene–ethyl acetate (1·4 l.) first afforded a gum (38 mg.) and then fractions (R_F 0·27; 920 mg.) which crystallised from ethyl acetate to give a substance (625 mg.) identified as cucurbitacin J by paper chromatography and infrared spectrum, m. p. and mixed m. p. 200—202°, $[\alpha]_D$ −36° (*c* 1·0), $\lambda_{max.}$ 270 mμ (ε 8700 in ethanol) and 313 mμ (ε 6300 in 0·1N-potassium hydroxide in 50% ethanol), $\nu_{max.}$ 1695 and 1664 cm.$^{-1}$ (Found: C, 67·4; H, 8·2. Calc. for $C_{30}H_{44}O_8$: C, 67·6; H, 8·3%).

Elution of the column was continued with 2 : 1 benzene–ethyl acetate (3 l.), and all fractions (total 956 mg.) which showed mainly a spot at R_F 0·17 on paper chromatograms were combined and crystallised from dilute methanol (the substance failed to crystallise from non-aqueous solvents), to give fine needles (700 mg.) of indefinite m. p., sintering from *ca.* 143° and decomposing at *ca.* 195°, identified as cucurbitacin K by paper chromatography and infrared spectrum, $[\alpha]_D$ −74° (*c* 1·0), $\lambda_{max.}$ 270 mμ (ε 8000 in ethanol) and 312 mμ (ε 5900 in 0·1N-potassium hydroxide in 50% ethanol), $\nu_{max.}$ 1695 and 1664 cm.$^{-1}$ (Found: C, 66·4, 66·9; H, 8·3, 8·4. $C_{30}H_{44}O_8,\frac{1}{2}H_2O$ requires C, 66·6; H, 8·4%). The substance was dried at 110°/10^{-4} mm. Drying at higher temperatures led to slow decomposition.

Cucurbitacins J and K gave negative triphenyltetrazolium chloride tests, indicating the absence of a secondary α-hydroxy-ketone.

Cucurbitacin I diacetate from cucurbitacins J and K. Cucurbitacin J (58 mg.) was treated with sodium acetate (55 mg.) in acetic anhydride (2 ml.) for 1·5 hr. at 100°. The mixture was poured into benzene, washed with water, and dried (Na_2SO_4). Evaporation gave a crystalline

residue which was crystallised from benzene–ether, to give a diacetate (45 mg.), m. p. 260—261°, $[\alpha]_D$ −88° (*c* 1·0), $\lambda_{max.}$ 233 mμ (ε 22,400) (Found: C, 68·0; H, 7·8. Calc. for $C_{34}H_{46}O_9$: C, 68·2; H, 7·7%). The substance was identified as cucurbitacin I diacetate (mixed m. p. and identical infrared spectrum).

Acetylation of cucurbitacin K (59 mg.) as above also gave cucurbitacin I diacetate (47 mg.), m. p. and mixed m. p. 261—262°, $[\alpha]_D$ −85° (*c* 1·0), $\lambda_{max.}$ 233 mμ (ε 22,800) (Found: C, 67·8; H, 8·0. Calc. for $C_{34}H_{46}O_9$: C, 68·2; H, 7·7%).

Treatment of cucurbitacins J and K with hot alkali. Cucurbitacin K (99 mg.) in 0·5N-sodium hydroxide was boiled for 1 hr. during which a slow stream of nitrogen and steam was led through the solution. The distillate was collected in a solution of 2,4-dinitrophenylhydrazine (50 mg.) in 5N-hydrochloric acid (5 ml.) which, when heated for 1 hr. on a steam-bath, gave an orange precipitate which was collected and crystallised from nitrobenzene to give the biacetyl bisdinitrophenylhydrazone (16 mg.), m. p. and mixed m. p. 328—330°, further identified by its infrared spectrum (KBr disc).

The above alkaline solution was acidified with dilute hydrochloric acid and the product isolated with ether and crystallised from dilute methanol, to give ecballic acid (56 mg.), m. p. 261—262°, identified by mixed m. p. and infrared spectrum.

Treatment of cucurbitacin J (101 mg.) as above also gave biacetyl bis-2,4-dinitrophenylhydrazone (15 mg.) and ecballic acid (35 mg.).

Cucurbitacin L from cucurbitacin I. Cucurbitacin I (115 mg.) was hydrogenated over 5% palladised calcium carbonate (40 mg.) in ethanol (50 ml.) (0·91 mol. absorbed in 45 min.), and the product crystallised from dilute methanol, to give cucurbitacin L (102 mg.), needles of indefinite m. p., sintering slowly from *ca.* 120° to give a clear melt at *ca.* 140°, $[\alpha]_D$ −49° (*c* 1·0), $\lambda_{max.}$ 270 mμ (ε 8050 in ethanol) and $\lambda_{max.}$ 313 mμ (ε 5850 in 0·1N-potassium hydroxide in 50% ethanol), $\nu_{max.}$ 1692 and 1661 cm.$^{-1}$ (Found: C, 68·8; H, 8·7. Calc. for $C_{30}H_{44}O_7,\frac{1}{2}H_2O$: C, 68·6; H, 8·6%).

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102. *Reaction of* 1- *and* 3-*Phenylallyl Chloride with Di- and Tri-ethylamine.*

By G. VALKANAS and E. S. WAIGHT.

THE reaction of 1-methylallyl chloride (I; R = Me, X = Cl) with diethylamine [1] gives but-2-enyldiethylamine (II; R = Me, X = NEt_2); an abnormal bimolecular substitution (S_N2') has been postulated but a cyclic mechanism may be involved.[2] The analogous reaction with triethylamine [3] gives a mixture of allylic products (I and II; R = Me, X = $NEt_3^+Cl^-$); in this case the abnormal bimolecular substitution cannot involve specific hydrogen bonding in the transition state. In neither reaction is isomerization of the chloride observed. We have studied the reactions of 1- and 3-phenylallyl chloride (I and II; R = Ph, X = Cl) which present a somewhat different picture.

(I) R·CHX·CH:CH_2 R·CH:CH·CH_2X (II)

The light-absorption intensity (at 2530 Å) of solutions of 1-phenylallyl chloride in triethylamine initially increased, reached a maximum value which decreased with increasing temperature, and then declined according to a first-order rate law. Extinction coefficients ($E^{1\%}_{1\,cm.}$) were calculated on the amount of chloride originally present, no

[1] Young, Webb, and Goering, *J. Amer. Chem. Soc.*, 1951, **73**, 1076.
[2] Kepner, Winstein, and Young, *J. Amer. Chem. Soc.*, 1949, **71**, 115; Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953; DeWolfe and Young, *Chem. Rev.*, 1956, **56**, 753.
[3] Young and Clement, *Science*, 1952, **115**, 488; Young, Clement, and Shih, *J. Amer. Chem. Soc.*, 1955, **77**, 3061.

account being taken of precipitation of the product which was insoluble in triethylamine. The only non-nitrogenous product isolated after the intensity maximum had been reached was cinnamyl chloride. The first part of the reaction represents the isomeric rearrangement of 1-phenylallyl chloride to cinnamyl chloride; the second concerns the reaction of the latter with triethylamine. First-order rate constants calculated from the second part (Table 1) agree well with those determined separately for the reaction of cinnamyl chloride

TABLE 1.

Reaction of 1-phenylallyl chloride (concn. 0·15 mole/l.) with triethylamine.

Temp.	90°	80°	70°	60°	35°	80°
$t_{max.}$ *	400	530	1630	2400	~5000	—
$E^{1\%}_{1\,cm.}$	620	710	765	830	~950	—
10^3k †	—	1·02	0·51	0·26	—	1·02 ‡

* Time (in min.) at which max. value of $E^{1\%}_{1\,cm.}$ is attained. † First-order rate constant (min.$^{-1}$) for reaction of cinnamyl chloride formed. ‡ Starting from pure cinnamyl chloride.

with triethylamine. Infrared and ultraviolet spectra of the quaternary salt isolated indicated the presence initially of about 50% of the unconjugated isomer. The latter was unstable, giving a product which had an infrared spectrum almost identical with that of cinnamyldiethylmethylammonium iodide and was evidently cinnamyltriethylammonium chloride. Previous workers [4] have isolated only cinnamyl products from the reaction of the chloride with tertiary amines, and this is to our knowledge the first demonstration of isomeric rearrangement in an allylic quaternary ammonium salt. Rearrangement also occurred in chloroform solution; in hydroxylic solvents there was a competing solvolysis but no detailed investigation was made.

