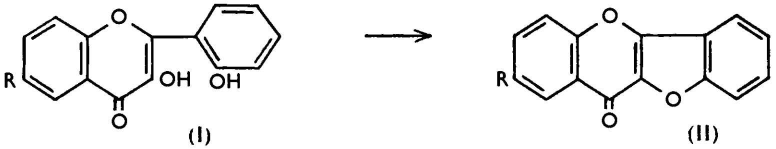
NOTES

617. *Aluminium Complexes of Flavonols.*

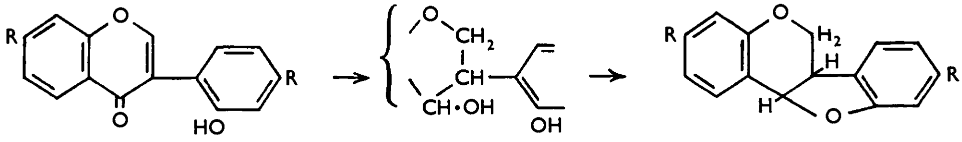
By J. A. BALLANTINE and W. B. WHALLEY.

OUR interest [1,2] in the properties of 2′-methoxyphenylpyrones led us to investigate the possibility of dehydrating 3 : 2′-dihydroxyflavones (I) to linear dehydro-analogues (II) of the homopterocarpin ring system [3] (V), since it is possible that the biogenesis of homopterocarpin and pterocarpin follows a comparable route (III) ⟶ (IV) ⟶ (V) (cf. King and Bottomley [4]).

3 : 2′-Dihydroxy-6-methylflavone (I; R = Me), prepared in the usual manner from 2′-hydroxy-2-methoxy-5′-methylchalkone, was, however, recovered from solution in cold and hot (100°) concentrated sulphuric acid, and was unaffected by phosphoric oxide in boiling benzene and by refluxing syrupy phosphoric acid, and acetic anhydride furnished the diacetate. In an effort to effect a type of " cyclodehydration," heating the dimethyl ether with aluminium chloride in nitrobenzene gave a crystalline complex of the dihydroxyflavone and aluminium of the probable type (Flavone–2H)$_3$Al, although on the basis of



(I) (II)



(III) (R = OMe) (IV) (V) (R = OMe)

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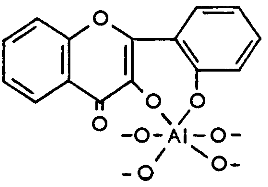
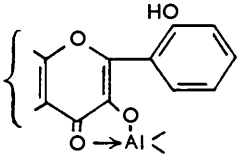
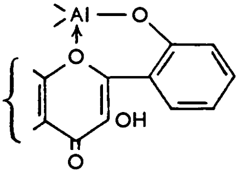
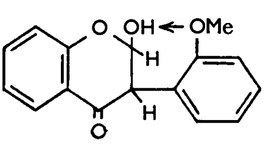
[1] Whalley, *J.*, 1953, 3366; Simpson and Whalley, *J.*, 1955, 166.
[2] Whalley, *J. Amer. Chem. Soc.*, 1953, **75**, 1059.
[3] Späth and Schläger, *Ber.*, 1940, **73**, 1; McGookin, Robertson, and Whalley, *J.*, 1940, 787.
[4] King and Bottomley, *J.*, 1954, 1400.

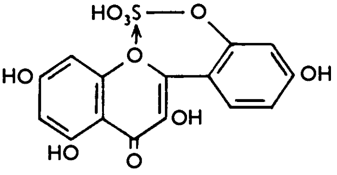
the analytical figures closely allied formulæ cannot be excluded. 3 : 2′-Dihydroxyflavone furnished an analogous crystalline complex, from which the aluminium was not easily removed. The absence of chlorine and methoxyl groups and of hydroxyl absorption bands in the infrared spectra of these compounds, the negative ferric reaction, and the insolubility in aqueous sodium hydroxide indicate that the 3- and the 2′-hydroxyl group are concerned in this complex formation. These observations are satisfactorily accommodated by a formula of type (VI), although other formulations cannot be entirely excluded. Formulæ of types (VII) and (VIII) were eliminated by the failure of 3- and 2′-hydroxy-6-methylflavone to yield analogous compounds with aluminium. The fluorescence of hydroxyflavones in the presence of various metal ions is well established and morin (3 : 5 : 7 : 2′ : 4′-pentahydroxyflavone) has long been used for the detection of metal ions (particularly aluminium) because of the unique intensity of the fluorescence [5] exhibited in the presence of these ions in both acid and alkaline solution. Undoubtedly this effect may be ascribed to complex formation of the type described above and we have found that morin furnishes an intensely fluorescent, solid, non-crystallisable complex with aluminium.


(VI)


(VII)


(VIII)


(IX)


(X)

These observations directed our attention to the constitution of the anhydrosulphate of morin,[6] which has been allocated the structure (X) by Robinson and Venkataraman.[7] Unfortunately repeated attempts to prepare a crystalline sulphate from 3 : 2′-dihydroxy-6-methylflavone were unsuccessful, but the production of normal sulphates by 3- and 2′-hydroxy-6-methylflavone, the latter of which might be expected to furnish an anhydrosulphate of type (X) by analogy with morin,[7] suggests that Robinson's formula should be treated with reserve.

It is noteworthy that in 3 : 2′-dihydroxyflavones the hydroxyl groups which interact with aluminium in this novel manner occupy the same relative positions as the hydroxyl and the methoxyl group in 2-hydroxy-2′-methoxy*iso*flavanones (IX) where hydrogen bonding of these two groups has been suggested [2] as a major contributary factor to the abnormal stability of the 2-hydroxy*iso*flavanone system. In each case a seven-numbered ring is involved.

Experimental.—3 : *2′-Dihydroxy-*6-*methylflavone.* A solution of potassium hydroxide (10 g.) in water (10 ml.) was added to a solution of 2-acetyl-*p*-cresol (OH = 1) (5 g.) and *o*-methoxybenzaldehyde (8 g.) in alcohol (20 ml.) (cooling as required), and 2 hr. later the product was

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[5] Neelakantam and Row, *Indian Acad. Sci.*, 1942, **14**, *A*, 307; Schantl, *Mikrochem.*, 1924, **2**, 174.
[6] Perkin and Pate, *J.*, 1895, **67**, 644.
[7] Robinson and Venkataraman, *ibid.*, 1929, 61.

isolated by acidification of the cold solution and purified from methanol to furnish *2'-hydroxy-2-methoxy-5'-methylchalkone* (7 g.) in yellow needles, m. p. 103° (Found: C, 76·2; H, 6·1. $C_{17}H_{16}O_3$ requires C, 76·0; H, 6·0%).

When hydrogen peroxide (100-vol.; 100 ml.) was added gradually to a warm solution (30°) of 2'-hydroxy-2-methoxy-5'-methylchalkone (5 g.) in 30% aqueous sodium hydroxide (100 ml.) and the mixture acidified 30 min. later, the precipitated *3-hydroxy-2'-methoxy-6-methylflavone* separated from methanol in pale yellow prisms (5·2 g.), m. p. 200° (Found: C, 72·6; H, 4·8. $C_{17}H_{14}O_4$ requires C, 72·3; H, 5·0%).

Methylation of this by methyl sulphate–potassium carbonate–acetone furnished a quantitative yield of *3 : 2'-dimethoxy-6-methylflavone* in needles, m. p. 124°, from methanol (Found: C, 72·7; H, 5·6. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%).

The demethylation of either 3 : 2'-dimethoxy-6-methyl- or of 3-hydroxy-2'-methoxy-6-methyl-flavone (5 g.) during 1 hr. with boiling hydriodic acid (25 ml.; *d* 1·7)–acetic acid (from 20 ml. of acetic anhydride) furnished *3 : 2'-dihydroxy-6-methylflavone* which separated from methanol in pale yellow needles (4·5 g.), m. p. 200°, having an intense green-brown ferric reaction in alcohol (Found: C, 71·8; H, 4·6. $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%). The mixed m. p. with 3-hydroxy-2'-methoxy-6-methylflavone was *ca.* 170°.

The *diacetate* separated from aqueous methanol in needles, m. p. 128°, having a negative ferric reaction in alcohol (Found: C, 65·3; H, 5·0. $C_{20}H_{16}O_6,H_2O$ requires C, 64·9; H, 4·9%).

A solution of 3: 2'-dimethoxy-6-methylflavone (1 g.) in nitrobenzene (30 ml.) containing aluminium chloride (4 g.) was heated on the steam-bath for 4 hr. After isolation in the usual manner followed by the removal of the nitrobenzene in steam the green-yellow solid was purified from benzene (sparingly soluble) to give the *complex* (0·6 g.) in intense yellow prisms, m. p. >330° [Found: C, 69·4; H, 4·3; Al, 3·8. $(C_{16}H_{10}O_4)_3Al$ requires C, 69·8; H, 3·7; Al, 3·3%]. This compound is moderately soluble in methanol, ethanol, acetone, and chloroform, and the solutions exhibit an intense green fluorescence, even in very high dilution. The complex is recovered quantitatively after chromatography in chloroform on activated aluminium, has no ferric reaction in alcohol, is insoluble in hot 2N-sodium hydroxide, and gives rise quantitatively to 3 : 2'-dihydroxy-6-methylflavone when the solution in acetic–hydrochloric acid (1 : 1) is refluxed for 10 min.

3-Hydroxy-2'-methoxy-6-methyl- and 3 : 2'-dihydroxy-6-methyl-flavone afforded the same complex under similar conditions.

Similarly 3 : 2'-dihydroxyflavone [1] gave rise to a *complex* which separated from benzene in bright yellow needles, m. p. >330° [Found: C, 68·4; H, 3·6; Al, 4·4. $(C_{15}H_8O_4)_3Al$ requires C, 68·9; H, 3·1; Al, 3·5%].

3-Hydroxy-6-methylflavone. Prepared by the condensation of 2-acetyl-*p*-cresol (5 g.) and benzaldehyde (8 g.) with potassium hydroxide (10 g.) in water (10 ml.) and alcohol (20 ml.), *2'-hydroxy-5'-methylchalkone* separated from methanol in orange tablets (6 g.), m. p. 110° (Found: C, 80·3; H, 5·8. $C_{16}H_{14}O_2$ requires C, 80·7; H, 5·9%).

Oxidation of this chalkone (1 g.) with 100-vol. hydrogen peroxide in the usual manner gave 3-hydroxy-6-methylflavone (0·6 g.), m. p. 197°. Auwers and Müller [8] record m. p. 197—198° for a specimen prepared by another method.

The *sulphate* separated from sulphuric–acetic acid in bright yellow plates, m. p. *ca.* 120° (decomp.) (Found: C, 53·5; H, 4·2. $C_{15}H_{12}O_3,H_2SO_4$ requires C, 54·9; H, 4·0%).

Similarly the *sulphate* of 2'-hydroxy-6-methylflavone [9] separated from sulphuric–acetic acid in bright yellow plates, m. p. 226° (decomp.) (Found: C, 54·7; H, 3·9%).

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[*Received, March 9th,* 1956.]

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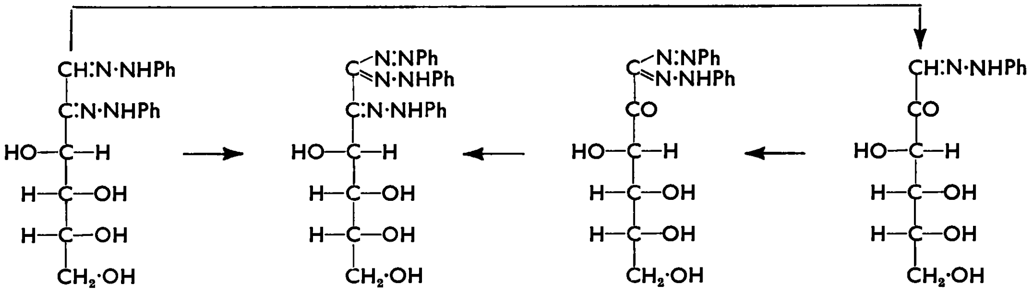
[8] Auwers and Müller, *Ber.*, 1908, **41**, 4239.

[9] Baker and Besley, *J.*, 1940, 1103.

618. *Proof of the Structure of* " D-*Glucosazone-formazan* " (1-*Phenylazo*-D-*glucosazone*) *by Synthesis.*

By L. MESTER and Á. MAJOR.

" D-GLUCOSAZONE-FORMAZAN " (1-phenylazo-D-glucosazone) (II) was prepared by one of us [1] by coupling D-glucosazone (I) with benzenediazonium chloride in alkaline alcohol. A few simple representatives of this class were synthesised long ago by Bamberger and Lorenzen [2] by condensing α-keto-formazans with phenylhydrazine : *e.g.*, acetylformazan, NPh:N·CAc:N·NHPh, gave " methylglyoxalosazone-formazan " [1-phenylazo-1 : 2-(di-*N*′-phenylhydrazono)propane]. Similarly we now find that coupling D-glucosone 1-phenylhydrazone [3] with diazotised aniline in cold pyridine yields the " glucosone-formazan " (IV) as red needles, which with phenylhydrazine gives the known violet " D-glucosazone-formazan " (II). The identity of the two products not only proves the structure of " D-glucosazone-formazan," but leaves no doubt that in Henseke and Lorenzen's D-glucosone phenylhydrazone the hydrazine group is attached to $C_{(1)}$ since aldehyde phenylhydrazones, but not ketone phenylhydrazones, yield formazans.[4, 5] This open-chain structure of the phenylhydrazone [6] may be in equilibrium with the 2 : 6-pyranoside structure but the latter is not able to afford the formazan—the cyclic structure was postulated by Henseke and Liebenow for D-glucosone 1-*N*′-methyl-*N*′-phenylhydrazone.



