NOTES.

84. *Some Reactions of Xanthhydryl Chloride.*

By G. W. H. Cheeseman.

Replacement of chlorine occurred when xanthhydryl chloride [1] was treated with silver nitrate in ether at room temperature, and xanthone crystallised from the solution. At 0°, silver chloride was also formed, and evaporation of the resulting solution in air gave xanthone. As the chloride was at least partly converted into nitrate in these experiments, it seems likely that xanthhydryl nitrate very readily decomposes into xanthone. Xanthone was also isolated on reaction of the chloride and silver nitrate in methyl cyanide, together with some *N*-xanthhydrylacetamide. Kny-Jones and Ward [1] isolated xanthone, xanthen, and some xanthhydrol after the action of water on xanthhydryl chloride; in this case xanthone and xanthen were produced by the ready acid-catalysed dismutation of the xanthhydrol formed in the primary reaction. It has now been found that treatment of the chloride in ether at room temperature with morpholine, thiophenol, or 1 : 3 : 5-trimethoxybenzene gave 4-xanthhydrylmorpholine, phenyl xanthhydryl sulphide, and 1 : 3 : 5-trimethoxy-2-xanthhydrylbenzene, respectively. When ethereal solutions of the chloride and phenylmagnesium bromide were mixed and heated under reflux for 3 hr., 9-phenylxanthen was formed.

Experimental.—Xanthhydryl chloride was freshly prepared [1] and used without purification.

Reaction of xanthhydryl chloride with silver nitrate. (*a*) In ether. Powdered silver nitrate (8·5 g.) was added to a solution of xanthhydryl chloride (from xanthhydrol, 5·0 g.) in dry ether (50 ml.). The mixture was shaken for 4 hr. at room temperature and then filtered. The solid obtained by filtration was extracted with benzene (Soxhlet). The extract yielded xanthone (1·65 g.), m. p. and mixed m. p. 174—176°. The residual silver chloride weighed 2·65 g. after being washed with water. Acetamide (6·0 g.) was added to the original filtrate, solvent was removed, and the residue heated at 100° for 30 min. Successive extraction of the mixture with water and acetone (50 ml.) gave *N*-xanthhydrylacetamide (1·2 g.), m. p. 246—248°. The m. p. was unchanged by crystallisation from 96% ethanol and was undepressed on admixture with an authentic sample.[2]

When an ethereal solution of xanthhydryl chloride (from xanthhydrol, 5·0 g.) was stirred with powdered silver nitrate (8·5 g.) for 1 hr. at 0°, 1·25 g. of silver chloride were formed. The filtered solution was divided into two portions. One portion was allowed to evaporate at room temperature: crystallisation of the residue from 96% ethanol gave xanthone as needles, m. p. 168—174°. The remainder was stirred with powdered sodium toluene-*p*-sulphinate at room temperature for 1 hr., then set aside at room temperature overnight; the mixture was filtered and the solid obtained extracted with water; successive crystallisation from acetone (40 parts) and ethanol (100 parts) gave *p*-tolyl xanthhydryl sulphone, m. p. 213—214° (undepressed on admixture with an authentic sample [3]) (Found: C, 71·6; H, 5·1; S, 9·35. Calc. for $C_{20}H_{16}O_3S$: C, 71·4; H, 4·8; S, 9·5%).

[1] Kny-Jones and Ward, *J.*, 1930, 535.
[2] Vogel, " Practical Organic Chemistry," Longmans, Green & Co., London, 1948, p. 398.
[3] Balfe, Kenyon, and Thain, *J.*, 1952, 790.

(*b*) In methyl cyanide. Xanthhydryl chloride (from xanthhydrol, 6·0 g.) dissolved rapidly in a solution of silver nitrate (7·0 g.) in methyl cyanide (20 ml.). The mixture was set aside for 90 min. at room temperature and then filtered. The solid obtained was extracted with benzene (Soxhlet) and, on cooling, *N*-xanthhydrylacetamide (0·6 g.), m. p. 243—245°, separated from the extract. Concentration of the mother-liquor gave xanthone (1·15 g.), m. p. (mainly) 169—173°. The original filtrate was evaporated; decomposition occurred during the attempted crystallisation of the residue from light petroleum (b. p. 60—80°), and only xanthone (1·8 g.), m. p. (mainly) 169—173°, was isolated.