With diethylamine, either neat or diluted with a solvent such as chloroform or cyclohexane, 1-phenylallyl chloride ultimately afforded cinnamyldiethylamine. The reaction was followed spectrometrically and titrimetrically and first-order rate constants, $k_{spec.}$ and $k_{tit.}$, respectively, are given in Table 2. $k_{spec.}$ exceeds $k_{tit.}$ but both are lower than

TABLE 2.

Reactions with diethylamine.

Temp.	Solvent	[Chloride] (mole/l.)	[Amine] (mole/l.)	$10^3k_{spec.}$	$10^3k_{tit.}$
(*a*) *1-Phenylallyl chloride.*					
30°	Et_2NH	0·0135	—	2·85	—
40	,,	0·0197	—	7·96	—
30	$CHCl_3$	0·191	0·92	6·6	4·95
,,	,,	0·160	0·46	4·3	3·0
,,	,,	0·146	—	0·87	—
40	,,	0·166	1·84	22·1	11·0
,,	,,	0·157	0·83	10·1	6·5
,,	,,	0·140	—	1·65	—
70	Cyclohexane	0·091	0·39	2·9	—
80	,,	0·076	0·39	8·1	—
(*b*) *Cinnamyl chloride.*					
30	$CHCl_3$	0·156	0·92	—	8·85
,,	,,	0·197	0·46	—	4·4

$k_{tit.}$ for the reaction of cinnamyl chloride under the same conditions. Since nominal samples of 1-phenylallyl chloride contained about 20% of the isomeric chloride the true rate constants for reaction of the former are lower than the values recorded. The kinetic data suggest that isomeric rearrangement competes with substitution and this is confirmed by the finding of cinnamyl chloride in excess of the amount originally present in the products of incomplete reaction. It is difficult to say how much of the conjugated

[4] Klages and Klenk, *Ber.*, 1906, **39**, 2552; Claisen and Tietze, *Ber.*, 1926, **59**, 2344; Crossley, U.S.P. 2,609,392/1952.

amine, which is the only product from cinnamyl chloride, is formed after rearrangement and how much is obtained directly, perhaps by abnormal bimolecular substitution. The amine isolated by distillation before complete reaction gave a methiodide which from its infrared spectrum was a mixture of isomers (I and II; R = Ph, X = $NMeEt_2^+I^-$). Attempts to separate the mixture of amines on an acidic ion-exchange resin were unsuccessful; the unconjugated amines seemed to isomerize readily, especially in the presence of acids, which was to be expected in view of the excellence of quaternized amino as a leaving group, for example in Hofmann eliminations.

Reaction of 1-phenylallyl chloride with amines is analogous to that with oxygen compounds.[5] Isomeric rearrangement predominates at the expense of substitution in media of low ionizing power. With cinnamyl chloride, which has a greater tendency to undergo bimolecular displacements,[6] both ionizing power and nucleophilicity of the medium are important in determining product composition. Diethylamine is more basic than triethylamine [7] and presumably also has the higher ionizing power.

Experimental.—1-Phenylallyl chloride had b. p. 50—60°/0·35—0·5 mm., $\lambda_{max.}$ 2530 Å (ε 3500—6000).[5]

Cinnamyl chloride had b. p. 70—71°/0·2 mm., n_D^{23} 1·5830, $\lambda_{max.}$ 2530 Å (ε 20,000 in hexane).

Cinnamyldiethylamine. Diethylamine (30 g.) and cinnamyl chloride (10 g.) were kept in chloroform (80 ml.) at 70° for 15 hr., then washed with water, dried, and distilled. The *amine* (9·1 g.) had b. p. 126—128°/12 mm., n_D^{23} 1·5313, $\lambda_{max.}$ 2560 Å (ε 18,250), $\nu_{max.}$ 965 cm.$^{-1}$ (*trans*-CH:CH, pure liquid) (Found: C, 82·5; H, 10·0; N, 7·3. $C_{13}H_{19}N$ requires C, 82·5; H, 10·0; N, 7·4%). On treatment with methyl iodide in pentane at room temperature the semi-solid methiodide separated and after crystallization from methanol had m. p. 130—132°, $\lambda_{max.}$ 2560 Å (ε 16,800), $\nu_{max.}$ 985 cm.$^{-1}$ (*trans*-CH:CH, Nujol mull).

Isolation of products. (*a*) 1-Phenylallyl chloride (1·02 g.) and triethylamine (20 ml.) were kept at 80° for 740 min. The solution was cooled, diluted with ether, washed with water, dried, and distilled. The product, b. p. 58—60°/0·05 mm., n_D^{22} 1·5814, $\lambda_{max.}$ 2530 Å (ε 19,700), had an infrared spectrum identical with that of cinnamyl chloride.

(*b*) Cinnamyl chloride (5 g.) and triethylamine (30 ml.) were kept at 80° for 2 hr. The excess of solvent was decanted and the residue dissolved in chloroform (10 ml.) and reprecipitated with light petroleum (100 ml.). This purification was repeated four times and the hygroscopic salt, after 6 hr. under a vacuum, had $\lambda_{max.}$ 2550 Å (ε 8200, in freshly prepared ethanolic solution) (Found: N, 5·2; Cl, 14·9. $C_{15}H_{24}ClN$ requires N, 5·6; Cl, 14·0%). The quaternary salt (3 g.; ε 9100) was kept in a desiccator for three weeks at room temperature. The needles formed had $\lambda_{max.}$ 2550 Å (ε 16,700 in EtOH) and an infrared spectrum different from that of the starting material, particularly in the 10 μ region, but very similar to that of cinnamyldiethylmethylammonium iodide. A 10% solution of the quaternary salt (ε 8400) in chloroform was kept at 70° for 8 hr. (sealed tube). The product had $\lambda_{max.}$ 2550 Å (ε 16,300) and was very similar to the material obtained above.

Kinetic measurements. Chloroform was washed with concentrated sulphuric acid, kept over calcium chloride in the dark for one week, and distilled from phosphoric oxide. Cyclohexane was a grade suitable for spectroscopic measurements. Di- and tri-ethylamine were distilled twice from barium oxide. Spectrometric and titrimetric rate constants were determined as described previously,[5] by measuring the light-absorption intensity at 2530 Å of samples diluted with cyclohexane; and by determining the concentration of chloride ion liberated, by titration with silver nitrate solution with potassium chromate as indicator, after separation of unchanged organic chloride.

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[5] Valkanas and Waight, *J.*, 1959, 2720; Valkanas, Waight, and Weinstock, *J.*, 1963, 4248.
[6] Vernon, *J.*, 1954, 423, 4462.
[7] Hall, *J. Phys. Chem.*, 1956, **60**, 63.

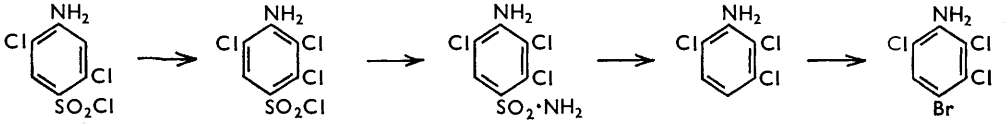
103. *Synthesis of 4-Bromo-2,3,5- and 4-Bromo-2,3,6-trichloroaniline.*

By JAMES H. SHORT.

4-BROMO-2,3,6- (V) and 4-BROMO-2,3,5-TRICHLOROANILINE (IX) were needed in connexion with other work, and their preparation is reported here.