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

Experimental.—1-*Phenylazo*-D-*glucosone* 1-*phenylhydrazone*. D-Glucosone 1-*N*′-phenylhydrazone (1·62 g., 0·006 mole), dissolved in pyridine (16·2 ml.), was coupled at −5° with diazotised aniline (0·6 g., 0·006 mole + 7·5%). After ½ hr. the solution was poured on ice and water, and 24 hr. later the sticky material was collected. Dissolving it in absolute alcohol (0·3 ml.) gave 1-*phenylazo*-D-*glucosone* 1-N′-*phenylhydrazone* as red needles (0·22 g.) which, twice recrystallised from 50% alcohol, had m. p. 166° (0·20 g.) (Found : N, 14·8. $C_{18}H_{20}O_5N_4$ requires N, 15·05%).

1-*Phenylazo*-D-*glucosazone*. The preceding product (0·15 g., 0·0004 mole) in warm acetic acid (6 ml.) and alcohol (1·5 ml.) was treated with phenylhydrazine (0·05 g., 0·0004 mole + 10%). After 4½ hr. the product crystallised in violet needles (0·03 g.). The mother-liquor was poured into water (40 ml.), and the precipitate filtered off. The two products were combined and recrystallised from pyridine (5 parts)–alcohol (15 parts) and then had m. p. 187—188° alone or mixed with the " formazan " prepared by the previous method.

The authors thank Professor G. Zémplen for his advice and interest, Assistant Professor G. Henseke for information, and Miss Ilona Batta for microanalyses.

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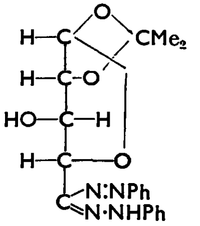
[1] Mester, *J. Amer. Chem. Soc.*, 1955, **77**, 4301.
[2] Bamberger and Lorenzen, *Ber.*, 1892, **25**, 3542.
[3] Personal communication from G. Henseke; M. Winter, Diplomarbeit, Greifswald, 1954.
[4] Von Pechmann, *Ber.*, 1892, **25**, 3181
[5] Mester and Major, *J. Amer. Chem. Soc.*, 1956, **78**, 1403.
[6] *Idem*, *J. Amer. Chem. Soc.*, 1955, **77**, 4297.
[7] Henseke and Liebenow, *Chem. Ber.*, 1954, **87**, 1068.

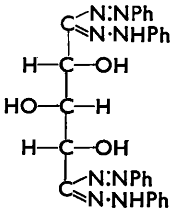
619. *Two Novel Carbohydrate Formazans.*

By L. Mester and E. Móczár.

The product obtained from 1 : 2-*O*-*iso*propylidene-D-glucose by periodic acid [1] has been converted by us into the monophenylhydrazone derived from 1 : 2-*O*-*iso*propylidene-D-*xylo*trihydroxyglutardialdehyde and into D-*xylo*trihydroxyglutardialdehyde bisphenylhydrazone which were obtained earlier by using lead tetra-acetate as the oxidant.[2,3,4]

(I)





(II)

Reaction of the crystalline monophenylhydrazone with diazotised aniline in pyridine–ethanol (cf. preceding communication) gave 75% of the compound (I), and the bisphenylhydrazone gave the bis-compound (II). The former product is the first sugar derivative to contain the formazan group at the highest-numbered carbon atom: the latter belongs to a novel class of sugar derivatives. Use of these compounds as biological redox indicators is being investigated.[5,6]

Experimental.—1 : 2-*O*-*iso*Propylidene-D-glucose was oxidised with periodic acid as described by Sowden,[1] and from the product the monophenylhydrazone and, after hydrolysis, the bisphenylhydrazone were prepared by Iwadare's method.[2]

5-*Deoxy*-5-*phenylazo*-5-N′-*phenylhydrazono*-1 : 2-*O*-iso*propylidene*-D-*xylofuranose.* To 5-deoxy-5-*N*′-phenylhydrazono-1 : 2-*O*-*iso*propylidene-D-xylofuranose (17 g.) in pyridine (120 ml.) and ethanol (180 ml.) at −5° was added a diazo-solution from aniline (6 g., 1·075 mol.). The mixture at once became red and after 20 min. was poured on ice. Next day the *product* (7·5 g., 74·5%) was collected and thrice recrystallised from alcohol, forming red needles, m. p. 202° (Found: N, 14·5; C, 62·9; H, 5·4. $C_{20}H_{22}O_4N_4$ requires N, 14·7; C, 62·9; H, 5·3%).

The "formazan" (0·5 g.) with pyridine (5 ml.) and acetic anhydride (5 ml.) in 24 hr. at room temperature gave a *monoacetate* (0·8 g.) which after three crystallisations from alcohol had m. p. 152° (0·15 g.) (Found: N, 13·5; C, 62·9; H, 5·7. $C_{22}H_{24}O_6N_4$ requires N, 13·2; C, 62·55; H, 5·2%).

1 : 5-*Diphenylazo*-D-xylo*trihydroxyglutardialdehyde bis*-N′-*phenylhydrazone.* D-*xylo*Trihydroxyglutardialdehyde bisphenylhydrazone (0·48 g.) in pyridine (7 ml.) and alcohol (7 ml.) was added with ice-salt cooling to a diazo-solution (3 ml.) from aniline (0·3 g.). After 1 hr. the red solution was poured on ice-water; the precipitate, washed several times with water, solidified in 2 days (yield, 0·3 g., 38%). Recrystallisation from ethanol yielded the *product* (0·18 g.), m. p. 181—182° (Found: N, 20·3. $C_{29}H_{28}O_3N_8$ requires N, 20·8%). With pyridine (1 ml.) and acetic anhydride (1 ml.) it (0·05 g.) gave the *triacetate*, m. p. 163—164° (Found: N, 16·4. $C_{35}H_{34}O_6N_8$ requires N, 16·8%).

We thank Professor G. Zemplén for valuable advice and Miss Ilona Batta for the microanalyses.

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[1] Sowden, *J. Amer. Chem. Soc.*, 1951, **73**, 5496; 1952, **74**, 4377.
[2] Iwadare, *Bull. Chem. Soc. Japan*, 1941, **16**, 40.
[3] Grosheintz and Fischer, *J. Amer. Chem. Soc.*, 1948, **70**, 1476.
[4] Brocca and Dansi, *Ann. Chim.* (*Italy*), 1954, **44**, 120.
[5] Zemplén, Mester, and Eckhart, *Chem. Ber.*, 1953, **86**, 472.
[6] Jámbor and Mester, *Acta Chim. Acad. Sci. Hung.*, 1955, **6**, 263.

620. *Critical Concentrations of Some Alkylpyridinium Iodides in Water and in Xylene evaluated from Solubility Measurements.*

By C. C. Addison and C. G. L. Furmidge.

At the critical concentration for the formation of micelles in solution there is a sharp increase in the solubility of long-chain electrolytes.[1] This is well established for salts containing long-chain anions [2,3] and long-chain cations,[3] but experimental data on the latter are more limited; the measurements by Adam and Pankhurst [3] included few solubility values below the critical concentration. During a separate investigation,[4] solubility measurements on some alkylpyridinium salts were extended to lower ranges than those previously used, so that the critical concentrations could be evaluated by this method; the solubilities of some of the salts in water or xylene have not previously been measured. This note records these new data.

Fig. 1.

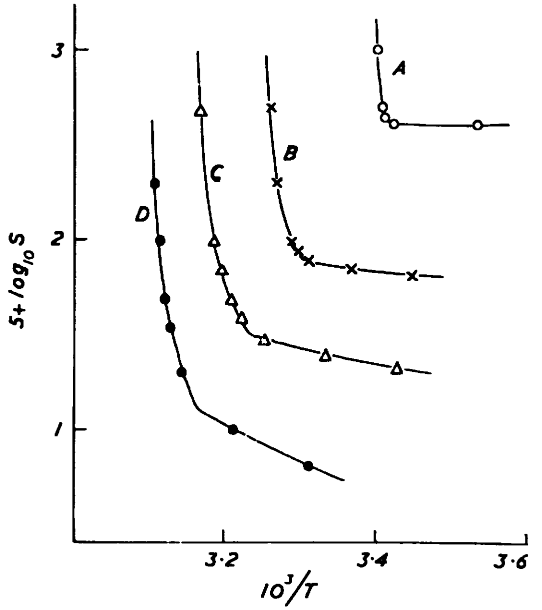
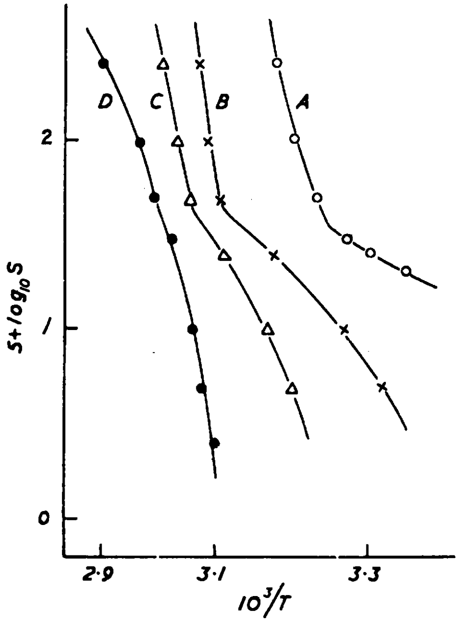


Fig. 2.



Experimental.—Alkylpyridinium chlorides were prepared (free from homologues) by reaction between the alkyl chloride and pyridine,[5] and then converted into the iodide.[4] Crystals of the alkylpyridinium iodides are not readily wetted by water, and preparation of dilute solutions by direct dissolution of a small weighed quantity of the iodide may lead to error; concentrated solutions were therefore diluted. Glass tubes containing 10 ml. of the solution were sealed and then cooled until solute crystallised. In some cases the tubes stood several days near 0° before crystallisation occurred. The solubility temperatures quoted are those at which crystals dissolved when warmed. The tubes were immersed in a thermostat controlled to ±0·1°, and were constantly agitated. Since the quantity of suspended crystals was often extremely small, the tubes were viewed by microscope, with transverse lighting. Over the low concentration ranges, solubility temperatures were accurate to ±0·5°, and above the critical concentration to ±0·1°.

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[1] Murray and Hartley, *Trans. Faraday Soc.*, 1935, **31**, 183.
[2] Tartar and Wright, *J. Amer. Chem. Soc.*, 1939, **61**, 539.
[3] Adam and Pankhurst, *Trans. Faraday Soc.*, 1946, **42**, 523.
[4] Addison and Furmidge, *J. Sci. Food Agric.*, 1954, **5**, 212.
[5] Knight and Shaw, *J.*, 1938, 683.

Results.—The variation in solubility S (molar) in water with temperature is shown in Fig. 1 for dodecyl-, tetradecyl-, hexadecyl-, and octadecyl-pyridinium iodides (curves A, B, C, and D, respectively). When log S is plotted against $1/T$, the breaks in the curves and the chain length effect are clearly shown, and solubility values extend to sufficiently low temperatures to enable critical concentrations to be evaluated with accuracy. These are compared in Table 1 with corresponding values from interfacial tension measurements; data for three related halides are also given. After allowance for temperature differences, agreement is good. The published value for cetylpyridinium bromide [6] appears to be too high.

TABLE 1.

Alkylpyridinium halide	Critical concn. (molar)		
	from water solubility	from interfacial tension	Published values
$(C_{12}H_{25}\cdot C_5H_5N)^+\ I^-$	0·0041(18·0°)	0·0043(18·5°)	0·0055(25°) [a]
$(C_{14}H_{29}\cdot C_5H_5N)^+\ I^-$	0·00079(28·0°)	0·0012(40·0°)	—
$(C_{16}H_{33}\cdot C_5H_5N)^+\ I^-$	0·00031(35·0°)	0·00044(50·0°)	—
$(C_{18}H_{37}\cdot C_5H_5N)^+\ I^-$	0·00013(45·5°)	—	—
$(C_{14}H_{29}\cdot C_5H_5N)^+\ Br^-$	0·0032(14·0°)	0·0031(18·5°)	—
$(C_{16}H_{33}\cdot C_5H_5N)^+\ Br^-$	0·00048(27·0°)	0·00047(30·0°)	0·00075(35°) [b]
$(C_{16}H_{33}\cdot C_5H_5N)^+\ Cl^-$	0·00084(13·0°)	0·00085(18·5°)	0·0009(25°) [c]

[a] From absorption spectra and dye solubilisation; Harkins, Krizek, and Corrin, *J. Colloid Sci.*, 1951, **6**, 576. [b] From conductivity measurements; Hartley, Collie, and Samis, *Trans. Faraday Soc.*, 1936, **32**, 798. [c] From azobenzene solubilisation; Hartley, *J.*, 1938, 1968.

Addition of sodium iodide to an alkylpyridinium iodide solution in water reduces both solubility and critical concentration. At high concentrations the solubility temperature is modified only slightly, but there are pronounced differences at concentrations below the critical concentration in water alone (Table 2).

TABLE 2.

Concn. of alkylpyridinium iodide (10^{-3}M)	Solubility temp.						
	2·0	1·0	0·8	0·6	0·4	0·2	0·1
Tetradecylpyridinium iodide							
(*a*) in water	32·7°	32·1°	29·5°	8·0°	—	—	—
(*b*) in 0·007molar NaI solution	35·3°	34·9°	34·6°	33·0°	27·9°	—	—
Cetylpyridinium iodide							
(*a*) in water	41·1°	40·7°	40·6°	39·7°	36·9°	3·0°	—
(*b*) in 0·007molar NaI solution	44·3°	44·0°	44·0°	43·9°	43·8°	43·7°	42·2°

Solubility of the four alkylpyridinium iodides discussed here is lower in xylene (mixture of isomers; b. p. 138°) than in water (Fig. 2). Aggregation of long-chain compounds to spherical or lamellar micelles in organic solvents is much less pronounced than in water, the micelle often consisting of about 3—6 molecules only.[7] Published evidence leaves some doubt as to whether such micelle formation occurs at a critical concentration in organic solvents, but the breaks in the curves in Fig. 2 suggest that a critical concentration does exist in these systems. The breaks are much less pronounced than those in aqueous solution, but in contrast the critical concentrations are not greatly influenced by alteration in chain length, and micelle formation occurs less abruptly as chain length is increased.