Reaction of xanthhydryl chloride with morpholine. Xanthhydryl chloride (from xanthhydrol, 2·0 g.) was caused to react with morpholine (3 ml.) in ether at room temperature. After 18 hr., solvent was removed, the residue extracted with water, and the product (2·2 g.) filtered off. Crystallisation from ethanol (15 parts) gave 4-*xanthhydrylmorpholine* (1·4 g., 52%), m. p. 139—140° (Found: C, 76·6; H, 6·65; N, 5·3. $C_{17}H_{17}O_2N$ requires C, 76·4; H, 6·4; N, 5·2%).

Reaction of xanthhydryl chloride with thiophenol. Xanthhydryl chloride (from xanthhydrol, 2·85 g.) was caused to react similarly with thiophenol (2 ml.). After 18 hr., the mixture was poured into water and ether. The organic layer was separated, washed with water, dried, and evaporated. Light petroleum (b. p. 40—60°) was added to the residue, and, after cooling to 0°, the crystalline precipitate (2·8 g., 67%), m. p. 74—76°, filtered off. Crystallisation from 96% ethanol (6 parts) gave phenyl xanthhydryl sulphide, m. p. 78—79° (Found: C, 78·5; H, 5·0; S, 10·9. Calc. for $C_{19}H_{14}OS$: C, 78·6; H, 4·85; S, 11·0%). Sawicki and Oliverio [4] give m. p. 77—78°. The sulphide was converted into xanthone, m. p. 176—177°, on oxidation with hydrogen peroxide in glacial acetic acid.

Reaction of xanthhydryl chloride with 1 : 3 : 5-*trimethoxybenzene.* Xanthhydryl chloride (from xanthhydrol, 4·0 g.) was caused to react similarly with 1 : 3 : 5-trimethoxybenzene (3·4 g.). After 18 hr., the product (5·1 g.) was filtered off. Crystallisation from butan-1-ol gave 1 : 3 : 5-*trimethoxy*-2-*xanthhydrylbenzene* (4·8 g., 68%), m. p. 159—161°. The m. p. was raised to 163—164° by further crystallisation from butan-1-ol (7 parts) (Found: C, 76·1; H, 6·1. $C_{22}H_{20}O_4$ requires C, 75·8; H, 5·8%).

Reaction of xanthhydryl chloride with phenylmagnesium bromide. A solution of xanthhydryl chloride (from xanthhydrol, 5·0 g.) in ether (30 ml.) was added dropwise to one of phenylmagnesium bromide (prepared from magnesium, 1·25 g.) in ether (50 ml.). The mixture was heated under reflux for 3 hr., then cooled and decomposed with 2N-sulphuric acid. The ethereal layer was separated, washed free from acid, dried, and evaporated. Benzene (5 ml.) was added to the residue and the crystalline product (2·8 g., 43%), m. p. 140—144°, filtered off in two crops. Crystallisation from ethanol (25 parts) gave 9-phenylxanthen, m. p. 146—147° (Found: C, 88·2; H, 5·6. Calc. for $C_{19}H_{14}O$: C, 88·35; H, 5·5%). Ullmann and Engi [5] give m. p. 145°.

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[*Received, August 25th,* 1958.]

[4] Sawicki and Oliverio, *J. Org. Chem.*, 1956, **21**, 183.
[5] Ullmann and Engi, *Ber.*, 1904, **37**, 2371.

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85. *Structure of Fulminate Ion.*

By KARTAR SINGH.

NEF [1] assigned a structure $\bar{O}$–N=C to fulminate ion. Pauling and Hendricks [2] suggested an alternative formula $\bar{C}$=N=O based on calculations of potential energy of three nuclei which suggested that $^-$CNO is the most stable configuration. Our infrared results for various fulminates rule out Nef's structure, and studies of ultraviolet absorption spectra

[1] Nef, *Annalen*, 1894, **280**, 263, 305; Wohler, *Ber.*, 1906, **39**, 2522.
[2] Pauling and Hendricks, *J. Amer. Chem. Soc.*, 1926, **48**, 641.

of fulminates and quantum mechanical calculations suggest that the most probable one is $-\bar{O}-N\equiv C$.