Attempts to introduce a 4-bromo-substituent into 2,5-dichloroacetanilide [1] gave no pure product. 2,3-Dichloroacetanilide [1] gave no monobromo-derivative but 4,6-dibromo-2,3-dichloroaniline was obtained.

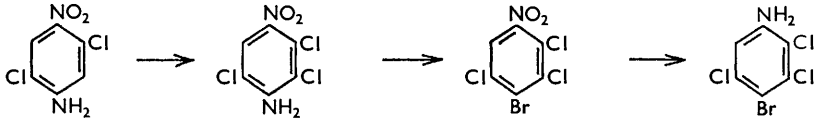
Monobromination of *m*-chloroacetanilide was successful, and deacetylation gave the known 4-bromo-3-chloroaniline.[2] The latter was allowed to react with sulphuryl chloride, and a substance was obtained which gave a satisfactory analysis for the amine (V), but gas–liquid chromatography (g.l.c.) indicated that it was only 80% pure, two additional components being present. That the major component was the amine (V) was shown by



(I) (II) (III) (IV) (V)

gas–liquid chromatography after the pure compound had been obtained. The synthetic scheme which led to the pure compound started with 2,5-dichlorosulphanilic acid which was converted to the chloride (I); this with sulphuryl chloride afforded 2,3,5-trichlorosulphanilyl chloride (II), and the latter with ammonia gave 2,3,5-trichlorosulphanilamide (III). The sulphonamide group was removed in hot 70% sulphuric acid, and 2,3,6-trichloroaniline (IV) was obtained. Bromination then gave the desired 4-bromo-2,3,6-trichloroaniline (V), in this case, chromatographically pure.

In the first attempt to obtain 4-bromo-2,3,5-trichloroaniline (IX), 2,6-dichloro-4-nitroaniline was diazotized in the presence of hydrobromic acid, and the resulting 2-bromo-1,3-dichloro-5-nitrobenzene was hydrogenated, affording 4-bromo-3,5-dichloroaniline. Attempts to monochlorinate this gave only unchanged starting material or 4-bromo-2,3,5,6-tetrachloroaniline. Monochlorination of the *N*-acetyl derivative was also unsuccessful. We next devised a scheme which would avoid selective chlorination: sulphuryl chloride and 2,5-dichloro-4-nitroaniline (VI) gave 2,3,6-trichloro-4-nitroaniline (VII).



(VI) (VII) (VIII) (IX)

When the diazotisation procedure which had been used to convert 2,6-dichloro-4-nitroaniline into 2-bromo-1,3-dichloro-5-nitrobenzene was applied to this product, the nitro-group, as well as the amino-group, was lost and the substance appeared to be mostly 1,4-dibromo-2,3,5-trichlorobenzene. However, the desired compound (VIII) was obtained when the reaction was carried out at a lower temperature. Hyrogenation then gave 4-bromo-2,3,5-trichloroaniline (IX).

Experimental.—*4,6-Dibromo-2,3-dichloroacetanilide.* 2,3-Dichloroacetanilide [1] (4·0 g., 0·02 mole) and bromine (3·2 g., 0·02 mole) in acetic acid (10 c.c.) were heated on the steam-bath for

[1] Beilstein and Kurbatow, *Annalen*, 1879, **196**, 214.
[2] Wheeler and Valentine, *Amer. Chem. J.*, 1899, **22**, 273.

1 hr., and then the solution was diluted with water (30 c.c.). An oil was precipitated that readily solidified. The solid *product* was recrystallized once from aqueous isopropyl alcohol and once from benzene, to give needles (1·3 g., 18%), m. p. 207° (Found: C, 26·5; H, 1·4; Br, 44·0; Cl, 19·9; N, 3·7; O, 4·5. $C_8H_5Br_2Cl_2NO$ requires C, 26·55; H, 1·4; Br, 44·2; Cl, 19·6; N, 3·9; O, 4·4%). No monobromo-derivative was isolated.

2,5-*Dichlorosulphanilyl chloride* (I). A solution of sodium 2,5-dichlorosulphanilate (132 g., 0·5 mole) (Distillation Products Industries) in chlorosulphonic acid (500 c.c.) was heated at 120—130° for 4 hr., then poured on ice, and the product was collected (107 g., 82·5%; m. p. 135—137°). Two recrystallizations from benzene–Skellysolve B (petroleum ether, b. p. 60—68°) (charcoal) gave a light yellow *chloride*, m. p. 141·5—142·5° (Found: C, 27·9; H, 1·5; Cl, 41·1; N, 5·3; O, 12·3; S, 12·1. $C_6H_4Cl_3NO_2S$ requires C, 27·7; H, 1·5; Cl, 40·8; N, 5·4; O, 12·3; S, 12·3%).

2,3,5-*Trichlorosulphanilyl chloride* (II). To a solution of 2,5-dichlorosulphanilyl chloride (50 g., 0·19 mole) in chloroform (560 c.c.) was added sulphuryl chloride (180 c.c.), and the solution was heated under reflux for 4 hr. The chloroform was removed and the residue was recrystallized from benzene–Skellysolve B (charcoal), to afford thick, cream-coloured needles (32·5 g., 58%) of the *trichloro-compound*, m. p. 121·5—122° (Found: C, 24·25; H, 1·2; Cl, 47·9; N, 4·7; S, 11·1. $C_6H_3Cl_4NO_2S$ requires C, 24·4; H, 1·0; Cl, 48·1; N, 4·75; S, 10·9%).

2,3,5-*Trichlorosulphanilamide* (III). A solution of 2,3,5-trichlorosulphanilyl chloride (32·5 g., 0·11 mole) in liquid ammonia (100 c.c.) was left at room temperature until the ammonia had evaporated. Recrystallization from aqueous ethanol gave the *amide* (16·0 g., 54%), m. p. 219·5—220·5° (Found: C, 26·0; H, 1·9; Cl, 38·7; N, 10·3; S, 11·9. $C_6H_5Cl_3N_2O_2S$ requires C, 26·15; H, 1·8; Cl, 38·6; N, 10·2; S, 11·6%).

2,3,6-*Trichloroaniline* (IV). 2,3,5-Trichlorosulphanilamide (6·7 g., 0·024 mole) in 70% sulphuric acid (80 c.c.) was heated under reflux for 18 hr. The solution was poured into water, giving the *amine* as a precipitate (4·2 g., 88%), m. p. 63° (lit.,[3] 63—64°) (Found: C, 36·8; H, 2·3; Cl, 54·2; N, 7·2. Calc. for $C_6H_4Cl_3N$: C, 36·7; H, 2·1; Cl, 54·1; N, 7·1%).

4-*Bromo*-2,3,6-*trichloroaniline* (V). (A) A solution of 4-bromo-3-chloroaniline [2] (2·0 g., 0·01 mole) in aqueous acetic acid (25 c.c. of glacial acid, 5 c.c. of water) was heated at 65—70° for 2 hr. as chlorine gas was bubbled through it. Grey needles were obtained when the solution was chilled (yield 1·2 g., 44%; m. p. 88—90°). Recrystallization from aqueous acetic acid (charcoal) raised the m. p. of the product to 92·5—93° (Found: C, 26·3, 26·0; H, 1·4, 1·3; Br, 28·9; Cl, 38·9; N, 4·9, 4·9. $C_6H_3BrCl_3N$ requires C, 26·2; H, 1·1; Br, 29·0; Cl, 38·6; N, 5·1%). This substance was only 80% pure (g.l.c.). Similar results were obtained when the chlorination was carried out in chloroform with sulphuryl chloride.

(B) 2,3,6-Trichloroaniline (7·1 g., 0·036 mole) was dissolved in glacial acetic acid (140 c.c.), and bromine (6·0 g., 0·037 mole) was added. After 1 hr. at room temperature, the precipitate was collected. A second crop was isolated from the filtrate. The combined material was recrystallized from aqueous ethanol, to give a *product* (9·4 g., 94%; m. p. 95·5—96·5°). Recrystallization from aqueous acetic acid (charcoal) gave needles, m. p. 96—96·5° (Found: C, 26·2; H, 1·2; Br, 29·2; Cl, 38·6; N, 5·1%). No impurities were detected (g.l.c.).