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[6] Hartley, Collie and Samis, *Trans. Faraday Soc.*, 1936, **32**, 798.

[7] Gonick, *J. Colloid Sci.*, 1946, **1**, 393; Palit, *Proc. Roy. Soc.*, 1951, *A*, **208**, 542; Martin and Pink *J.*, 1948, 1750; Van der Waarden, *J. Colloid Sci.*, 1950, **5**, 448; Arkin and Singleterry, *J. Amer. Chem. Soc.*, 1948, **70**, 3965; Mattoon and Mathews, *J. Chem. Phys.*, 1949, **17**, 496.

621. *Interaction of Acetyl Peroxide with But-3-enoic Acid and Crotonic Acid. A New Example of Allylic Shift of Olefinic Bond in Free-radical Reactions.*

By K. B. L. MATHUR and R. S. THAKUR.

INSTANCES of allylic shift during a free-radical reaction have been recorded for the action of acetyl peroxide on allylbenzene [1] [giving radical (I)] and for the action of a Grignard reagent on cinnamyl chloride in the presence of cobaltous chloride [2] [giving radical (II)]. In both reactions the dimerised product was a mixture of 1 : 4-diphenyl- and 1 : 6-diphenylhexa-1 : 5-diene, but no 3 : 4-diphenylhexa-1 : 5-diene was obtained.[1] The formation of the 1 : 4-diphenyl derivative is explicable only if radicals (I) and (II) are interconvertible.

$$\text{(I)}\quad \cdot CHPh\cdot CH{:}CH_2 \rightleftharpoons CHPh{:}CH\cdot CH_2\cdot \quad \text{(II)}$$

We now record another example of the allylic shift in the reaction of acetyl peroxide and but-3-enoic acid (6 mol.) at 90—95°.

A solid and some viscous polymeric material are obtained. The solid was proved to be subercolic acid (IV) by comparison of its properties,[3] by its reduction to suberic acid, and by comparison with an authentic sample. The reaction can be represented as shown :

$$CH_2{:}CH\cdot CH_2\cdot CO_2H \xrightarrow{Me\cdot} \underset{\text{(III)}}{CH_2{:}CH\cdot \dot{C}H\cdot CO_2H} \longrightarrow \cdot CH_2\cdot CH{:}CH\cdot CO_2H \longrightarrow \underset{\text{(IV)}}{[-CH_2\cdot CH{:}CH\cdot CO_2H]_2}$$

Crotonic acid which also has a reactive γ-hydrogen atom does not give subercolic acid when similarly treated. The products consist of a viscous water-soluble fraction and an unsaturated solid whose composition approximates to $[C_5H_8O_2]_{4-5}$. It therefore seems probable that the methyl radical has added stoicheiometrically to crotonic acid. Therefore, the subercolic acid isolated from experiments with but-3-enoic acid cannot have arisen by prior isomerisation to crotonic acid, and the reaction of acetyl peroxide and but-3-enoic acid thus furnishes another example of allylic shift in a free-radical reaction.

Experimental.—But-3-enoic acid, b. p. 69—70°/12 mm., and crotonic acid, m. p. 72°, were prepared as described by Vogel.[4] Acetyl peroxide, m. p. 26°, was prepared by Gambergen's method.[5] Suberic acid was obtained by the oxidation of castor oil with nitric acid;[6] a product of m. p. 139° was obtained only by again triturating the sample obtained by this method with chloroform and recycling the residue. Subercolic acid, m. p. 252—253°, was obtained from ethyl dibromosuberate by Goss and Ingold's method.[3]

Interaction of but-3-enoic acid with acetyl peroxide. A solution of acetyl peroxide (5·9 g.) in but-3-enoic acid (15·66 g., 3·6 mols.) was added during 5 hr. to but-3-enoic acid (10·44 g., 2·4 mols.) maintained at 90—95° (bath temp.) and the mixture heated thereafter for a further 3 hr., no colour being then given with starch–iodide paper. After being kept overnight the mixture contained a suspension of crystals (0·35 g.) which were recrystallised from water, giving needles, m. p. 253°, of an unsaturated acid (Found: C, 56·6; H, 6·1. Calc. for $C_8H_{10}O_4$: C, 56·5; H, 5·9%). A mixture with authentic subercolic acid had m. p. 251—252°. Distillation of the filtrate gave unchanged butenoic acid (16 g.); the residue (8 g.) was viscous and could not be crystallised. The product of fusion with resorcinol and sulphuric acid when made alkaline gave a red colour with only a faint fluorescence.

No other product of the dimerisation or rearrangement and dimerisation of the free radical (III) could be detected.

Reduction of the acid, m. p. 253°, by sodium amalgam. The acid (0·25 g.) was dissolved in hot water (50 ml.) and treated at the boiling point with 4% sodium amalgam (50 g.) during

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[1] Koch, *J.*, 1948, 1111.
[2] Kharasch *et al.*, *J. Org. Chem.*, 1945, **10**, 298.
[3] Cf. Goss and Ingold, *J.*, 1926, 1472.
[4] Vogel, " Practical Organic Chemistry," Longmans, London, 1951, p. 451.
[5] Gambergen, *Ber.*, 1909, **42**, 4010.
[6] Edmund, Kon, and Stevenson, *J.*, 1920, **117**, 641.

4 hr. The liquor was acidified and extracted with ether, and the ether removed. The white residue when crystallised from water had m. p. 140°. A mixture with authentic suberic acid had m. p. 139°.

Interaction of acetyl peroxide and crotonic acid in benzene solution. Acetyl peroxide (2·9 g.) in benzene (20 ml.) was added during 8 hr. to crotonic acid (4·3 g., 2 mols.) in boiling benzene (20 ml.), and the boiling continued for a further 8 hr. The benzene was removed by distillation and the unchanged crotonic acid by steam distillation. The residual liquor was digested with saturated sodium hydrogen carbonate solution (3 × 20 ml.) and filtered, and the extract acidified with concentrated hydrochloric acid, an oil being precipitated. This oil, when kept over phosphoric oxide in a vacuum desiccator, solidified to a brittle mass (*A*), m. p. 68—70° [Found: C, 61·3; H, 8·6; Br absorption ($KBr-KBrO_3$), 39%; *M* (Rast), 450; equiv., 133. $(C_5H_8O_2)_x$ requires C, 60·0; H, 8·0%], which did not yield any characteristic derivative. From the acidified residual liquors a viscous water-soluble product (*B*) was obtained by extraction with ether. Both products behaved in the fluorescence test (fusion with resorcinol and sulphuric acid) like dibasic acids.

The reaction products from β-chlorocrotonic acid, methyl γ-bromocrotonate, and tetrolic acid were viscous.

The authors thank Professor T. R. Seshadri for his interest in the work and for facilities.

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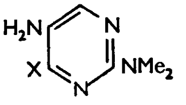
622. *Preparation of 4-Substituted 2-Dimethylamino-5-nitro- and -5-amino-pyrimidines.*

By D. G. SAUNDERS.

MOST of the conventional photographic colour developers are based on the *NN*-dialkyl-*p*-phenylenediamine structure. However, the proposal by Wilmanns, Fricke, and Birr [1] to use 2 : 5-diaminopyrimidines as " black-and-white " developers, encouraged us to think that the 5-amino-2-dialkylaminopyrimidines might prove useful as colour developers.

Previous work in this laboratory had indicated that in order to give oxidation products which would couple readily, it was necessary that the 5-amino-2-dialkylaminopyrimidine should not be substituted in both the 4- and the 6-position. Since the strong electron-attraction of the two ring-nitrogen atoms would be expected to weaken the reducing power of the pyrimidine developers compared with that of their benzenoid analogues, the introduction of a strongly electron-releasing group in the 4-position would be desirable.


(I)

The preparation of 4-substituted 5-amino-2-dimethylaminopyrimidines (I; X = OH, OMe, and NH_2) was undertaken. Of these, the triamine (I; X = NH_2) was known.[2]

2-Dimethylamino-4-hydroxypyrimidine [3,4] was nitrated to the 5-nitro-derivative, reduction of which with Raney nickel and hydrogen gave the 5-amino-derivative, isolated as the hydrochloride. 2-Dimethylamino-4-hydroxy-5-nitropyrimidine with phosphorus oxychloride yielded the 4-chloro-compound, which with Raney nickel and hydrogen in the presence of excess of triethylamine gave crude 5-amino-2-dimethylaminopyrimidine in poor yield. When 4-chloro-2-dimethylamino-5-nitropyrimidine was refluxed with the exact equivalent of sodium methoxide in methanol, 2-dimethylamino-4-methoxy-5-nitropyrimidine was obtained. Use of excess of sodium methoxide resulted in a high-melting compound, probably 2 : 4-dimethoxy-5-nitropyrimidine.

Catalytic reduction of 2-dimethylamino-4-methoxy-5-nitropyrimidine, as for the

[1] Wilmanns, Fricke, and Birr, U.S.P. 2,139,870.
[2] Albert, Brown, and Cheeseman, *J.*, 1951, 474.
[3] Davidson and Baudisch, *J. Amer. Chem. Soc.*, 1926, **48**, 2379.
[4] Overberger and Kogon, *ibid.*, 1954, **76**, 1065.

4-hydroxy-compound, gave 5-amino-2-dimethylamino-4-methoxypyrimidine isolated as the hydrochloride.

When 4-chloro-2-dimethylamino-5-nitropyrimidine was shaken with alcoholic ammonia overnight it was completely converted into 4-amino-2-dimethylamino-5-nitropyrimidine, despite the extremely low solubility of the chloropyrimidine and the product in the medium; the product was reduced to 4 : 5-diamino-2-dimethylaminopyrimidine, isolated as the hydrochloride.

All the 5-amino-2-dimethylaminopyrimidines acted as weak colour-developers.

EXPERIMENTAL

Experimental.—2-Dimethylamino-4-hydroxypyrimidine was prepared essentially by Overberger and Kogon's method,[4] but on pouring the reaction mixture into water no solid separated. The pH was adjusted to about 5 by adding excess of solid sodium carbonate followed by a few drops of acetic acid. The solution was evaporated to dryness and the solids obtained were extracted with acetone. The concentrated and cooled acetone solution produced crude 2-dimethylamino-4-hydroxypyrimidine which was recrystallized from acetone, to give white needles, m.p. 173—175°, in 81% yield.

2-*Dimethylamino*-4-*hydroxy*-5-*nitropyrimidine.* To fuming nitric acid (8 c.c.; *d* 1·5) and concentrated sulphuric acid (8 c.c.), cooled in ice, 2-dimethylamino-4-hydroxypyrimidine (10 g.) was added, the temperature being kept below 70°. The mixture was then heated on the steam-bath for 45 min. (subsequent experiments indicated that heating for 4 hr. improved the yield by 5—7%), then poured into water, to give the yellow *nitro-derivative* which was washed with water and dried. It (9 g., 68%) had m. p. 304—311° (Found: C, 39·2; H, 4·3; N, 29·95. $C_6H_8O_3N_4$ requires C, 39·1; H, 4·35; N, 30·4%).

4-*Chloro*-2-*dimethylamino*-5-*nitropyrimidine.* 2-Dimethylamino-4-hydroxy-5-nitropyrimidine (12·0 g.) and phosphorus oxychloride (120 c.c.) were refluxed together until hydrogen chloride ceased to be evolved. When the solution was cooled the 4-chloro-derivative separated as needles and was filtered off. Owing to the greater solubility of the product in phosphoric acid than in phosphorus oxychloride, it was almost impossible to obtain a second crop of crystals. The mother-liquor was therefore poured on ice, the remainder of the product being instantly hydrolysed to the starting material which was precipitated. This was then re-used. In some preparations it was necessary to repeat this process several times in order to obtain good yields. The crops of 4-chloro-2-dimethylamino-5-nitropyrimidine were combined and extracted (Soxhlet) with light petroleum (b. p. 60—80°). Cooling gave the *chloro-compound* as pale yellow needles (7·3 g., 55%), m. p. 143°, which became darker on exposure to light (Found: C, 35·3; H, 3·2; N, 27·9; Cl, 17·9. $C_6H_7N_4Cl$ requires C, 35·55; H, 3·5; N, 27·65; Cl, 17·5%). 2-Dimethylamino-4-hydroxy-5-nitropyrimidine (1 g.) was recovered.

2-*Dimethylamino*-4-*methoxy*-5-*nitropyrimidine.* Sodium (115 mg.) was dissolved in methyl alcohol (30 c.c.) and 4-chloro-2-dimethylamino-5-nitropyrimidine (1·0 g.) was refluxed in the solution overnight. Needles of the *methoxypyrimidine* were obtained together with a coarse solid. The fine crystals were decanted off, and the filtrate was refluxed with the coarse solid, more dissolving. Needle-shaped crystals separated from the cooled solution. The process was repeated until all the coarse solid had dissolved. The needles, slightly contaminated with salt, were extracted (Soxhlet) and recrystallized from acetone as yellow needles, m. p. 178—179°, in 72% yield (Found: C, 42·25; H, 4·5; N, 28·2. $C_7H_{10}O_3N_4$ requires C, 42·4; H, 5·05; N, 28·25%).

A trace of a fine crystal mat of a high-melting solid, m. p. >310°, was obtained from the mother-liquors, possibly 2 : 4-dimethoxy-5-nitropyrimidine. If excess of sodium methoxide is used this becomes the main product.