On thermal decomposition mercury fulminate gives an insensitive and insoluble product, pyrofulmin. Langhans,[3] on the basis of colour reactions, suggested that pyrofulmin is probably a mixture of mercury oxycyanide with mercuric oxide. Its insolubility makes it difficult to apply usual chemical methods to elucidate its structure, but its infrared and ultraviolet spectra in the solid phase establish the presence of $-N=C=N-$ and $-C\equiv N$ groups.

Mercury fulminate was purified by dissolving a fresh sample in aqueous ammonia followed by precipitation with 20% acetic acid and washing with water. Silver and lead fulminates were prepared as described in the literature.[4] Pyrofulmin was obtained by heating mercury fulminate at 88° ± 0·5° *in vacuo*. Samples decomposed to different extents were also examined.

FIG. 1.

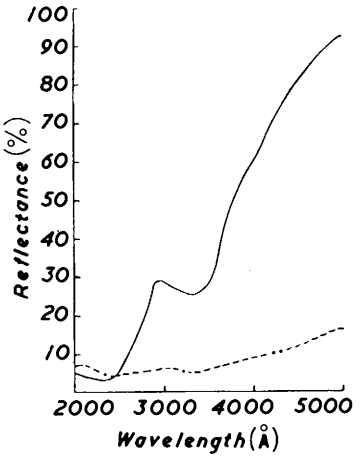
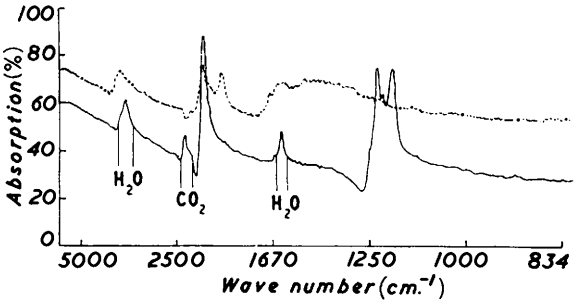


FIG. 2.



Infrared spectra (2—15 μ) were examined in potassium bromide discs [5] containing 0·7% of the sample (w/w) with a Hilger H 800 double-beam spectrograph. Ultraviolet absorption spectra were determined by reflections from pellets with a Hilger Uvispek Spectrophotometer No. H.700/304 (Fig. 1). Mercury fulminate (full line) shows two broad and intense absorption bands centred at 3310 Å and 2400 Å, and pyrofulmin (broken line) absorbs at the same positions but the bands are indistinct.

The positions of peaks in the infrared spectra of fulminates are given in Table 1. Peaks arising from adsorbed water [6] (near 3450 cm.$^{-1}$ and 1640 cm.$^{-1}$) and adsorbed carbon dioxide (near 2350 cm.$^{-1}$) were neglected.

TABLE 1. *Positions (cm.$^{-1}$) of infrared absorption peaks of fulminates.*

Fulminate	$2\nu_1$	ν_3	ν_1	$2\nu_2$
Mercury	—	2147vs	1225vs	1181s
Silver	2215s	2132vs	1123vs	1111s
Lead	—	2172vs	1188vs	—

The peaks at 1225 and 2147 cm.$^{-1}$ for mercury fulminate may respectively be the fundamental frequencies representing symmetric (ν_1) and antisymmetric (ν_3) vibrations of –ONC group, and

[3] Langhans, *Z. ges. Schiess- and Sprengstoffw.*, 1922, **17**, 122.
[4] Taylor and Rinkenbeck, *Army Ordnance*, 1926, **6**, 448; Wohler and Martin, *Ber.*, 1917, **50**, 586.
[5] Stimson and O'Donnel, *J. Amer. Chem. Soc.*, 1952, **74**, 1805.
[6] Brame, Margrave, and Meloche, *J. Inorg. Nuclear. Chem.*, 1957, **5**, 49.