4-*Bromo*-2,3,5,6-*tetrachloroaniline*. Reduction of 2-bromo-1,3-dichloro-5-nitrobenzene,[4] as described below for 2-bromo-5-nitro-1,3,4-trichlorobenzene, gave 4-bromo-3,5-dichloroaniline.[5] A mixture of the latter (2·4 g., 0·01 mole) and sulphuryl chloride (10 c.c.) in chloroform (25 c.c.) was heated under reflux for 4 hr. On chilling, the *amine* (1·7 g., 55%), m. p. 226—231°, was obtained. No trace of monochlorinated material could be found in the filtrate. White needles were obtained from ethanol (charcoal), with m. p. 236—236·5° (Found: C, 23·3; H, 0·6; Br, 26·1; Cl, 45·6; N, 4·7. $C_6H_2BrCl_4N$ requires C, 23·3; H, 0·65; Br, 25·8; Cl, 45·8; N, 4·5%). Attempts to monochlorinate 4-bromo-3,5-dichloroacetanilide (m. p. 223—224°; lit.,[5] 220°) were unsuccessful.

2,3,6-*Trichloro*-4-*nitroaniline* (VII). 2,5-Dichloro-4-nitroaniline (73 g., 0·35 mole) (Aldrich Chemical Company) in chloroform (1·5 l.) was heated under reflux with stirring for 4 hr. as sulphuryl chloride (200 c.c.) was added. After being heated for 1 hr. longer, the solution was filtered and evaporated. The residue recrystallized from ethanol, giving material (34 g., 40%) melting at 143—146°. A portion recrystallized from ethanol (charcoal) as yellow needles,

[3] Hüffer, *Rec. Trav. chim.*, 1921, **40**, 457.
[4] Flürscheim and Simon, *J.*, 1908, **93**, 1481.
[5] Hurtley, *J.*, 1901, **79**, 1303.

m. p. 145·5—146·5° (lit.,[6] 143°) (Found: C, 30·0; H, 1·2; Cl, 44·2; N, 11·5; O, 13·5. Calc. for $C_6H_3Cl_3N_2O_2$: C, 29·8; H, 1·25; Cl, 44·05; N, 11·6; O, 13·25%).

2-Bromo-1,3,4-trichloro-5-nitrobenzene (VIII). 2,3,6-Trichloro-4-nitroaniline (20 g., 0·083 mole) was dissolved in glacial acetic acid (1·0 l.), and 48% hydrobromic acid (75 c.c.) was added. The solution was cooled to room temperature and sodium nitrite (18 g., 0·25 mole) was added in small portions during 1 hr. After being heated on the steam-bath the solution was diluted with water (1·0 l.) and chilled, to yield a yellow *product* (25 g., 99%), m. p. 62—63°. Recrystallization from ethanol raised the m. p. to 66·5—67° (Found: C, 23·6; H, 0·5; Br, 26·4; Cl, 35·0; N, 4·4; O, 10·6. $C_6HBrCl_3NO_2$ requires C, 23·6; H, 0·3; Br, 26·2; Cl, 34·8; N, 4·6; O, 10·5%).

4-Bromo-2,3,5-trichloroaniline (IX). 2-Bromo-5-nitro-1,3,4-trichlorobenzene (26·4 g., 0·085 mole) was hydrogenated in acetic acid (200 c.c.) at 2 atm. over 5% platinum–carbon (0·8 g.) (uptake complete in ~2 hr.). The catalyst was removed and the filtrate diluted with water (700 c.c.). The product was recrystallized (charcoal) from aqueous acetic acid and from ethanol, to give cream-coloured needles (14·1 g., 60%) of the *amine*, m. p. 116·5—117° (Found: C, 26·2, 25·95; H, 1·1, 1·0; Br, 28·8; Cl, 38·9; N, 5·3, 4·9. $C_6H_3BrCl_3N$ requires C, 26·2; H, 1·1; Br, 29·0; Cl, 38·6; N, 5·1%). The product was 97·5% pure (g.l.c.).

Analytical data were provided by Mr. Elmer Shelberg and Mr. Orville Kolsto and staff of the Abbott Microanalytical Laboratory. Catalytic hydrogenations were carried out by Mr. Morris Freifelder and Mr. George Stone. Mr. Walter Ranus, jun., assisted in the preparation of some of the intermediate compounds. G.l.c. analyses were provided by Mr. Preston Helgren and Mrs. Taimi Anderson.

ORGANIC CHEMISTRY DEPARTMENT, RESEARCH DIVISION, ABBOTT LABORATORIES,
NORTH CHICAGO, ILL., U.S.A. [*Received, June 27th,* 1963.]

[6] Hodgson and Kershaw, *J.*, 1929, **132**, 2920.

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104. *Unstable Intermediates. Part XXI.* Effect of Ion-pairing on the Electron Spin Resonance Spectrum of* m-*Dinitrobenzene Anion.*

By M. J. BLANDAMER, T. E. GOUGH, J. M. GROSS, and M. C. R. SYMONS.

THE monoanion of *m*-dinitrobenzene, prepared electrolytically in methyl cyanide,[1] has a spin resonance spectrum in accord with expectation. However, the radical formed by reaction between *m*-dinitrobenzene and sodium or potassium in dimethoxyethane [2,3] has a spectrum which differs from this especially in that the nuclear hyperfine coupling to one nitrogen is greatly enhanced whilst that to the other is extremely small. The magnitude in gauss of the coupling to ^{14}N is 4·68 for the ion in methyl cyanide and 9·0 ± 0·2 and 0·29 ± 0·02 for that in dimethoxyethane.[3]

This has been interpreted [2,4] in terms of ion-pair formation in the ether, the structure of the ion-pair being such that the sodium ion remains preferentially associated with one nitro-group for a long period compared with the inverse of the hyperfine interaction. However, the possibility that reaction with sodium results in chemical reduction of one nitro-group, although less attractive, cannot be eliminated.

In view of the potential importance of these results to the study of ion–ion interactions on the one hand and to molecular-orbital theory on the other, we have investigated the effect of varying the solvent composition on the spin resonance spectrum of the radical formed by reduction with sodium. In dimethoxyethane, a spectrum closely similar to Ward's [2] was obtained at room temperature. Methyl cyanide was added after removal

* Part XX, *J.*, 1963, 5594.

[1] Geske and Maki, *J. Chem. Phys.*, 1960, **33**, 825.
[2] Ward, *J. Amer. Chem. Soc.*, 1961, **83**, 1296.
[3] Ward, *J. Chem. Phys.*, 1962, **36**, 1405.
[4] Weissman, *Ann. Rev. Phys. Chem.*, 1961, **12**, 162.

of the excess of metal by filtration and of a portion of the ether by distillation. The spectrum of the radical in a 5 : 1 v/v mixture of methyl cyanide and dimethoxyethane was closely similar to that for the anion prepared electrolytically,[1] although the line-widths were somewhat greater.

This result is in accord with the ion-pair theory and eliminates the possibility that interaction with metal resulted in the reduction of one nitro-group.

Experimental.—Materials. *m*-Dinitrobenzene was twice recrystallised from 1,2-dimethoxyethane. The latter solvent was refluxed over calcium hydride for 48 hr. and fractionated through a 40-cm. Vigreux column and stored in a receiver attached to a vacuum-line over a mixture of sodium, potassium, and benzophenone. Methyl cyanide was similarly treated but stored over calcium hydride. Sinters, of porosity 3, were included in the vacuum-line to prevent transfer of suspended solids.

Solutions. Solutions were prepared in a high-vacuum all-glass apparatus. *m*-Dinitrobenzene was reduced by sodium in dimethoxyethane and the resulting solution transferred through a sinter, of porosity 2, into a second vessel. The solvent was slowly removed by condensing the vapour in a liquid-nitrogen trap. Rapid decomposition of the solution, indicated by a purple coloration, occurred above a critical concentration. Before the onset of this coloration, methyl cyanide was condensed into this vessel. In this way, it was possible to prepare solutions stable at room temperature with solvent ratios of methyl cyanide to 1,2-dimethoxyethane as high as 5 : 1 by volume.