4-*Amino*-2-*dimethylamino*-5-*nitropyrimidine.* 4-Chloro-2-dimethylamino-5-nitropyrimidine (3·0 g.), when shaken overnight with excess of saturated alcoholic ammonia, slowly dissolved, while the 4-amino-derivative was precipitated as pale yellow needles. These (2·5 g., 92%) were collected and washed with water to remove ammonium chloride. They had m. p. 214° (Found: C, 39·2; H, 4·4; N, 38·0. Calc. for $C_6H_9O_2N_5$: C, 39·35; H, 4·95; N, 38·25%).

5-*Amino*-2-*dimethylamino*-4-*hydroxypyrimidine dihydrochloride.* 2-Dimethylamino-4-hydroxy-5-nitropyrimidine (10·0 g.), suspended in ethanol (300 c.c.) together with Raney nickel in a hydrogenating bomb, was shaken for 3 hr. under hydrogen at 50—60°/10 atm. The solution was filtered hot through kieselguhr into a flask containing excess of alcohol saturated with hydrogen chloride. A faintly pink solid was precipitated and was filtered off and washed with a little alcohol. The *dihydrochloride* (11·2 g., 88·5%) had m. p. >310° (Found : C, 30·0; H, 6·1; N, 23·2; Cl, 28·6. $C_6H_{10}ON_4,2HCl,H_2O$ requires C, 29·4; H, 5·75; N, 22·85; Cl, 28·95%).

5-*Amino-2-dimethylaminopyrimidine hydrochloride.* 4-Chloro-2-dimethylamino-5-nitropyrimidine (4·0 g.) was hydrogenated and isolated as above in the presence of triethylamine (6·3 c.c.). A pink powder was obtained (0·5 g.) which acted as a colour-developer in alkaline solution. The analysis, however, was unsatisfactory.

5-*Amino-2-dimethylamino-4-methoxypyrimidine dihydrochloride dihydrate.* 2-Dimethylamino-4-methoxy-5-nitropyrimidine (3·0 g.) was reduced as was the 4-hydroxy-compound. Concentration of the solution under reduced pressure gave a pale orange powder (2·8 g., 67%), m. p. >300°, of the *diamine dihydrochloride dihydrate* (Found : C, 30·85; H, 6·55; N, 20·6; Cl, 24·9. $C_7H_{12}ON_4,2HCl,2H_2O$ requires C, 30·35; H, 6·55; N, 20·2; Cl, 25·6%).

4 : 5-*Diamino-2-dimethylaminopyrimidine dihydrochloride.* 4-Amino-2-dimethylamino-5-nitropyrimidine (4·5 g.) was hydrogenated in the same manner as 2-dimethylamino-4-hydroxy-5-nitropyrimidine. When the solution was filtered into alcoholic hydrogen chloride a white precipitate of dihydrochloride was formed (m. p. 260°; 4·4 g., 88%) (Found : C, 32·3; H, 6·2; Cl, 31·4. Calc. for $C_6H_{11}N_5,2HCl$: C, 31·85; H, 5·8; Cl, 31·35%).

Analyses were by Mr. C. B. Dennis of these Laboratories.

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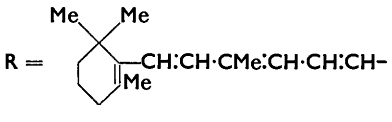
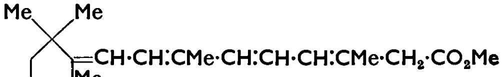
623. *Synthesis of all*-trans-, 2-cis-(*or* neo-), *and* 6-cis-[2-^{14}C]*Vitamin A.*

By C. F. GARBERS.

THE Arens and van Dorp synthesis of vitamin A acid [1] has often been improved.[2,3] The C_{18} ketone (I) used in our work was prepared from *trans*-C_{18} ketone semicarbazone by mild acid hydrolysis, was chromatographed and distilled in a high vacuum, and then gave a semicarbazone of m. p. 185—186° in over 90% yield,[4] and was therefore assigned the all-*trans*-configuration. The ketone was condensed with methyl bromo[2-^{14}C]acetate to give the labelled ester (II). Iodine, phosphorus oxychloride, and toluene-*p*-sulphonic acid were tried as dehydrating agents in preliminary experiments, and the last was found most suitable on a small scale. The mixed vitamin A acid methyl esters (III) produced were purified and converted into the acids (IV), which were fractionally crystallised. Three labelled geometric isomers of vitamin A acid were isolated. Isomerisations leading to the formation of these isomers must have occurred during the condensation and/or dehydration step, it being noted that both iodine and acids have been employed to effect *cis–trans*-isomerisations of polyenes.[5] Alternatively, it is possible that the C_{20} hydroxy-ester (II) is

R = 

$$\begin{tikzcd}
\text{(I)}\ R{\cdot}COMe \arrow[r] & HO{\cdot}CRMe{\cdot}CH_2{\cdot}CO_2Me\ \text{(II)} \arrow[d] \\
\text{(IV)}\ R{\cdot}CMe{:}CH{\cdot}CO_2H & R{\cdot}CMe{:}CH{\cdot}CO_2Me\ \text{(III)} \arrow[l]
\end{tikzcd}$$



(V)

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[1] Arens and van Dorp, *Nature*, 1946, **157**, 190; *Rec. Trav. chim.*, 1946, **65**, 338.

[2] Schwarzkopf, Cahnmann, Lewis, Swidinsky, and Wüest, *Helv. Chim. Acta*, 1949, **32**, 443.

[3] Inhoffen, Bohlmann, and Bohlmann, *Annalen*, 1950, **568**, 47.

[4] Inhoffen, Bohlmann, and Bartram, *Annalen*, 1949, **561**, 13.

[5] Zechmeister, *Chem. Rev.*, 1944, **34**, 267.

dehydrated to *retro*vitamin A acid methyl ester (V) which then becomes catalytically isomerised to a *cis–trans*-mixture of vitamin A acid esters.[2, 6, 7]

Recently Robeson *et al.*[6] have reported the synthesis of four isomeric vitamin A acids. This has enabled us to identify the three isomers as the all-*trans*-, the 2-*cis*- (or *neo*-), and the 6-*cis*-form severally. The only *cis*-isomer of vitamin A acid obtained from the Arens and van Dorp synthesis[3] was not found in our dehydration product.

The yield of pure [2-^{14}C]vitamin A acid isomers (radioactivity : 1·07 mc/mmole) was 20% based on the methyl bromo[2-^{14}C]acetate used. The synthesis of all-*trans*-[2-^{14}C]vitamin A acid (radioactivity : 0·314 mc/mmole) in a yield of 8·7% has already been reported.[8]

Reduction of the three radioactive vitamin A esters gave the corresponding [2-^{14}C]vitamin A alcohols. It is believed that no *cis–trans*-isomerisation occurred during the esterification and reduction because the absorption maxima of the three alcohols were the same as those recorded.[6]

Experimental.—All experiments were carried out in a nitrogen atmosphere. Ultraviolet absorption spectra were determined in 96% EtOH on the Unicam S.P. 500 spectrophotometer.

C_{18} *Ketone* (I). This ketone (2·8 g.; kindly supplied by Messrs. Hoffmann-La Roche Ltd., Basle) was prepared from *trans*-C_{18} ketone semicarbazone by hydrolysis[4] and purified by chromatography on alumina and distillation in a high vacuum. Light absorption : $\lambda_{max.}$ 346 mμ, $E^{1\%}_{1\,cm.}$ = 1100 (reported :[9] 346 mμ, 1200).

C_{20} *Hydroxy-*[2-^{14}C]*ester* (II). To a mixture of activated zinc (0·155 g.), C_{18} ketone (0·46 g.), and benzene (5 ml.) was added a solution of methyl bromo[2-^{14}C]acetate (0·256 g., containing 2 mc of radioactivity from The Radiochemical Centre, Amersham; activity 1·56 mc/mmole), in benzene (7·5 ml.), under a Liebig condenser through which hot water was circulated. The mixture was magnetically stirred, and heated, benzene (3·2 ml.) being slowly distilled off. The reaction started during the distillation, and cold water was then circulated through the condenser. The mixture was refluxed for a further ½ hr., and worked up in the usual way [yield 0·580 g.; $\lambda_{max.}$ 290 mμ, $E^{1\%}_{1\,cm.}$ = 850 (reported for the ethyl ester, 289 mμ,[10] 648; 291 mμ,[2] 810; 290 mμ,[9] 872)].

[2-^{14}C] *Vitamin A acid methyl ester* (III). Toluene-*p*-sulphonic acid monohydrate (0·0027 g.) was dehydrated by melting in a vacuum. The residue was cooled and dissolved in dry benzene (2 ml.), the mixture heated to boiling, and the labelled hydroxy-ester (II) (0·580 g.) in dry benzene (3·8 ml.) added. The solution was boiled for 5 hr., cooled, washed with water, dried, and taken to dryness. The residue was chromatographed in hexane on neutral alumina (20 g.; Merck), and elution effected by gradually increasing the benzene concentration in the hexane. The eluate was observed spectrophotometrically and corresponding fractions were combined to yield [2-^{14}C]vitamin A acid methyl esters (0·260 g.) and [2-^{14}C]*retro*vitamin A acid methyl ester (V) (0·038 g.). The latter was again treated with toluene-*p*-sulphonic acid (0·5 mg. in 2 ml. of benzene), and the vitamin A acid ester produced separated by chromatography.[7] The total yield was 274 mg., and $\lambda_{max.}$ 353 mμ, $E^{1\%}_{1\,cm.}$ 1110.

Geometric isomers of [2-^{14}C]*vitamin A acid* (IV). The esters (III) were heated with methanolic potassium hydroxide for 2 hr. Hydrolysed material was separated, and the crude acids (IV) taken up in ether. The ether solution was washed and evaporated. The crystalline residue was dried in a vacuum and recrystallised from ether under pressure at 100°. The all-*trans*-isomer crystallised first (51·2 mg.), m. p. 175—178·5°.

The mother-liquor was concentrated to yield a mixture (80 mg.) of various geometric isomers resolved by repeated fractional recrystallisation from ether and mechanical separation of the different crystal forms into all-*trans*-, 2-*cis*-, and 6-*cis*-[2-^{14}C]vitamin A acid. These results can be summarised thus : (*a*) All-*trans* (59·8 mg.), yellow needles, m. p. 175—178·5° (Found : C, 79·7; H, 9·0. Calc. for $C_{20}H_{28}O_2$: C, 80·0; H, 9·4%), $\lambda_{max.}$ 351 mμ, $E^{1\%}_{1\,cm.}$ 1440; (*b*) 2-*cis*-(or *neo*) (32 mg.), orange-red crystals, m. p. 174—176° (Found : C, 79·8; H, 9·6%), $\lambda_{max.}$ 352·5 mμ, $E^{1\%}_{1\,cm.}$ 1350; (*c*) 6-*cis* (10 mg.), almost white needles, m. p. 186—188° (Found : C, 79·75; H, 9·5%), $\lambda_{max.}$ 346 mμ, $E^{1\%}_{1\,cm.}$ 1260.

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[6] Robeson, Cawley, Weisler, Stern, Eddinger, and Chechak, *J. Amer. Chem. Soc.*, 1955, **77**, 4111.

[7] B.P. 650,302.

[8] Wolf, Johnson, and Kahn, 2nd Radioisotope Conference, Oxford, 1954.

[9] Baxter, *Fortschr. Chem. organ. Naturstoffe*, 1952, **9**, 41.

[10] Wendler, Slates, Trenner, and Tishler, *J. Amer. Chem. Soc.*, 1951, **73**, 719.

[2-^{14}C] *Vitamin A alcohol isomers.* The following operations were all carried out in the dark room: Vitamin A acid (10 mg.) was esterified as described by Schwarzkopf *et al.*[3] A 0·35M-solution of lithium aluminium hydride (6 ml.) was added to this ester in ether (2 ml.) at −80°. After ½ hr. the temperature was raised and kept at −40° for 1 hr. Excess of hydride was destroyed with ethyl acetate, and the ethereal solution washed successively with aqueous potassium hydroxide and water. Tocopherol (0·5 mg.) was added, and the solution filtered through a short column of anhydrous sodium sulphate, and evaporated. The ultraviolet spectrum of the residue was determined and a correction for the tocopherol content made. By reduction of the corresponding acids (IV) the following alcohols were obtained: All-*trans*, $\lambda_{max.}$ 325·5 mμ, $E^{1\%}_{1\,cm.}$ 1580; *neo*, $\lambda_{max.}$ 328 mμ, $E^{1\%}_{1\,cm.}$ 1475; 6-*cis*, $\lambda_{max.}$ 323 mμ, $E^{1\%}_{1\,cm.}$ 1350.

This paper is published with the permission of the South African Council for Scientific and Industrial Research. The author thanks Professor J. Gillman and Dr. D. A. Sutton for suggesting the problem and for many helpful discussions, Dr. M. Peisach for radioactivity determinations, and Miss Hughes who carried out the elementary analysis.

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PRETORIA.
[*Received, March 6th,* 1956.]

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624. 8-*Mercaptoquinoline.*

By G. M. BADGER and R. G. BUTTERY.

ALTHOUGH 8-hydroxyquinoline forms colourless crystals, Edinger [1] has described 8-mercaptoquinoline as a violet liquid which forms a bright red dihydrate. We have prepared 8-mercaptoquinoline by Edinger's method but with great care to purify the intermediate quinoline-8-sulphonyl chloride and eliminate all of the 5-isomer. Reduction with stannous chloride gave a tin complex which was benzoylated to give 8-benzoylthioquinoline. On hydrolysis this gave 8-mercaptoquinoline. In a second and new synthesis, the pure 8-sulphonyl chloride was reduced with stannous chloride and the resulting tin complex oxidised with iodine to give di-8-quinolyl disulphide, which was reduced to 8-mercaptoquinoline with glucose. In each case the product was obtained as a bright red dihydrate and the anhydrous material was a pale violet liquid.