Electron spin resonance spectra were recorded at room temperature on a Varian Associates V-4502 spectrometer.

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Department of Chemistry,
The University, Leicester. [*Received, July 5th,* 1963.]

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105. *Urinary Steroids and Related Compounds. Part IV.*[1] *Tetrahydrocorticosterone.*

By J. C. Danilewicz and W. Klyne.

Tetrahydrocorticosterone (3α,11β,21-trihydroxy-5β-pregnan-20-one, commonly called " tetrahydro-B " in clinical biochemistry) has been found in human urine in various pathological conditions.[2] It has been identified with synthetic material, the preparation of which has not been described.[3] The needs of the Medical Research Council Steroid Reference Collection led to the preparation of this compound from the corresponding 11-oxo-derivative by the method now described.

3α,21-Dihydroxy-5β-pregnane-11,20-dione was transformed into its 20-ethylene ketal.[4] The 11-keto-group was reduced with lithium aluminium hydride, to give the 11β-hydroxy-20-ketal, which was an intractable gum. The crude product was briefly hydrolysed under acid conditions to the required 20-ketone, which was separated by partition chromatography. This material gave a positive blue tetrazolium reaction. On treatment with acetic anhydride in pyridine it gave the diacetate; this had an infrared spectrum [$\nu_{max.}$ (in CS_2) 3600, 1750, and 1730 cm.$^{-1}$] identical with that of the diacetate of a sample prepared by Dr. Seymour Lieberman (Columbia Medical Centre, New York), from corticosterone

[1] Part III, Danilewicz and Klyne, *J.*, 1962, 4950.

[2] Dohan, Touchstone, Richardson, Bulaschenko, Landolt, and Applin, *J. Clin. Invest.*, 1955, **34**, 485; Dohan, Touchstone, Richardson, and Bulaschenko, *Arch. Biochem. Biophys.*, 1959, **81**, 5; Engel, Carter, and Fielding, *J. Biol. Chem.*, 1955, **213**, 99.

[3] Unpublished synthesis by Dr. D. Taub (Merck and Co., Rahway, N.J.) (1955). We are grateful to Dr. Taub for information regarding this work.

[4] Antonucci, Bernstein, Heller, Lenhard, Littell, and Williams, *J. Org. Chem.*, 1953, **18**, 69.

by incubation with a rat-liver enzyme preparation.* Brief oxidation of the diacetate with chromium trioxide in acetic acid gave a compound identical with the diacetate of the starting material, as determined by thin-layer chromatography and infrared spectroscopy [$\nu_{max.}$ (in CS_2) 1750, 1730, and 1700 cm.$^{-1}$; no hydroxyl band].

Experimental.—M. p.s were determined on a Kofler apparatus and are corrected; infrared spectra were taken on an Infracord spectrophotometer. Microanalyses were carried out by Dr. M. M. Coombs, Imperial Cancer Research Fund Laboratories, London W.C.2.

3α,21-*Dihydroxy*-5β-*pregnane*-11,20-*dione* 20-*ethylene ketal.* 3α,21-Dihydroxy-5β-pregnane-11,20-dione (480 mg.) and toluene-*p*-sulphonic acid (17 mg.) were dissolved in a mixture of ethane-1,2-diol (4 c.c.) and benzene (30 c.c.). The benzene was distilled off at a rate of 10 c.c. per hour, with periodic addition of dry benzene to maintain the original volume. After 5 hr. the mixture was cooled, poured into water, and extracted with chloroform–ether (1 : 4). The organic phase was washed with saturated sodium hydrogen carbonate solution and then with water till neutral. Drying (Na_2SO_4) and evaporation gave a residue which on recrystallization from benzene–light petroleum afforded the 20-*ketal* as needles (360 mg., 64%), m. p. 184—188°. An analytical sample had m. p. 182—185° (Found: C, 70·7; H, 9·0. $C_{23}H_{36}O_5$ requires C, 70·4; H, 9·2%).

3α,11β,21-*Trihydroxy*-5β-*pregnan*-20-*one* 20-*ethylene ketal.* The preceding ketal (300 mg.) was dissolved in dry ether (50 c.c.). Lithium aluminium hydride (600 mg.) was slowly added, and the mixture refluxed for 3 hr. The excess of reagent was destroyed with ethyl acetate, followed by a little water. The suspension was poured into water and extracted with ether. The ether extract was washed successively with 2N-sulphuric acid, water, saturated aqueous sodium hydrogen carbonate, and water. After drying (Na_2SO_4) and evaporation of the solution the residue was chromatographed on alumina. Gradient elution with ether ⟶ 15% methanol in ether afforded a crude fraction (195 mg.), $\nu_{max.}$ (KBr) 3600 cm.$^{-1}$ (no C=O band), which could not be recrystallized. This was used directly for the next stage.

3α,11β,21-*Trihydroxy*-5β-*pregnan*-20-*one.*—The above crude triol ketal (360 mg.) in methanol (110 c.c.) was refluxed with 8% (v/v) sulphuric acid (12 c.c.) for 40 min. After cooling, sodium hydrogen carbonate was added and the suspension filtered. The filtrate was evaporated to a small volume under a vacuum, poured into water, and extracted with chloroform, and the organic phase was washed several times with water and evaporated to dryness. The residue was chromatographed by partition in the system toluene–light petroleum (b. p. 80—100°)–methanol–water (5 : 5 : 7 : 3) supported on Celite. The material eluted was detected by thin-layer chromatography, with silica gel G (Merck & Co., according to Stahl) and development with 4% of methanol in chloroform. Three uncharacterized compounds were initially eluted, followed by a main fraction (R_F 0·17); this on recrystallization from ether–light petroleum gave 3α,11β,21-*trihydroxy*-5β-*pregnan*-20-*one* as a white hydrated amorphous powder (94 mg.), m. p. 70—90° with evolution of solvent. The molten mass recrystallized on continued heating to fine tetragonal prisms m. p. 153—155°. An analytical sample had m. p. 156—158° (Found: C, 71·7; H, 9·5. $C_{21}H_{34}O_4$ requires C, 71·9; H, 9·8%).

We are indebted for a gift of starting material to Messrs. Merck, Sharp & Dohme, Rahway, New Jersey.

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Westfield College, Hampstead, London N.W.3. [*Received, July 24th,* 1963.]

* We thank Dr. A. E. Kellie (Courtauld Institute of Biochemistry, Middlesex Hospital, London) for this comparison.

106. *Anhydrous Chromium(III) Nitrate.*

By C. C. Addison and D. J. Chapman.

Anhydrous chromium(III) nitrate has been prepared for the first time. Dinitrogen pentoxide vapour, prepared by dehydration of fuming nitric acid with phosphoric oxide, was treated with ozonised oxygen to oxidise the dinitrogen tetroxide impurity. The gas stream was passed into dry carbon tetrachloride (100 ml.) to give a practically colourless solution containing 3—3·5 g. of dinitrogen pentoxide. A solution of chromium carbonyl (1 g.) in dry carbon tetrachloride (100 ml.) was added, with stirring, at room temperature. Reaction began immediately; gases were evolved and a green suspension was formed. The reaction mixture (protected from the atmosphere) was allowed to stand for 12 hours, when the suspension coagulated and settled. The product was filtered off in a closed system and washed with carbon tetrachloride. The latter was removed under a vacuum to leave anhydrous chromium(III) nitrate as a pale green powder. Nitrogen content was determined by the Kjeldahl technique, and chromium by oxidation to dichromate (Found: Cr, 21·9; N, 17·5. $Cr(NO_3)_3$ requires Cr. 21·8; N, 17·6%).

In spite of the excess of dinitrogen pentoxide, there was no evidence that a chromium nitrate–dinitrogen pentoxide addition compound had been formed at any stage in the reaction. The final drying of the precipitate involved vacuum treatment at room temperature for a few minutes only, so that the stability of any such addition compound must be very low. By contrast, chromium carbonyl reacts with dinitrogen tetroxide to give the addition compound $Cr(NO_3)_3,2N_2O_4$. This has a high stability, and no method has yet been devised for removal of the tetroxide without simultaneous decomposition of the metal nitrate.[1]

Anhydrous chromium(III) nitrate is exceedingly deliquescent. It dissolves in dry ethyl acetate, methyl cyanide, and dimethyl sulphoxide without apparent decomposition, and is insoluble in benzene, carbon tetrachloride, and chloroform. It reacts with diethyl ether, and reaction is vigorous when a little ether is added to excess of the solid (compare cupric nitrate[2]). The molar susceptibility, χ_M, is 6032×10^{-6} at 19°; $\mu_{eff.} = 3{\cdot}77$ B.M., corresponding to the chromium(III) oxidation state with three unpaired electrons.

The infrared spectrum was determined using a Unicam S.P. 100 spectrophotometer. Mulls were prepared in Nujol, and in Halocarbon Oil, Series 11—14. Potassium bromide cell windows were protected by Polythene sheets.[3] The observed bands ($cm.^{-1}$) are as follows (assignments in parentheses): 2820w, 2600w ($\nu_2 + \nu_4$), 2514w ($2\nu_1$), 2258w, 2096w.sp ($2\nu_2$), 1914w, 1795m, 1631s, 1560vs, and 1544vs (ν_4), 1507sh, 1283vs, and 1249vs (ν_1), 1044s, and 990s (ν_2), 782s (ν_6), 727m (ν_3 or ν_5). All nitrate groups are covalently bonded, and the value of ν_4–ν_1 (~300 $cm.^{-1}$) indicates that bonding is strong.[4] The given assignments employ the nomenclature normally adopted for unidentate bonding.[5] However, the splitting of the ν_1, ν_2, and ν_4 frequencies into two bands of similar intensity, and the presence of the strong band at 1631 $cm.^{-1}$, implies that more than one type of bonding is involved. It is feasible that bidentate and/or bridging nitrate groups may feature prominently in the structure of the solid, thus enabling the chromium ions to achieve a co-ordination number greater than three.

A feature of particular interest is the very low thermal stability of the compound. It is not volatile; when heated in a vacuum or in an atmosphere of nitrogen, it begins to decompose rapidly at 60°, and the decomposition rate is at a maximum at 100° [compare

[1] Addison and Norbury, unpublished results.
[2] Addison, "Free Radicals in Inorganic Chemistry," Advances in Chemistry Series No. 36, American Chemical Society, 1962, p. 131.
[3] Addison and Walker, *J.*, 1963, 1220.
[4] Katzin, *J. Inorg. Nuclear Chem.*, 1962, **24**, 245.
[5] Herzberg, "Infra-red and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945, pp. 65, 179.

$La(NO_3)_3$, 420°; $Pr(NO_3)_3$, 375°; $Nd(NO_3)_3$, 380°].[6] The lanthanide nitrates are ionic, and the ionic or covalent character of the nitrate bond no doubt has a pronounced effect on thermal stability so far as the tervalent metals are concerned. However, the ready availability of higher metal oxidation states may be an even more important factor, since this permits the simple decomposition step:

$$M^{n+}\text{–O–NO}_2 \longrightarrow M^{(n+1)+}O + NO_2$$

In the case of chromium(III) nitrate, thermal decomposition is considered to proceed through a series of oxide nitrates, though thermogravimetric analysis indicates that none of the possible intermediates is sufficiently stable to give a plateau on the weight–temperature curve. The first plateau is obtained at 200°, and corresponds to the oxide Cr_3O_8.

THE UNIVERSITY, NOTTINGHAM. [*Received, July 31st,* 1963.]

[6] Wendlandt, *Analyt. Chim. Acta*, 1956, **15**, 435.

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107. *Preparation and Purification of Diborane.*

By B. J. DUKE, J. R. GILBERT, and I. A. READ.

DIBORANE has been prepared by the action of potassium borohydride on concentrated sulphuric or phosphoric acid, $H^+ + BH_4^- = \frac{1}{2}B_2H_6 + H_2$, for use in a study of its reactions with alcohols. Weiss and Shapiro [1] reported good yields of diborane when sulphuric acid was used, but with impurities of sulphur dioxide and, if the potassium borohydride was added rapidly, hydrogen sulphide. We find that the use of phosphoric acid provides a safe and convenient preparation of diborane free from impurities which would affect the reactions with alcohols; it is superior to methods used previously [2] in this laboratory.

Experimental.—Following the method outlined by Jolly,[3] the preparation line consisted of a 250-ml. flask connected to a vacuum line through three traps. The reaction mixture was stirred with a magnetic stirrer. Potassium borohydride was placed in an L-shaped side-arm, and it could be added to the flask by rotating the side-arm. " AnalaR " concentrated sulphuric acid was placed in the flask and the apparatus evacuated. The potassium borohydride was added during half an hour, and the products, after passage through a trap cooled to −126° with a liquid nitrogen–methylcyclohexane slush, were collected at liquid-nitrogen temperature. The hydrogen was pumped off and the diborane purified by distillation from a trap cooled to −126°.

Samples were analysed on an A.E.I. M.S.2 mass spectrometer. The total condensable product, without purification, contained 15% of sulphur dioxide, 2% of hydrogen sulphide, and a trace of carbon dioxide. Purification as described above removed all the sulphur dioxide but very little of the hydrogen sulphide and carbon dioxide. The vapour pressures of diborane, hydrogen sulphide, and carbon dioxide at −126° are 70 mm., 6 mm., and 5 mm., respectively, and their removal by fractional distillation is thus troublesome.

To obtain a purer sample, the method of Weiss and Shapiro [1] was followed exactly, except that phosphoric acid was used instead of sulphuric acid. Unpurified condensable samples contained no impurities except the trace of carbon dioxide found previously; no phosphine was present. The carbon dioxide (<1% by volume) was thought to come from carbonate impurity in the potassium borohydride; it increased in amount when the yield of diborane was small.

[1] Weiss and Shapiro, *J. Amer. Chem. Soc.*, 1959, **81**, 6167.
[2] Danby, Gobbett, and Linnett, *J.*, 1962, 2076.
[3] Jolly, " Synthetic Inorganic Chemistry," Prentice-Hall, New Jersey, 1960, p. 158.

The yield for both methods was 50—70%, although low yields were obtained from phosphoric acid if the reaction flask contained large quantities of acid, resulting in inefficient stirring. The reaction with phosphoric acid proceeded smoothly, the whole mixture frothing, whereas with sulphuric acid it proceeded vigorously on the surface.

One of us (B. J. D.) thanks the Gas Council for a Scholarship

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[*Received, August 7th,* 1963.]

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108. *Isotope-dilution Analysis of Amino-acids. Part II.*[1] *The Sensitivity of the Method.*

By W. R. WATERFIELD.

PREVIOUS work [1] has shown that it is possible, by using reverse isotope-dilution techniques, to detect the presence of less than 0·1% of a D-amino-acid in its isotopically labelled L-enantiomorph. The method has now been extended to the optical analysis of radiochemically inactive amino-acids through the formation of [α-^{14}C]benzyloxycarbonyl derivatives, as illustrated by the following analysis of D-asparagine.