Edinger's observations have therefore been confirmed. In absolute ethanol the ultraviolet spectrum (see Figure) of 8-mercaptoquinoline is very similar to that of 8-hydroxyquinoline,[2] but there is a low-intensity (Q) band in the visible region ($\lambda_{max.}$ 5000 Å), which is absent from the spectrum of 8-hydroxyquinoline and is responsible for the red-violet colour of the solution. In 50% aqueous ethanol, the intensity of the Q band is increased ten times; but the maximum is shifted 300 Å hypsochromically, and the solution is therefore red. 8-Mercaptoquinoline also forms a red solution in acetic acid, but it gives colourless solutions in hexane, nitrobenzene, and in " absolute " chloroform. In chloroform containing ethanol it forms a red-violet solution at room temperature, but at the boiling point this becomes almost colourless. It seems that pronounced absorption in the visible region may be associated with the formation of some sort of complex between the mercaptoquinoline and a compound ROH. When R = H the complex is reasonably stable and the dihydrate can be isolated. In chloroform containing ethanol, however, the complex dissociates when heated.

The spectra of some related compounds have also been examined for the presence of a Q band. In aqueous ethanol, 1-mercaptonaphthalene gave the expected ultraviolet absorption curve, with a maximum at 2980 Å (log ε 3·78), and it showed no absorption in the visible region. An aqueous-ethanolic solution of di-8-quinolyl disulphide was also

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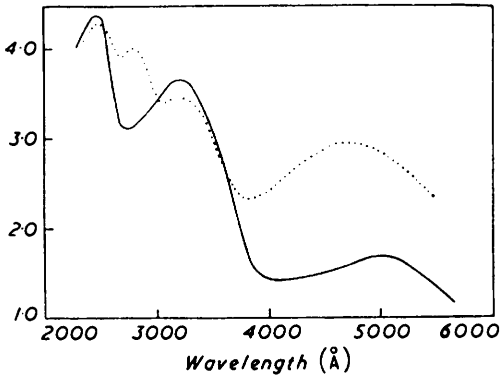
[1] Edinger, *Ber.*, 1908, **41**, 937.
[2] Ewing and Steck, *J. Amer. Chem. Soc.*, 1946, **68**, 2181.

transparent in the visible region, as was that of *m*-nitrobenzenethiol. On the other hand 8-benzoylthioquinoline resembled the parent 8-mercaptoquinoline to some extent: in 50% ethanol its absorption curve showed maxima at 2280 (log ε 4·46) and 2780 Å (log ε 4·03), and it also gave an absorption band at 4680 Å (log ε 2·16); in absolute alcohol, however, it showed no Q band: its ultraviolet absorption was similar [$\lambda_{max.}$ 2280 (log ε 4·49), 2820 (log ε 4·01)] but it showed no absorption in the visible region. The results in aqueous ethanol appear to prove that a C:C·C:S chromophore cannot be involved in the formation of the Q band.



Absorption curves of 8-*mercaptoquinoline in absolute alcohol* (——) *and in* 50% *aqueous alcohol* (· · · ·).

Experimental.—*Di*-8-*quinolyl disulphide.* Quinoline was sulphonated and the resulting quinoline-8-sulphonic acid washed very thoroughly with water to remove the 5-isomer. Quinoline-8-sulphonyl chloride was then prepared by Edinger's method[1] and purified by repeated crystallisation from light petroleum until its m. p. was sharp and constant at 128·5—129° (Edinger[1] gives m. p. 122°; McCasland[3] gives 124—126°). The pure chloride was reduced with stannous chloride to give the tin complex (Edinger[1]) which was then oxidised as follows by the method used by Riegel *et al.*[4] to prepare di-(4-chloro-8-quinolyl) disulphide.

Iodine (5 g.) was added with stirring to a solution of sodium hydroxide (30 g.) in water (250 c.c.) at 0°. When dissolution was complete the tin complex (50 g.) was added, with stirring, during 15 min., at 0°. After a further hour the yellow solid was collected, dissolved in 6N-hydrochloric acid, heated on the steam-bath, and treated with activated charcoal. The resulting solution was basified with ammonia, and the colourless product collected. The disulphide separated from light petroleum as colourless needles, m. p. 205—206° (Edinger[1] gives m. p. 206°).

8-*Mercaptoquinoline.* (i) This was prepared by Edinger's method[1] with the modification described above. 8-Mercaptoquinoline dihydrate was obtained as bright red needles, which, dried in a vacuum (without a desiccating agent), had m. p. 58—59°, in agreement with Edinger's report.[1] When the hydrate was dried in a vacuum over sodium hydroxide, anhydrous 8-mercaptoquinoline was obtained as a pale violet liquid. Both materials were oxidised to the disulphide in air in a few days.

(ii) Sodium hydroxide (1 g.) in water (10 c.c.) and glucose (1 g.) in water (10 c.c.) were added to a suspension of the disulphide (0·5 g.) in methanol (50 c.c.). Nitrogen was bubbled through the refluxing mixture for 3 hr. After cooling, water (50 c.c.) was added and the methanol distilled off under nitrogen. The mixture was then rapidly filtered (under nitrogen), and carbon dioxide bubbled through the solution. The resulting red 8-mercaptoquinoline dihydrate had m. p. 58—59°.

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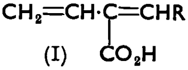
[3] McCasland, *J. Org. Chem.*, 1946, **11**, 277.

[4] Riegel, Lappin, Albisetti, Adelson, Dodson, Ginger, and Baker, *J. Amer. Chem. Soc.*, 1946, **68**, 1229.

625. *Derivatives of Buta*-1 : 3-*diene*-2-*carboxylic Acid.*

By E. A. Braude and E. A. Evans.

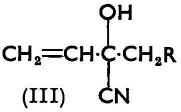
No synthetic derivatives of the 2-carboxybuta-1 : 3-diene system $-CH{=}CH{\cdot}C(CO_2H){=}CH-$ appear to be known and doubt has recently been thrown on the postulated presence of this system in certain natural products.[1] Previous work [2] has shown that reactions designed to yield 2-carboxypenta-1 : 3-diene derivatives $-CH_2{\cdot}CH{=}CH{\cdot}C(CO_2H){=}CH-$ afford, instead, the 2-carboxypenta-2 : 4-diene isomers, $-CH{=}CH{\cdot}CH{=}C(CO_2H){\cdot}CH_2-$, indicating that the cross-conjugated system rearranges with great ease to the electronically stabler straight-conjugated one and that the 2-carboxybuta-1 : 3-diene system is unlikely to survive unless such a migration is structurally precluded. We therefore attempted to synthesise the parent compound, buta-1 : 3-diene-2-carboxylic acid (I; R = H), as well as two of its homologues (I; R = Me and Pr^i) in which the desired system would be retained even if a 1 : 5-prototropic shift occurred.


$CH_2{=}CH{\cdot}\underset{CO_2H}{C}{=}CHR$

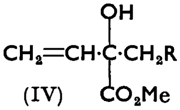
(I)

$CH_2{=}CH{\cdot}CO{\cdot}CH_2R$

(II)

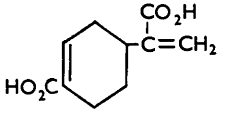

$CH_2{=}CH{\cdot}\overset{OH}{\underset{CN}{C}}{\cdot}CH_2R$

(III)

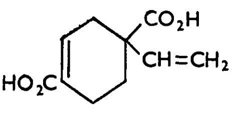

$CH_2{=}CH{\cdot}\overset{OH}{\underset{CO_2Me}{C}}{\cdot}CH_2R$

(IV)

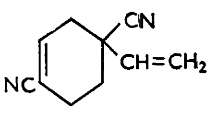
Treatment of methyl vinyl ketone with anhydrous hydrogen cyanide gave the cyanohydrin (III; R = H) which was hydrolysed by concentrated hydrochloric acid to the hydroxy-acid and then converted into the corresponding methyl ester (IV; R = H) with diazomethane. The ester was recovered unchanged after prolonged heating under reflux with naphthalene-2-sulphonic acid, and the homologue (IV; R = Me) obtained from ethyl vinyl ketone (II; R = Me) similarly resisted dehydration by naphthalene-2-sulphonic acid, phosphorus oxychloride in pyridine, or even pyrolysis at 400°. Pyrolysis of the acetyl derivative of (IV; R = H) at 500°, however, resulted in the elimination of acetic acid. Hydrolysis of the product afforded, not the desired acid (I; R = H), but a dimer, m. p. 228°, containing *two* ethylenic bonds (microhydrogenation). This dimer appears to be identical with that first isolated by Reppe [3] and subsequently by Yakubovich and Volkova [4] by reaction of nickel carbonyl with vinylacetylene. Reppe did not record the physical properties of his dimer, to which he assigned the structure (V). The Russian workers gave m. p. 235° and prepared a dimethyl ester, the physical properties of which agree closely with those observed here; they showed that treatment with sulphuric acid at 130° gives *p*-ethylbenzoic acid and preferred structure (VI). The physical properties of our product are in good agreement with those expected [5] for (VI); the ultraviolet absorption ($\lambda_{max.}$ 2150 Å, ε 11,000) indicates the presence of *one* conjugated $C{=}C{\cdot}CO_2H$ grouping, while the infrared absorption of the ester indicates the presence of a conjugated $-C{=}C-$ ($\nu_{max.}$ 1653 cm.$^{-1}$) as well as of a $-CH{=}CH_2$ ($\nu_{max.}$ 1638, 996, and 926 cm.$^{-1}$) group. The frequencies associated with C–H bending in the vinyl group are higher than usual;



(V)



(VI)



(VII)

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[1] Braude in " Progress in Organic Chemistry " (J. W. Cook, Ed.), Chapter 4, Vol. III, Butterworths Scientific Publications, London, 1955.

[2] Braude and Evans, *J.*, 1954, 607; 1955, 3324.

[3] Reppe, " Acetylene Chemistry," Mayer, New York, 1949; *Annalen*, 1953, **582**, 1.

[4] Yakubovich and Volkova, *Doklady Akad. Nauk U.S.S.R.*, 1952, **84**, 1183; *Chem. Abs.*, 1953, **47**, 3278.

[5] Cf. Braude and Coles, *J.*, 1950, 2014; Braude and Evans, *J.*, 1955, 3331.

similar shifts are also found in the acid (IV; R = H) and its ester (IV; R = Me) and have been noted [6] in other systems of the type $R_3C{\cdot}CH{=}CH_2$.

The dimer (VI) is evidently a Diels–Alder self-adduct of the acid (I; R = H). Analogous dimers have been obtained [7] on carboxylation of pent-3-en-1-yne and ethynyl*cyclo*hexene, and it is of interest that 2-cyanobuta-1 : 3-diene also undergoes [8, 9] dimerisation with great ease to the dinitrile (VII) which has been hydrolysed to a diacid, m. p. 236°, almost certainly identical with that obtained above.* It thus appears that buta-1 : 3-diene-2-carboxylic acid and its derivatives possess an exceptional tendency to undergo diene addition, which represents a further limitation to the structural and environmental conditions under which such systems are likely to exist.

Experimental.—*Methyl* 2-*hydroxy*-2-*methylbut*-3-*enoate* (IV; R = H). Anhydrous methyl vinyl ketone (90 g.; obtained by keeping an aqueous commercial product with excess of acetic anhydride for 3 days followed by fractionation), hydrogen cyanide (60 ml.), potassium hydroxide (4 g.), and sodium cyanide (3 g.) were kept overnight at 5—10°. The mixture was acidified with phosphoric acid, dried (Na_2SO_4), and fractionated, giving the cyanohydrin (35 g.), b. p. 72—74°/10 mm., n_{D}^{24} 1·4248. Very little cyanohydrin was obtained under the conditions described by Leupold and Vollmann [11] who give b. p. 140°/760 mm., $n_{\mathrm{D}}^{17 \cdot 5}$ 1·4264.

The cyanohydrin (34 g.) was heated at 90° with concentrated hydrochloric acid (100 ml.) for 40 min., then diluted with water (250 ml.) and extracted with ether. The ether extract was dried (Na_2SO_4) and an excess of a diazomethane in ether was added at 0°. Fractionation of the product gave *methyl* 2-*hydroxy*-2-*methylbut*-3-*enoate* (23 g.), b. p. 53—54°/8 mm., n_{D}^{21} 1·4348 (Found: C, 55·1; H, 7·9. $C_6H_{10}O_3$ requires C, 55·4; H, 7·8%). Infrared light absorption (liquid film): strong bands at 3509 (O–H stretching), 1736 (CO_2Me), 1642 ($CH{=}CH_2$ stretching), 992, 978, and 934 (C–H bending in $CH{=}CH_2$) cm.$^{-1}$. The ester showed no absorption with $\varepsilon > 100$ in the ultraviolet (2000—4000 Å).

The ester (2 g.) was refluxed with naphthalene-2-sulphonic acid (50 mg.) for 2 hr. On fractionation, most of the ester (85%), b. p. 155—156°/550 mm., n_{D}^{21} 1·4362, was recovered.