Slightly less than the theoretical quantity of [α-^{14}C]benzyloxycarbonyl chloride, Ph·^{14}CH$_2$·O·COCl, reacted quantitatively with 7 mg. of optically pure D-asparagine monohydrate, to give [α-^{14}C]benzyloxycarbonyl-D-asparagine. This product was added to an excess of carrier benzyloxycarbonyl-L-asparagine and the mixture recrystallised until all trace of the D-enantiomorph had been removed, as determined by the specific activity of the mixture. After ten recrystallisations, the specific activity of the residual benzyloxycarbonyl asparagine was less than 0·001% of the original homogenised sample. Since there is no evidence that benzyloxycarbonyl chloride reacts at different rates with the D- and the L-forms of amino-acids, the above result indicates that the sample of D-asparagine investigated contains less than one part in 100,000 of the L-enantiomorph, and further confirms the observation [1,2] that no racemisation occurs during the benzyloxycarbonylation of amino-acids. The value of 0·001% represents the practical limit of sensitivity of the reverse isotope-dilution method with standard scintillation counting procedures and microcurie amounts of ^{14}C-labelled derivatives at a readily attainable specific activity. The attempted detection of smaller quantities of optical impurities gives spurious results caused by radio-active contamination.

Enzymic methods [3] for the determination of the optical purity of amino-acids to the above degree of sensitivity require several millimoles of substrate; thus isotope-dilution analysis of a suitable derivative has great advantages when only a few milligrams of (expendable) amino-acid are available. The method can also be extended to the investigation of amino-acid mixtures, and has been successfully used for the optical analysis of peptide hydrolysates.[4]

Experimental.—M. p.s were observed on a Kofler block. Analytical-reagent grade solvents were used throughout. Carbon-14 samples were directly measured in a β-liquid scintillation counter (IDL Counter Type 6012), with [1-^{14}C]hexadecane (Radiochemical Centre CFR 5) as internal standard. The scintillant was a solution of naphthalene 10%, 2,5-diphenyloxazole 0·7%, and 2,2′-*p*-phenylenedi-(5-phenyloxazole) 0·03% in dioxan.

[1] Part I, Waterfield, *J.*, 1963, 2731.
[2] Bergmann and Zervas, *Ber.*, 1932, **65**, 1192.
[3] Cf. Greenstein and Winitz, "Chemistry of the Amino-Acids," John Wiley and Sons, Inc., New York, 1961, Vol. II, p. 1738.
[4] Waterfield, unpublished results.

Benzyloxycarbonylasparagines. Benzyloxycarbonyl-L-asparagine, m. p. 164°, $[\alpha]_D^{18}$ +7·5° (in 2% AcOH), and benzyloxycarbonyl-D-asparagine, m. p. 162°, $[\alpha]_D^{18}$ −7·6° (in 2% AcOH), were prepared in sodium hydrogen carbonate solution by a standard procedure.[5]

[α-^{14}C]*Benzyloxycarbonyl chloride.* [α-^{14}C]Benzyl alcohol (0·5 mc., 18·3 mg., 2·95 mc/mmole; Radiochemical Centre CFA 133) was treated with carbonyl chloride (0·36 g.) in benzene (3 ml.) and kept at room temperature for 48 hr. The benzene was fractionated off and the residue treated with dry benzene (3 ml.), and the solvent again distilled off to remove traces of carbonyl chloride. The oily product was dissolved in dry benzene (3·9 g.), and a portion (216 mg.) of this solution was treated with aqueous ammonia (*d* 0·88), yielding [α-^{14}C]benzyl carbamate. This product was homogenised in ethyl acetate with carrier benzyl carbamate [6] (217 mg.), and recrystallised to constant specific activity from benzene–hexane. The homogenised sample had a specific activity of 14·8 μc/mmole which decreased to 13·6 μc/mmole after recrystallisation, demonstrating that the bulk benzene solution contained 0·4 mc (80%) of carbon-14, of which 0·368 mc (92%) was present as [α-^{14}C]benzyloxycarbonyl chloride. The radiochemical purity of this material was satisfactory for the following preparation, and was assumed to have a specific activity equal to that of the [α-^{14}C]benzyl alcohol.

[α-^{14}C]*Benzyloxycarbonyl-D-asparagine.* To a solution of D-asparagine monohydrate (7 mg., 0·047 mmole), freshly recrystallised (8 times) from water without change of specific rotation ($[\alpha]_D^{20}$ +5·4°), and sodium hydrogen carbonate (30 mg.) in water (1 ml.), was added a solution of [α-^{14}C]benzyloxycarbonyl chloride (115 μc, 2·95 mc/mmole, 0·039 mmole) in benzene (1·1 g.). The mixture was shaken for 2 hr. at room temperature, most of the benzene was removed in a stream of nitrogen, water (0·5 ml.) was added, and shaking continued for 2 hr. The solution was washed with benzene (3 × 1 ml.), acidified to pH 1 with 2N-hydrochloric acid, and extracted with ethyl acetate (7 × 2 ml.). A negligible amount of radioactivity was present in the seventh extract. The extracts were combined, dried (Na_2SO_4), and filtered. A portion (0·55 g.) of the combined extracts (11·2 g.) was homogenised with carrier benzyloxycarbonyl-D-asparagine (74 mg.). The homogenised sample had a specific activity of 20·3 μc/mmole which remained unchanged on crystallisation from ethyl acetate–hexane, demonstrating the presence of 100% radiochemically pure [α-^{14}C]benzyloxycarbonyl-D-asparagine (114 μc, 98%) in the combined extracts.

Determination of the L-content of [α-^{14}C]*benzyloxycarbonyl-D-asparagine.* [α-^{14}C]Benzyloxycarbonyl-D-asparagine (108 μc, 9·8 mg., 2·95 mc/mmole) was homogenised in ethyl acetate with carrier benzyloxycarbonyl-L-asparagine (408 mg., dilution factor [1] 42) and crystallised 3 times from ethyl acetate–hexane. The product was transferred to a new crystallisation vessel and the process repeated 3 times. The product was transferred to a second new vessel, "scavenger" [1] benzyloxycarbonyl-D-asparagine (1 mg.) was added, and the mixture was again recrystallised (twice). After addition of more benzyloxycarbonyl-D-asparagine (1 mg.), followed by further recrystallisation (twice), the residual benzyloxycarbonyl-L-asparagine (40 mg.) contained less than 1×10^{-4} μc of carbon-14.

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[5] Greenstein and Winitz, "Chemistry of the Amino-Acids," John Wiley and Sons, Inc., New York, 1961, Vol. II, p. 891.
[6] Carter, Frank, and Johnston, *Org. Synth.*, 1943, **23**, 13.

109. *A New Synthesis of Acetylenes. Part III. Diacetylenes.*

By S. T. D. Gough and S. Trippett.

We previously showed[1] that β-ketoalkylidenephosphoranes, $Ph_3P{:}CR^1{\cdot}COR^2$ (I), at ~280° give triphenylphosphine oxide and disubstituted acetylenes provided that the acetylenic bond formed is conjugated with an aromatic nucleus or a carbonyl group or its equivalent. The synthesis has now been extended to the preparation, in moderate yield, of a number of diacetylenes, starting from αβ-acetylenic acid chlorides.

The required β-ketoalkylidenephosphoranes (II) were prepared by reaction of the αβ-acetylenic acid chlorides (III; R^1 = Ph, Bu) with one mol. of the phosphorane (IV; R^2 = Ph, CN, or CO_2Et) in the presence of triethylamine which obviates the need for a second mol. of phosphorane. Pyrolysis at 280—300° under reduced pressure then gave the diacetylenes in 9—30% yield. Where unknown, these were characterised by hydrogenation. Oxalyl chloride and ethoxycarbonylmethylenetriphenylphosphorane gave the expected bisphosphorane which, however, gave no diacetylenedicarboxylate on pyrolysis.

$$\underset{\text{(III)}}{R^1{\cdot}C{:}C{\cdot}COCl} + \underset{\text{(IV)}}{Ph_3P{:}CHR^2} \xrightarrow{Et_3N} \underset{\text{(II)}}{Ph_3P{:}CR^2{\cdot}CO{\cdot}C{:}CR^1} \longrightarrow Ph_3PO + R^1{\cdot}C{:}C{\cdot}C{:}CR^2$$

β-Ketoalkylidenetriphenylphosphoranes (I) in which R^1 is hydrogen do not give monosubstituted acetylenes on pyrolysis.[2] The phosphoranes (I; R^1 = H, R^2 = Me or Ph) have now been shown to give triphenylphosphine in high yield on decomposition, but no other volatile product was observed.

Experimental.—1-*Cyano*-2-*oxo*-4-*phenylbut*-3-*ynylidenetriphenylphosphorane.* Phenylpropionyl chloride (17·4 g.) in benzene (20 ml.) was added slowly to a stirred solution of cyanomethylenetriphenylphosphorane (30·1 g.) and triethylamine (10·1 g.) in benzene (500 ml.), and the solution was set aside at room temperature overnight. Filtration gave the acetylenic *phosphorane* (26·0 g.), m. p. (from chloroform–ethyl acetate) 246—247° (decomp.), $\lambda_{max.}$ 4·5, 4·6, 6·6 μ (Found: C, 81·3; H, 4·8. $C_{29}H_{20}NOP$ requires C, 81·2; H, 4·7%). The filtrate was washed with water, dried, and evaporated. Crystallisation of the residue from chloroform–ethyl acetate gave a further 8·5 g. of the product (total yield 80·5%).

In a similar way the following were obtained: 1-*ethoxycarbonyl*-2-*oxo*-4-*phenylbut*-3-*ynylidenetriphenylphosphorane* (71%), m. p. (from ethyl acetate–light petroleum) 178—178·5°, $\lambda_{max.}$ 4·6, 6·0, and 6·6 μ (Found: C, 78·2; H, 5·3. $C_{31}H_{25}O_3P$ requires C, 78·2; H, 5·25%); 2-*oxo*-1,4-*diphenylbut*-3-*ynylidenetriphenylphosphorane* (60%), m. p. (from chloroform–light petroleum) 241—242°, $\lambda_{max.}$ 4·55 and 6·6 μ (Found: C, 84·65; H, 4·9. $C_{34}H_{25}OP$ requires C, 85·0; H, 5·2%); 1-*cyano*- (76%), m. p. (from benzene–light petroleum) 202—203°, $\lambda_{max.}$ 4·55, 4·65, and 6·5 μ (Found: C, 79·05; H, 5·75. $C_{27}H_{24}NOP$ requires C, 79·4; H, 5·85%), and 1-*ethoxycarbonyl*-2-*oxo*-*oct*-3-*ynylidenetriphenylphosphorane* (76%), m. p. (from benzene–light petroleum) 137—138°, $\lambda_{max.}$ 4·55, 6·0, and 6·6 μ (Found: C, 75·15; H, 6·25. $C_{29}H_{29}O_3P$ requires C, 75·3; H, 6·4%); 2-*oxo*-1-*phenyloct*-3-*ynylidenetriphenylphosphorane* (57%), m. p. (from aqueous ethanol) 207—208°, $\lambda_{max.}$ 4·5 and 4·8 μ (Found: C, 83·3; H, 6·3. $C_{32}H_{29}OP$ requires C, 83·5; H, 6·3%).

Pyrolysis of 1-*cyano*-2-*oxo*-4-*phenylbut*-3-*ynylidenetriphenylphosphorane.* The phosphorane (30·0 g.) was heated at 280°/0·35 mm. for 1 hr., the distillate (10·6 g.) being collected in a receiver cooled in liquid nitrogen. The distillate, in benzene solution, was then placed on a column of neutral alumina (grade III). Elution with benzene gave 5-*phenylpent*-2,4-*diynonitrile* (30%), m. p. (from ether at −40°) 65—66°, $\lambda_{max.}$ 243, 270, 287, 303, and 323 mμ (ε 48,200, 7030, 13,400, 18,800, and 13,800 in EtOH), 4·43 and 4·53 μ (Found: C, 87·2; H, 3·55; N, 9·2. $C_{11}H_5N$ requires C, 87·5; H, 3·3; N, 9·2%). The nitrile (1·009 g.) was reduced in ethanol in the presence of a palladium catalyst (uptake of hydrogen 4·2 mol.). The resulting saturated

[1] Gough and Trippett, Part I, *J.*, 1962, 2333; Part II, *J.*, 1962, 2337.
[2] Trippett and Walker, *J.*, 1959, 3874.

nitrile ($\lambda_{max.}$ 4·5 μ) gave, on alkaline hydrolysis, δ-phenylvaleric acid, m. p. and mixed m. p. (from water) 60°.

In a similar way pyrolysis of the above phosphoranes gave the following diacetylenes: diphenyldiacetylene (24%), m. p. (from methanol) 89° (lit.,[3] 88°), having the recorded [4] ultraviolet spectrum; ethyl 5-phenylpenta-2,4-diynoate (9%), $\lambda_{max.}$ 252, 265, 276, 290, and 310 mμ (ε 9250, 11,450, 11,900, 12,370, and 9175 in EtOH), 4·5 and 5·9 μ [the ester absorbed 4·0 mol. of hydrogen (Pd–C in ethanol); alkaline hydrolysis then gave δ-phenylvaleric acid, m. p. and mixed m. p. 60°]; *ethyl nona-2,4-diynoate* (16%), b. p. 76—78°/0·05 mm., $\lambda_{max.}$ 235, 247, 261, and 277 mμ (ε 1750, 4000, 5680, and 3850 in EtOH) 4·52 and 5·9 μ (Found: C, 74·05; H, 7·8. $C_{11}H_{14}O_2$ requires C, 74·25; H, 7·9%) [the ester absorbed 4·2 mol. of hydrogen (Pd–C in ethanol); the saturated ester ($\lambda_{max.}$ 5·72 μ) was hydrolysed by alkali and the resulting nonanoic acid identified as the amide, m. p. and mixed m. p. (from aqueous ethanol) 99—100°]; 1-phenylocta-1,3-diyne (23%), m. p. 3—4°, b. p. 120°/0·6 mm., $\lambda_{max.}$ 244, 257, 272, and 288 mμ (ε 11,520, 19,820, 28,970, and 23,710 in ethanol), 4·45 μ [lit.,[5] $\lambda_{max.}$ 245, 257, 271, and 288 mμ (ε 7500, 19,000, 26,000, and 23,000)], n_D^{25} 1·5925 (lit.,[5] n_D^{23} 1·5922). Pyrolysis of 1-cyano-2-oxo-oct-3-ynylidenetriphenylphosphorane gave, probably, nona-2,4-diynonitrile (23%), b. p. 63—64°/1 mm., $\lambda_{max.}$ 200 mμ (ε 68,170 in hexane), 4·55 and 4·6 μ (Found: C, 81·1; H, 6·7. Calc. for C_9H_9N: C, 82·6; H, 6·85%).

1,4-*Diethoxycarbonylbut*-2,3-*dioxobutanediylidenebistriphenylphosphorane*. Oxalyl chloride (2·7 g.) in benzene (10 ml.) was added over 30 min. to a stirred solution of ethoxycarbonyl methylenetriphenylphosphorane (30 g.) in benzene (300 ml.), and the mixture stirred for a further 2 hr. Filtration gave ethoxycarbonylmethyltriphenylphosphonium chloride (~100%), m. p. and mixed m. p. (from acetone–benzene) 90°. Evaporation of the filtrate and crystallisation of the residue from aqueous ethanol gave the *bisphosphorane* (8·1 g.), m. p. 248—249°, $\lambda_{max.}$ 5·98 and 6·4 μ (Found: C, 73·8; H, 5·3. $C_{46}H_{40}O_6P_2$ requires C, 73·6; H, 5·35%).

Pyrolysis of phenacylidenetriphenylphosphorane. The phosphorane (20 g.) was heated at 300°/2 mm. for 1 hr., leaving a black intractable residue. Recrystallisation of the distillate from ethanol gave triphenylphosphine (81%), m. p. and mixed m. p. 80°.

Similarly acetonylidenetriphenylphosphorane gave 59%, and *p*-bromophenacylidenetriphenylphosphorane gave 79%, of triphenylphosphine.

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[3] Hollemann, *Ber.*, 1887, **20**, 3087.
[4] Armitage, Entwistle, Jones, and Whiting, *J.*, 1954, 150.
[5] Black, Horn, and Weedon, *J.*, 1954, 1704.