Dimer of buta-1 : 3-*diene*-2-*carboxylic acid.* The foregoing ester was acetylated with acetyl chloride in benzene–pyridine,[12] and the crude acetate (4 g.), b. p. 71—72°/8 mm., was passed during 10 min. in a stream of nitrogen through a 6-inch column packed with glass helices and heated electrically at 500°. The products were collected in a trap cooled in methanol–solid carbon dioxide and were then refluxed with 12% aqueous potassium hydroxide (20 ml.) and methanol (10 ml.). The solution was diluted with water, acidified with concentrated hydrochloric acid at 0°, and extracted with ether. The solvent was removed and the solid residue was sublimed at 10^{-4} mm., giving (i) at 90° (bath-temp.), a solid (3 mg.), m. p. 48—49°, which showed no absorption with $\varepsilon > 100$ at 2000—4000 Å, and (ii) at 160° (bath-temp.), the dimer (0·9 g.), m. p. 222—223°, which after re-sublimation, crystallised from acetone–light petroleum (b. p. 100—120°) in plates, m. p. 228° [Found: C, 60·4; H, 6·5%; *M* (in camphor), 240; equiv. (KOH), 109; hydrogenation number (PtO_2–AcOH), 121. Calc. for $C_{10}H_{12}O_4$: C, 61·2; H, 6·2%; *M*, 196].† Ultraviolet light absorption (in EtOH): $\lambda_{\max.}$ 2150 Å (ε 11,000). Infrared absorption (paraffin mull): maxima at 1684 (CO_2H) and 1640 cm.$^{-1}$ (C=C stretching). Treatment with ethereal diazomethane gave the dimethyl ester, b. p. 106—108°/0·1 mm., n_{D}^{23} 1·4918 (Found: C, 64·5; H, 7·3. Calc. for $C_{12}H_{16}O_4$: C, 64·3; H, 7·2%). Yakubovich and Volkova [4] give b. p. 120°/1 mm., n_{D}^{20} 1·4901. Infrared light absorption (liquid film): maxima at 1723 (CO_2Me), 1653 (conjugated C=C), 1638 ($CH{=}CH_2$), 996 and 926 cm.$^{-1}$ ($CH{=}CH_2$).

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* It seems probable that (VI) is also the structure of the diacid, m. p. 234°, obtained by Pummerer [10] by the oxidation of a dialdehyde $C_{10}H_{12}O_2$ formed in the reaction of crotonaldehyde with formaldehyde. This dialdehyde may be the dimer of 2-formylbuta-1 : 3-diene, the latter being formed by addition of formaldehyde to the double bond of crotonaldehyde, followed by dehydration.

† High values of the molecular weight as determined by the Rast method appear to be common for dicarboxylic acids; thus the ratios of $M_{\mathrm{obs.}}/M_{\mathrm{calc.}}$ were: dimer, 1·22; diphenic acid, 1·19; phthalic acid, 1·17; succinic acid, 1·38; adipic acid, 1·51; benzoic acid (for comparison), 1·05.

[6] Davison and Bates, *J.*, 1953, 2607.

[7] Jones, Shen, and Whiting, *J.*, 1951, 763.

[8] Marvel and Brace, *J. Amer. Chem. Soc.*, 1948, **70**, 1775.

[9] Price, Cypher, and Krishnamurti, *ibid.*, 1952, **74**, 2987.

[10] Pummerer, G.P. 821,204; *Chem. Abs.*, 1954, **48**, 12,171.

[11] Leupold and Vollmann, U.S.P. 2,166,600.

[12] Cf. Mills, *J.*, 1951, 2332.

Methyl 2-ethyl-2-hydroxybut-3-enoate (IV; R = Me). Ethyl vinyl ketone, b. p. 102°/740 mm., n_D^{20} 1·4192, was prepared in 22% yield from ethylene and propionyl chloride.[13] The ketone (15 g.), benzene (50 ml.), anhydrous hydrogen cyanide (12 ml.), and potassium cyanide (0·3 g.) were kept for 3 hr. at 0° with frequent shaking. The mixture was acidified with syrupy phosphoric acid, and the benzene layer was immediately decanted and dried (Na_2SO_4). Solvent and unchanged ketone were removed under reduced pressure and the residue was refluxed for 45 min. with concentrated hydrochloric acid (30 ml.). The solution was diluted with water and extracted with ether. The ethereal solution was extracted with 2N-sodium hydroxide, and the alkaline solution was acidified at 0° with concentrated hydrochloric acid and extracted with ether. The solvent was evaporated and the residue was crystallised from pentane at −60° to give *2-ethyl-2-hydroxybut-3-enoic acid* (0·6 g.), m. p. 56—57° [Found: C, 55·5; H, 7·9%; *M* (in camphor), 161. $C_6H_{10}O_3$ requires C, 55·4; H, 7·8%; *M*, 130]. Infrared light absorption (paraffin mull): strong bands at 3356 (OH), 2577, 1730 (CO_2H), 1645 (C=C), 1425, 1004, 995, 983, 946 ($CH=CH_2$), and 916 cm.$^{-1}$ (hydrogen-bonded acid dimer).

The acid with diazomethane in ether at 0° gave the *methyl ester*, b. p. 56°/10 mm., n_D^{16} 1·4358 (Found: C, 58·2; H, 8·7. $C_7H_{12}O_3$ requires C, 58·3; H, 8·4%). Infrared light absorption (liquid film): strong bands at 3472 (OH), 1862, 1733 (CO_2Me), 1034, 991 and 930 cm.$^{-1}$ ($CH=CH_2$). Most of the ester was recovered unchanged after distillation from naphthalene-2-sulphonic acid, refluxing with phosphorus oxychloride in pyridine, and pyrolysis over glass helices at 400°.

2-Hydroxy-4-methylpentan-3-one. Lactonitrile (40 g.) in ether (100 ml.) was added dropwise to *iso*propylmagnesium bromide (from Mg, 3·3 g., and *iso*propyl bromide, 173 g.) in ether (600 ml.). The mixture was stirred for 36 hr. at room temperature, 6N-hydrochloric acid (600 ml.) was added, and stirring was continued for a further 6 hr. The ether layer was separated, dried (Na_2SO_4–K_2CO_3), and distilled, giving *2-hydroxy-4-methylpentan-3-one* (38 g., 58%), b. p. 51—53°/11 mm., n_D^{21} 1·4208 (Found: C, 62·0; H, 10·6. $C_6H_{12}O_2$ requires C, 62·0; H, 10·4%). The 2 : *4-dinitrophenylhydrazone* crystallised from aqueous methanol as orange needles, m. p. 151—152°, $\lambda_{max.}$ 3680 Å (ε 21,000 in $CHCl_3$) (Found: C, 48·6; H, 5·6; N, 19·0. $C_{12}H_{16}O_5N_4$ requires C, 48·6; H, 5·4; N, 18·9%). The *semicarbazone* crystallised slowly from water at 2° and had m. p. 208°, $\lambda_{max.}$ 2260 Å (ε 11,000 in EtOH) (Found: C, 48·7; H, 8·5; N, 24·6. $C_7H_{15}O_2N_3$ requires C, 48·5; H, 8·7; N, 24·3%).

3-Cyano-4-methylpentane-2 : 3-diol. The foregoing ketone (20 g.), anhydrous hydrogen cyanide (20 ml.), potassium cyanide (1 g.), and a few drops of triethylamine were kept overnight at 0°. The mixture was rendered just acid with sulphuric acid and distilled, giving the *cyanohydrin* (14 g., 57%), b. p. 60—68° (bath-temp.)/10^{-5} mm., n_D^{20} 1·4554 (Found: C, 58·9; H, 9·3; N, 9·8. $C_7H_{13}O_2N$ requires C, 58·7; H, 9·2; N, 9·8%). It showed no absorption with $\varepsilon > 100$ at 2000—4000 Å.

Attempted dehydration of the cyanohydrin with phosphorus oxychloride in pyridine gave only intractable tar.

DEPARTMENT OF CHEMISTRY, IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, LONDON, S.W.7. [*Received, March 14th*, 1956.]

[13] McMahon, Roper, Utermohlen, Hasek, Harris, and Braut, *J. Amer. Chem. Soc.*, 1948, **70**, 2971.

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626. *Hydrolysis of Aryl Sulphonates. Part II.* Kinetic Form of Hydrolysis.*

By C. A. BUNTON and V. A. WELCH.

IN Part I of this series it was shown that the sulphur–oxygen bond was broken in the alkaline hydrolysis of phenyl toluene-*p*-sulphonate. This observation has now been extended to the hydrolysis of phenyl methanesulphonate, which, when carried out in aqueous 70% dioxan containing isotopically enriched water, gave phenol with a normal isotopic abundance of oxygen:

$$Me{\cdot}SO_2 \vdots {-}OPh + {}^{18}OH^- \longrightarrow Me{\cdot}SO_2{}^{18}O^- + PhOH$$

The rates of alkaline hydrolysis of both esters were measured at various temperatures (see Table), and the slow neutral hydrolysis was followed at 99·5°. The small difference

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* Part I, *J.*, 1951, 1872.

between the hydrolysis rates of the two esters shows that a phenyl group attached to the sulphur atom of a sulphonate has little effect on the rate of nucleophilic attack on this atom. In the corresponding carbon system, *e.g.*, in carboxylic acid derivatives, the derivatives of the aromatic acids are hydrolysed more slowly than their aliphatic counterparts.[1] This is because the conjugation between the benzene ring and the carbonyl group reduces the susceptibility to nucleophilic attack. This conjugation appears to be absent in some aromatic sulphur compounds.[2] The replacement of the phenoxide by the hydroxide group may be synchronous, or may involve prior addition to the sulphur atom[3] —our results do not differentiate between these possibilities.

The variation of second-order rate constants with absolute temperature follows the equations: for phenyl methanesulphonate, $k_2 = 3{\cdot}6 \times 10^{10}e^{-18,400/RT}$ mole^{-1} l. min.$^{-1}$; and for phenyl toluene-*p*-sulphonate, $k_2 = 5{\cdot}5 \times 10^{10}e^{-19,500/RT}$ mole^{-1} l. min.$^{-1}$. These values of the Arrhenius activation energies for bimolecular attack on a sulphur atom are not very different from those observed in hydrolysis of some alkyl sulphonates by the S_N mechanisms,[4] despite the different positions of bond fission in the two systems.

Hydrolysis in aqueous dioxan.

Phenyl methanesulphonate.					
Temp.	99·5°	72·9°	44·6°	25·0°	99·5°
10^3k_2 (mole^{-1} l. min.$^{-1}$)	555 *	83·5	7·10	1·25	10^5k_1 (min.$^{-1}$) 1·30 †
*Phenyl toluene-*p*-sulphonate.*					
Temp.	99·5°	82·0°	72·9°		
10^3k_2 (mole^{-1} l. min.$^{-1}$)	191 ‡	54·0	26·7 ¶		

* Mean of 4 values. † Initially neutral. ‡ Mean of 4 values. ¶ Mean of 2 values.

Experimental.—Preparation of materials. The esters were prepared from phenol and the appropriate sulphonyl chloride. Phenyl methanesulphonate, recrystallised from methanol, had m. p. 61—62°, and phenyl toluene-*p*-sulphonate, recrystallised from aqueous ethanol, had m. p. 94·5—95·5°.

The experiments were carried out in aqueous dioxan (3 : 7 by volume), made up with dried, purified dioxan. Tracer experiments were carried out with the water enriched in ^{18}O. The isolated phenol was purified by distillation and dried over phosphoric oxide. It was pyrolysed on a hot carbon tube *in vacuo*, and the resultant carbon monoxide analysed mass-spectrometrically.

Kinetic measurements. Runs were carried out in sealed tubes (with the exception of the run at 25°), and the hydroxide ion determined by addition of excess of acid and back-titration with alkali, under nitrogen, with methyl-red as indicator. Because of the attack of alkali on the glass, and the partial conversion of hydroxide into phenoxide ion during the reaction, only the first part of the reaction was followed. The rate constants were determined graphically by using the integrated rate equation $k_2t(a - b) = \log_e b(a - x)/[a(b - x)]$, where a and b are the initial concentrations of hydroxide ion and ester respectively, and $a - x$ and $b - x$ are their concentrations at time t. The initial concentrations of hydroxide ion were varied between 0·0580 and 0·100M, and of ester between 0·0160 and 0·0410M. The results of a kinetic run on phenyl methanesulphonate are:

Temp. 72·9°, [OH$^-$] = 0·0596M, [Ester] = 0·0351M.

Time (min.)		15	30	45	60	75	92	114
Reaction (%)		7·4	15·1	20·85	22·5	30·2	34·5	38·4
log $(a - x)/(b - x)$	Found	0·244	0·262	0·275	0·280	0·304	0·316	0·331
	Calc. *	0·247	0·260	0·274	0·286	0·300	0·316	0·334

* Calc. for 10^2k_2 = 8·35 mole^{-1} l. min.$^{-1}$

Our rate of hydrolysis of phenyl methanesulphonate at 25° is qualitatively similar to that observed for hydrolysis of this ester in alkaline aqueous acetone.[5]

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[1] Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 212.
[2] Koch and Moffitt, *Trans. Faraday Soc.*, 1951, **47**, 7.
[3] Cf. Bender, *J. Amer. Chem. Soc.*, 1951, **73**, 1626.
[4] Robertson, *Canad. J. Chem.*, 1953, **31**, 589.
[5] Helferich and Papalanbrou, *Annalen*, 1942, **551**, 235.

The authors are indebted to Professors E. D. Hughes, F.R.S., and C. K. Ingold, F.R.S., for their interest and to Dr. D. R. Llewellyn for a generous supply of enriched water.

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University College, Gower St., London, W.C.1.

[*Received, March 14th*, 1956.]

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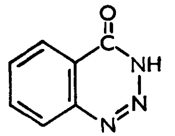
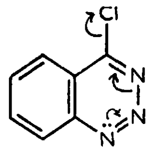
627. *The Reaction of* 3 : 4-*Dihydro*-4-*oxobenzo*-1 : 2 : 3-*triazine with Phosphorus Pentachloride and Phosphorus Oxychloride.*

By D. Buckley and M. S. Gibson.

The action of nitrous acid on *o*-aminobenzamide has been shown to give 3 : 4-dihydro-4-oxobenzo-1 : 2 : 3-triazine (I) (Ring Index No. 933). In comparing the structure (I) with those of the quinolones and quinazolones, Finger [1] speculated on the possibility of preparing 4-chlorobenzo-1 : 2 : 3-triazine (II) from it by reaction with phosphorus pentachloride. The conversion of the amide (I) into *o*-chlorobenzoic acid and nitrogen by hydrochloric acid (and related reactions), however, renders Finger's comparison somewhat misleading. Further, the lability of the chlorine atom to be expected in a substance (II) suggested that the reaction mentioned by Finger would rather yield *o*-chlorobenzonitrile, the mechanism resembling, formally at least, that of the decomposition of *o*-cyanobenzenediazonium chloride to *o*-chlorobenzonitrile in hydrochloric acid; the product is, in fact, *o*-chlorobenzonitrile.

(I)





(II)

It may be noted that the colour reaction reported for the compound (I) by Bamberger and Goldberger [2] may be considered as a hydrolytic fission of the heterocyclic ring followed by coupling of the resulting diazonium ion with α-naphthylamine to give an azo-dye.

Experimental.—3 : 4-Dihydro-4-oxobenzo-1 : 2 : 3-triazine formed needles (from ethanol), m. p. 212—213° (decomp.), as stated by Finger.[1] The ultraviolet absorption spectrum of an ethanolic solution showed peaks at 2230 (ε 1910) and 2780 Å (ε 590). The infrared absorption spectrum of a mull in Nujol showed bands at 1685 (C=O) and 3077 cm.$^{-1}$ (N–H); no hydroxyl absorption was evident, and a ferric chloride colour test was negative. The triazine gave a golden-brown colour when warmed with acetic anhydride containing a trace of concentrated sulphuric acid.

o-*Chlorobenzonitrile.* The triazine (0·73 g.), phosphorus pentachloride (2 g.), and phosphorus oxychloride (10 c.c.) were heated under reflux for 1 hr. The orange solution was poured on ice, basified, and extracted with ether. Isolated by chromatography on alumina from benzene solution, the nitrile (0·28 g.) formed colourless needles (from light petroleum), m. p. and mixed [3] m. p. 43—44°; the infrared spectrum was identical with that of the authentic specimen, showing a band at 2222 cm.$^{-1}$ (C≡N).

The triazine decomposed explosively when heated with phosphorus pentachloride alone.

Bamberger and Goldberger's reaction. As originally reported, the triazine gave a reddish-violet colour with α-naphthylamine in hot acetic acid. Analogous colour reactions can be more quickly carried out as follows: A solution of the triazine in concentrated hydrochloric acid is warmed with one of the coupling agent in acetic acid. The colours are as follows: α-naphthol,

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[1] Finger, *J. prakt. Chem.*, 1888, **37**, 431; cf. Weddige and Finger, *ibid.*, 1887, **35**, 262.

[2] Bamberger and Goldberger, *Ber.*, 1898, **31**, 2636.

[3] Montagne, *Rec. Trav. chim.*, 1900, **19**, 46.

magenta; α-naphthylamine, reddish-violet; β-naphthol, cherry-red; β-naphthylamine, wine-red; dimethylaniline, none. Addition of alkali to the coloured solutions from α- or β-naphthol discharges the colours with precipitation of scarlet dyes (cf. phenylazo-β-naphthol).

The authors are indebted to Professor R. B. Turner for his interest.

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628. *Four Anomalous Substitution Reactions.*

By F. BELL.

(a) *Bromination of 4-Acetoxydiphenyl.*—Although 4-acetoxydiphenyl undergoes chlorination [1] in position 4′, Hazlet and Kornberg [2] showed that, surprisingly, it undergoes bromination in position 3. P. W. Robertson [3] has suggested that the anomaly may be explained in the following way. When 4-acetoxydiphenyl is heated in acetic acid with bromine a trace of 4-hydroxydiphenyl is produced by hydrolysis and is immediately brominated in position 3; the resultant 3-bromo-4-hydroxydiphenyl then undergoes cross-acetylation to yield 4-acetoxy-3-bromodiphenyl with production of more 4-hydroxydiphenyl, and so on. According to this view, under acetylating conditions, which would prevent the formation of any free phenol, bromination should occur at position 4′. This is now found to be the case.

Bromine (1 mol.) was added to 4-acetoxydiphenyl (4 g.) dissolved in a slightly warm mixture of acetic acid (10 c.c.) and acetic anhydride (5 c.c.) containing a crystal of iodine. The colour was rapidly discharged and on cooling there separated 4-acetoxy-4′-bromodiphenyl (0·8 g.), m. p. 130° after recrystallisation from benzene; it was rapidly dissolved by warm sodium hydroxide solution, to give 4′-bromo-4-hydroxydiphenyl, m. p. 166° after recrystallisation from ethanol. The filtrate was poured into water and the precipitate found to be slightly impure 4-acetoxydiphenyl.

The above experiment was repeated with 3 mols. of bromine. The first crop of 4-acetoxy-4′-bromodiphenyl amounted to 1·5 g. and a further 1·35 g. was isolated by fractional crystallisation of the material obtained by pouring the filtrate into water. This corresponds to a yield of over 50% of the 4′-bromo-derivative.

(b) *Bromination of 2-Acetamido-5 : 6 : 7 : 8-tetrahydronaphthalene.*—Smith [4] found that *N*-acetyl-5 : 6 : 7 : 8-tetrahydro-2-naphthylamine on bromination gave 82% of the 1-bromo-derivative together with a 12% yield of, surprisingly, the 4-bromo-derivative. The latter was oriented by hydrolysis and elimination of the amino-group to give 5-bromo-1 : 2 : 3 : 4-tetrahydronaphthalene, b. p. 258—259° (Smith had recorded b. p. 238—239° for the 6-bromo-isomeride).

Kieffer and Rumpf [5] state that the isomeric bromo-bases obtained from Smith's acetamido-compounds have identical pK_a values and conclude that the compound described as the 4-bromo-derivative must in point of fact be the 3-bromo-derivative. This is now shown to be correct.

N-Acetyl-5 : 6 : 7 : 8-tetrahydro-2-naphthylamine was brominated by Smith's method, and the isomers were separated, hydrolysed, and deaminated. The products, which according to Smith are both 5-bromo-1 : 2 : 3 : 4-tetrahydronaphthalene and indeed show no significant difference in b. p., were nitrated by the method of Morgan, Micklethwait, and Winfield,[6] and

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[1] Savoy and Abernethy, *J. Amer. Chem. Soc.*, 1942, **64**, 2220, 2719.
[2] Hazlet and Kornberg, *ibid.*, 1939, **61**, 3037.
[3] P. W. Robertson, personal communication.
[4] Smith, *J.*, 1904, **85**, 729.
[5] Kieffer and Rumpf, *Compt. rend.*, 1950, **230**, 1874.
[6] Morgan, Micklethwait, and Winfield, *J.*, 1904, **85**, 746.

the products crystallised from light petroleum until of constant m. p. Smith's 1-bromo-*N*-acetyl-5 : 6 : 7 : 8-tetrahydro-2-naphthylamine gave a dinitro-compound which formed plates, m. p. 94—95°, and his second compound gave a dinitro-compound which formed needles, m. p. 102—103°. A mixture of the two dinitro-compounds had m. p. 63—70°. Morgan, Micklethwait, and Winfield give m. p. 91° (plates) for dinitro-5-bromo-1 : 2 : 3 : 4-tetrahydronaphthalene and m. p. 105—106° (with softening at 103°) (needles) for dinitro-6-bromo-1 : 2 : 3 : 4-tetrahydronaphthalene, and record a mixed m. p. 61—72°. Smith's 4-bromo-compound is, therefore, the 3-bromo-compound, and this conclusion was confirmed by showing that the bromo-5 : 6 : 7 : 8-tetrahydro-*N*-toluene-*p*-sulphonyl-2-naphthylamine derived from it is smoothly converted by the action of *N*-bromosuccinimide in pyridine into the compound, m. p. 195°, previously described as 1 : 3-dibromo-*N*-toluene-*p*-sulphonyl-5 : 6 : 7 : 8-tetrahydro-2-naphthylamine.[7]

The result of bromination of *N*-acetyl-5 : 6 : 7 : 8-tetrahydro-2-naphthylamine in acetic acid is, therefore, very similar to the result of nitration.[8]

(c) *Nitration of* 4-tert.-*Butylbenzoic Acid.*—Battegay and Haeffely[9] obtained 4-*tert.*-butyl-2-nitrobenzoic acid, m. p. 145°, by the oxidation of 4-*tert.*-butyl-2-nitrotoluene. The acid, m. p. 161°, obtained by Kelbe and Pfeiffer[10] by the nitration of *p-tert.*-butylbenzoic acid must, therefore, be, as expected, the 3-nitro-derivative.

Verley[11] obtained a crude 4-*tert.*-butylbenzyl bromide by bromination of *p-tert.*-butyltoluene. From this he prepared 4-*tert.*-butylbenzyl alcohol. He states that the bromide, the alcohol and, also, *p-tert.*-butylbenzoic acid with nitric acid all yield the same dinitro-*tert.*-butylbenzoic acid, which he regards as the 2 : 5-dinitro-acid. Beyond stating that the dinitro-acid can be recrystallised from ethanol he gives no other properties, not even the m. p. Although the 2 : 5-structure might be regarded as not unlikely for the compound derived from the bromide or alcohol if one nitro-group were introduced before oxidation, it remains an improbable structure for the product of nitration of *p-tert.*-butylbenzoic acid unless steric hindrance to the entry of the second nitro-group *ortho* to the *tert.*-butyl-group were the paramount factor. Results with related compounds[12] show that this is unlikely.

Re-examination of the bromination of *tert.*-butyltoluene under the conditions employed by Verley showed the product to be far from uniform and, therefore, it was decided to prepare 4-*tert.*-butyl-2 : 5-dinitrobenzoic acid and compare it with the product of nitration of *p-tert.*-butylbenzoic acid. The two were not identical and, therefore, the nitration of *p-tert.*-butylbenzoic acid almost certainly proceeds in a normal manner, *viz.*, at positions 3 : 5.

4-tert.-*Butyl-2 : 5-dinitrobenzoic Acid.*—4-*tert.*-Butyl-2-nitrobenzoic acid[9] (1·8 g.; m. p. 145—147°) was added, without cooling, to a mixture of fuming nitric acid (5 c.c.) and sulphuric acid (5 c.c.). After a short while the mixture was poured on ice, and the sticky precipitate repeatedly recrystallised from acetic acid, to give 4-tert.-*butyl-2 : 5-dinitrobenzoic acid* as needles, m. p. 232—234° (Found : C, 49·8; H, 4·2. $C_{11}H_{12}O_6N_2$ requires C, 49·3; H, 4·5%).

4-tert.-*Butyl-3 : 5-dinitrobenzoic Acid.*—This was obtained from 4-*tert.*-butyl-3-nitrobenzoic acid, m. p. 163°, by the same method. It crystallised from acetic acid in hexagonal prisms, m. p. 270—273°, and was clearly identical with the acid, m. p. 270—272·5°, obtained by Carpenter and Easter[13] as a by-product from the nitration of *p-tert.*-butylbenzaldehyde (Found : N, 10·0. Calc. for $C_{11}H_{12}O_6N_2$: N, 10·4%).

(d) *Chlorination of* N-*Toluene*-p-*sulphonyl-3 : 5 : 1-xylidine.*—The interaction of *N*-toluene-*p*-sulphonylxylidines with chlorine gives addition compounds of various types, the structures of which suggest that a nuclear methyl group tends to inhibit addition at a neighbouring carbon atom.[14] It might be expected, therefore, that 3 : 5-xylidine would undergo straightforward substitution without addition and such proved to be the case.

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[7] Bell and Gibson, *J.*, 1955, 26.
[8] Schroeter, *Annalen*, 1922, **426**, 39.
[9] Battegay and Haeffely, *Bull. Soc. chim. France*, 1924, **35**, 986.
[10] Kelbe and Pfeiffer, *Ber.*, 1896, **19**, 1726.
[11] Verley, *Bull. Soc. chim. France*, 1898, **19**, 69.
[12] Bell and Buck, *J.*, 1956, 1890.
[13] Carpenter and Easter, *J. Org. Chem.*, 1954, **19**, 91.
[14] Bell, *J.*, 1955, 2376.

3 : 5-*Xylidine*.—The following preparation appears more advantageous than that of Haller, Adams, and Wherry.[15] *N*-Toluene-*p*-sulphonyl-2 : 4-xylidine (40 g., powdered) was suspended in acetic acid (160 c.c.), and fuming nitric acid (10 c.c.) in acetic acid (15 c.c.) added. A clear solution resulted with considerable rise in temperature. On cooling, crystals separated, which after recrystallisation from ethanol had m. p. 138—139°. A further crop was obtained by dilution of the filtrate (yield, 105 g. from 120 g.). This nitro-compound (40 g.) was added with stirring to sulphuric acid (40 c.c.) and, after its dissolution, absolute ethanol (200 c.c.) was slowly poured in. The mixture was cooled to 5° and sodium nitrite (8·8 g.) in water (12 c.c.) introduced below the surface. After a few minutes copper powder was stirred in: vigorous decomposition occurred with temperature rise to 50°. The product, on distillation in steam, gave 5-nitro-1 : 3-xylene (14·4 g.), which was reduced in ethanolic solution with stannous chloride in hydrochloric acid to 3 : 5-xylidine (16·7 g. from 32·2 g.). With toluene-*p*-sulphonyl chloride in pyridine this gave N-*toluene*-p-*sulphonyl*-3 : 5-*xylidine*, m. p. 91° after recrystallisation from aqueous acetic acid (Found: C, 65·0; H, 6·0. $C_{15}H_{17}O_2NS$ requires C, 65·4; H, 6·2%).

Chlorination of N-*Toluene*-p-*sulphonyl*-3 : 5-*xylidine*.—(*a*) Sulphuryl chloride was added to the compound which rapidly dissolved. On evaporation of the excess of sulphuryl chloride a white solid remained, which after recrystallisation from acetic acid gave 2 : 4-*dichloro*-N-*toluene*-p-*sulphonyl*-3 : 5-*xylidine* in prisms, m. p. 125° (Found: C, 52·6; H, 4·3. $C_{15}H_{15}O_2NSCl_2$ requires C, 52·3; H, 4·4%).

(*b*) Chlorine (4 mols.) was passed into a solution of the compound in cold chloroform. The product was concentrated and diluted with light petroleum, to give crystals, which gave 2 : 4 : 6-*trichloro*-N-*toluene*-p-*sulphonyl*-3 : 5-*xylidine*, m. p. 171°, prisms from acetic acid or fine needles from ethanol (Found: C, 47·6; H, 3·7. $C_{15}H_{14}O_2NSCl_3$ requires C, 47·5; H, 3·7%). The mother-liquor gave the dichloro-derivative (above).

The author is indebted to Dr. J. W. Minnis for the microanalyses and to the Carnegie Trust for the Universities of Scotland for a grant.

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[15] Haller, Adams, and Wherry, *J. Amer. Chem. Soc.*, 1920, **42**, 184.

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629. *The Hydrolysis of* 3 : 5-*Dinitrobenzoates.*

By J. CASTELLS and G. A. FLETCHER.

DURING work on steroid chemistry a new method was developed for the hydrolysis of 3 : 5-dinitrobenzoates, which is effected by passing a benzene solution of the ester through alumina previously impregnated with alkali. The instantaneous violet coloration on contact of the solution with the alumina indicates that the hydrolysis is immediate, and the limitation of the coloured zone to the upper part of the column shows the reaction to be complete.

The method has been successfully applied to more than a dozen steroid and triterpenoid 3 : 5-dinitrobenzoates (with quantities from 10 mg. to 5 g.), and in all cases excellent yields were obtained. An illustration of the method is given in the case of cholestan-3β-yl 3 : 5-dinitrobenzoate.

Experimental.—*Alkaline alumina.* Alumina (1 kg.; P. Spence, grade H) was shaken for 2 hr. with a solution of potassium hydroxide (100 g.) in water (75 c.c.).

Cholestan-3β-*yl* 3 : 5-*dinitrobenzoate.* A mixture of cholestan-3β-ol (220 mg.), 3 : 5-dinitrobenzoyl chloride (400 mg.), and pyridine (2 c.c.) was kept overnight at room temperature. The dinitrobenzoate was precipitated with iced water, collected and crystallised twice from ethyl acetate–ethanol. *Cholestan*-3β-*yl* 3 : 5-*dinitrobenzoate* (210 mg.) was obtained as feathery needles, m. p. 188·5—190°, $[\alpha]_D$ +15° (*c*, 1·4 in $CHCl_3$) (Found: C, 70·2; H, 8·8; N, 4·85. $C_{34}H_{50}O_6N_2$ requires C, 70·1; H, 8·65; N, 4·8%).

Hydrolysis.—Cholestan-3β-yl 3 : 5-dinitrobenzoate (170 mg.) in benzene (3 c.c.) was adsorbed on to alkaline alumina (10 g.; 1·5 × 9 cm.). Elution with benzene–ether (3 : 1; 50 c.c.), and removal of the solvent gave (without crystallisation) cholestan-3β-ol (111 mg.), m. p. 139—140·5°,

$[\alpha]_D$ +22° (*c*, 1·0 in $CHCl_3$) (Found: C, 83·3; H, 12·3. Calc. for $C_{27}H_{48}O$: C, 83·4; H, 12·45%). The mixed m. p. with an authentic specimen of cholestan-3β-ol {m. p. 142—143°, $[\alpha]_D$ +23° (*c*, 0·7 in $CHCl_3$)} was 139·5—142·5°.

The authors are grateful to Professor E. R. H. Jones, F.R.S., for his interest in this work. Thanks are expressed for maintenance grants from the Department of Scientific and Industrial Research (to G. A. F.), and from the British Council and the Consejo Superior de Investigaciones Cientificas de España (to J. C.).

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630. *The Sulphonation of Diphenyl Sulphide.*

J. CHATT and A. A. WILLIAMS.

IN order to examine the formation of complex compounds of organic sulphides with silver ion in aqueous solution it was necessary to prepare a water-soluble organic sulphide. It seemed that the sodium salt of phenyl *p*-sulphophenyl sulphide would be suitable, and we record here its preparation.

In 1893 Otto and Tröger [1] treated diphenyl sulphide with concentrated sulphuric and also with chlorosulphonic acid, isolating a barium mono- and di-sulphonate of unknown orientation. They claimed that the disulphonate obtained by use of sulphuric acid differed from that obtained with chlorosulphonic acid: the former had one molecule of water of crystallisation and the latter three. Bourgeois and Petermann [2] later established that treatment with sulphuric acid at 15° gave the 2 : 4′- and 4 : 4′-disulphonate, but at 100° only the 4 : 4′-isomer. It seemed probable therefore that Otto and Tröger's mono-sulphonate would be the 4-sulphonic acid, of which we required the sodium salt. We found the barium, sodium, and *S*-benzylthiuronium salts of their acid to be identical with the salts of the 4-sulphonic acid prepared by the annexed unambiguous synthesis.

$$p\text{-}Cl{\cdot}C_6H_4{\cdot}NO_2 + NaSPh \longrightarrow p\text{-}PhS{\cdot}C_6H_4{\cdot}NO_2 \longrightarrow$$
$$p\text{-}PhS{\cdot}C_6H_4{\cdot}NH_2 \longrightarrow p\text{-}PhS{\cdot}C_6H_4{\cdot}SO_2H \longrightarrow p\text{-}PhS{\cdot}C_6H_4{\cdot}SO_3H$$

Phenyl *o*-sulphinophenyl sulphide and the corresponding sulphonic acid were also prepared by a similar synthesis. They were isolated and characterised as their *S*-benzylthiuronium salts.

Contrary to Otto and Tröger's observation, disulphonation of diphenyl sulphide with sulphuric acid and with chlorosulphonic acid gave us an identical product. Its barium salt crystallised with one molecule of water.

L. A. Duncanson kindly examined for us the infrared spectrum of the solid sodium salt of the 4-sulphonic acid, prepared by each method, and of the 4 : 4′-disulphonic acid. The spectra were consistent with the orientations assigned and had no bands in the 765—790 cm.$^{-1}$ region, where bands due to *m*-isomers would occur.

Experimental.—Microanalyses are by Messrs. W. Brown and A. G. Olney of these laboratories.

The sulphonic acids were isolated as their barium salts which were purified by repeated recrystallisation from water. A barium salt was converted into a sodium salt by treatment in hot aqueous solution with a slight deficiency of sodium sulphate, the precipitated barium sulphate being removed and the conversion completed by running the hot filtrate through a column of cation-exchange resin saturated with sodium ions. This method has the advantage that a moderately sized column of resin can be used without regeneration to convert relatively large batches of barium salts into the sodium salts. The aqueous solution on evaporation gave the pure sodium salt without recrystallisation. The sodium salts usually crystallised poorly

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[1] Otto and Tröger, *Ber.*, 1893, **26**, 993.
[2] Bourgeois and Petermann, *Rec. Trav. chim.*, 1903, **22**, 349, 356.

and had indefinite amounts of water of crystallisation. They were rendered anhydrous at 130°. The *S*-benzylthiuronium sulphonates were obtained by mixing a concentrated aqueous solution of the thiuronium hydrochloride with very slightly acid solutions of the barium or sodium sulphonate.

The equivalent weights of the salts were determined by running a known weight of the salt in hot aqueous solution through a column of the acid form of a cation-exchange resin (Zeo-Karb 225) and titrating the liberated acid with alkali.

4-*Sulphonates from diphenyl sulphide.* (1) Direct sulphonation. Diphenyl sulphide was sulphonated with chlorosulphonic acid (1 mol.), and the monosulphonic acid isolated as its barium salt by Otto and Tröger's method [Found: equiv., 333. Calc. for $\frac{1}{2}(C_{24}H_{18}O_6S_4Ba)$: equiv., 334]. The barium salt was converted into the *sodium salt* (Found: C, 49·8; H, 3·2%; equiv., 288. $C_{12}H_9O_3S_2Na$ requires C, 50·0; H, 3·2%; equiv., 288). The S-*benzylthiuronium salt*, recrystallised five times from aqueous ethanol, had m. p. 155° (Found: C, 55·6; H, 4·65. $C_{20}H_{20}O_3N_2S_3$ requires C, 55·5; H, 4·7%).

(2) Unambiguous synthesis. *p*-Nitrophenyl phenyl sulphide[3] was reduced to the amine which was converted[4] into its sulphate. This (20 g.) was suspended in dilute sulphuric acid (8·2 c.c. of concentrated acid; 112 c.c. of water), and diazotised at 3—4° by sodium nitrite (6 g.) in water (50 c.c.). The resultant suspension, when added to cold aqueous sulphuric acid (16·5 c.c. of concentrated acid; 22 c.c. of water), dissolved to a yellow, slightly cloudy solution. Sulphur dioxide was then passed through at 3—8° until 18 g. had been absorbed. Gattermann copper (25 g.) was added slowly with stirring, and the reaction completed by warming the solution until nitrogen evolution ceased.

The copper and other residues were filtered off and washed with water. The filtrate contained no sulphinic acid (no orange precipitate with ferric chloride) and was discarded. The copper was repeatedly extracted with 50 c.c. portions of dilute aqueous ammonia (*d* 0·880, 1 vol.; water, 3 vols.) until a fresh extract contained no sulphinic acid ($FeCl_3$ test on acidified sample). The extract was then run slowly with stirring into a strongly acid solution of ferric chloride (60% $FeCl_3$ solution, 100 c.c.; 18% hydrochloric acid, 400 c.c.) at room temperature, and the orange precipitate of the ferric sulphinate filtered off, washed, and air-dried. Drying was completed at 40° in air. At 100° decomposition to a black sticky solid occurred. The resultant ferric salt was finely ground and slowly added with vigorous stirring to dilute aqueous ammonia (500 c.c.) at just below its b. p. The suspension was digested for 4 hr., then filtered, and the filtrate evaporated to one-third of its volume, cooled, and filtered; this filtrate was evaporated further to 100 c.c. and, on cooling, deposited a white substance, presumably the ammonium sulphinate. This was not isolated but was re-dissolved by warming the suspension to 50° and small quantities ($\frac{1}{2}$—1 c.c.) of 10-vol. hydrogen peroxide were added. Five minutes after each addition the solution was spotted on a plate with ferric chloride. When such tests yielded only a faint opalescence (instead of a definite orange precipitate), the solution was heated to the b. p. and barium chloride solution added in excess. The crude barium sulphonate separated on cooling and was recrystallised from water (charcoal). The yield varied from 0 to 4 g. This product was extracted with acetone and then recrystallised from water until it had the correct equivalent weight (Found: C, 43·1; H, 2·8%; equiv., 332. Calc. for $C_{24}H_{18}O_6S_4Ba$: C, 43·15; H, 2·7%; equiv., 334). Prepared from it were the sodium salt (Found: C, 49·7; H, 3·5%; equiv., 290), and the benzylthiuronium salt (Found: C, 55·4; H, 4·5%). Its m. p. (155°) was unchanged on admixture with the benzylthiuronium salt of the acid obtained by direct sulphonation. The infrared spectrum of the sodium salt was identical with that of the sodium salt obtained by direct sulphonation.

S-*Benzylthiuronium salt of phenyl* o-*sulphophenyl sulphide.* This was prepared in rather poor yield from *o*-nitrophenyl phenyl sulphide by an analogous series of reactions. After the hydrogen peroxide oxidation, however, the solution was made just acid and the *benzylthiuronium salt* precipitated directly. The rather sticky crude product after six recrystallisations from aqueous ethanol gave white needles, m. p. 146° (Found: C, 55·4; H, 4·6; N, 6·6. $C_{20}H_{20}O_3N_2S_3$ requires C, 55·5; H, 4·7; N, 6·5%). The S-*benzylthiuronium* o-*sulphinate* was obtained by neutralising the ammonia extract of the Gattermann copper in the preparation of the sulphonate and treating it directly with aqueous thiuronium hydrochloride. The crude salt was recrystallised six times from aqueous ethanol to give white needles, m. p. 171·5—172° (Found: C, 57·7; H, 4·9; N, 7·0. $C_{20}H_{20}O_2N_2S_3$ requires C, 57·7; H, 4·8; N, 6·7%).

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[3] Willgerodt and Klinger, *J. prakt. Chem.*, 1862, **85**, 194.

[4] Waldron and Reid, *J. Amer. Chem. Soc.*, 1923, **45**, 2403.

Di-p-*sulphophenyl sulphide.* Diphenyl sulphide was treated with chlorosulphonic acid (2 mols.) as described by Otto and Tröger, and the disulphonic acid isolated as its barium salt (Loss at 130°, 4·0. Calc. for $C_{12}H_8O_6S_3Ba,H_2O$: H_2O, 3·6%). The salt was then anhydrous (Found : equiv., 241. Calc. for $C_{12}H_8O_6S_3Ba$: equiv., 241). Sulphonation with sulphuric acid at 100° gave the same product (Loss at 130° : 3·7%). This was converted into the *sodium salt* (Found : C, 36·6; H, 2·2%; equiv., 197. $C_{12}H_8O_6S_3Na_2$ requires C, 36·9; H, 2·1%; equiv., 195). The S-*benzylthiuronium salt,* recrystallised from aqueous ethanol, had m. p. 198·5—200·5° (Found : C, 49·8; H, 4·4; N, 8·4. $C_{28}H_{30}O_6N_4S_5$ requires C, 49·5; H, 4·4; N, 8·25%).

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631. *The Solubility of Tungsten Trioxide in Hydrochloric Acid.*

By (the late) S. E. S. EL WAKKAD and H. A. M. RIZK.

INCIDENTALLY to another investigation the solubility of tungsten trioxide in hydrochloric acid at room temperature has been determined. The results tabulated below show the minimum for 0·5M-acid.

HCl (M)	7·20	6·85	5·50	4·17	2·78	1·41	1·00	0·50	0·11	0·075	0·015
WO_3 (10^{-4} mole/l.)	38·4	27·6	18·4	15·3	10·8	9·0	7·11	5·37	8·59	9·20	11·0

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