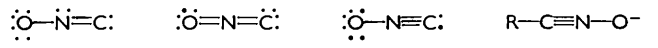
that at 1181 cm.$^{-1}$ the bending frequency $2\nu_2$. The high intensity of this peak is obviously due to Fermi resonance. The position of peaks in the infrared spectra of products formed on heating mercury fulminate to various losses are in Table 2. The infrared spectra of products formed at losses of 0·1 (full line) and 10·2% (broken line) are given in Fig. 2. When mercury fulminate has lost 1·2% in weight a new peak appears at 1988 cm.$^{-1}$, whose intensity increases

TABLE 2. *Positions (cm.$^{-1}$) of infrared peaks of decomposition products of mercury fulminate.*

Loss in wt. (%)	ν_3	$'\nu_3$	ν_1	$2\nu_2$	Loss in wt. (%)	ν_3	$'\nu_3$
0·1	2187vs	—	1218vs	1152s	7·8	2135s	1987s
0·3	2202vs	—	1221vs	1178s	10·2	2155s	1987s
1·8	2199vs	1988vw	1221vs	1181s			

on continued heating up to a loss of 10·2%. The peaks at 1225 and 1181 cm.$^{-1}$ fade out completely at a loss of 10·2%. The peak at 2147 cm.$^{-1}$ remains practically unaltered in position.

The three possible canonical structures for the fulminate ion are (I), (II), and (III). Preponderance of structure (I) implies an infrared absorption at about 1670 cm.$^{-1}$. Absence of infrared absorption signifies that structure (I) does not make a large contribution.



Nef Pauling and Hendricks

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

The observed values of symmetrical and antisymmetrical vibrations are comparable with those of carbon dioxide O=C=O [7] or to those of 2 : 4 : 6-trimethylbenzonitrile oxide which has been assigned [8] the structure (IV; R = 2 : 4 : 6-$Me_3C_6H_2$). The infrared spectra alone, therefore, do not provide definite evidence whether structure (II) or (III) or a resonance hybrid makes a major contribution. The presence of a strong, broad band centred at 3310 Å, probably arising from $\eta \longrightarrow \pi^*$ transitions,[9,10] indicates that structure (III) may predominate. A firm decision requires well-resolved ultraviolet band spectra and their quantitative interpretation.

The presence of peaks at 1987 cm.$^{-1}$ and 2155 cm.$^{-1}$ in the spectrum of pyrofulmin indicates that $-N=C=N-$ and $-C\equiv N$ groups may be present.

I thank Professors D. S. Kothari and C. H. Smith for encouragement.

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[*Received, May 28th*, 1958.]

[7] Mulligan, *J. Chem. Phys.*, 1951, **19**, 347.
[8] Califano, Moccia, Scarpate, and Speroni, *ibid.*, 1957, **26**, 1727.
[9] Trawick and Eberhardt, *ibid.*, 1954, **22**, 1162.
[10] Ito, Shimada, Kuraishi, and Mizushima, *ibid.*, 1957, **26**, 1508.

86. *The Rearrangement of Nitrones.*

By A. H. WRAGG and T. S. STEVENS.

MARTYNOFF [1] observed the formation of *O*-(*o*-methoxydiphenylmethyl)benzaldoxime, $MeO\cdot C_6H_4\cdot CHPh\cdot O\cdot N{:}CHPh$, as a by-product in the acid hydrolysis of the *N*-isomer, $MeO\cdot C_6H_4\cdot CHPh\cdot \overset{+}{N}(\bar{O}){:}CHPh$, and concluded that it arose by direct radical migration from nitrogen to oxygen. We had begun a general study of nitrones in order to define the

[1] Martynoff, *Ann. Chim.*, 1937, **7**, 424.

incidence of this analogue of the Meisenheimer rearrangement of amine oxides, when Cope and Haven [2] brought about the thermal rearrangement of *N*-diphenylmethylbenzophenone oxime, $Ph_2CH{\cdot}\overset{+}{N}(\overset{-}{O}){:}CPh_2$, but not that of *N*-benzylbenzophenone oxime. Our preliminary observations are now reported.

Rearrangement was not observed in the thermal treatment, under a variety of conditions, of *N*-phenyl-, *N*-benzyl-, *N*-diphenylmethyl-, or *N*-cinnamyl-benzaldoxime. The two first gave, respectively, some benzanilide and some *N*-benzylbenzamide, which could be products of a Beckmann change. *N*-9-Fluorenylhydroxylamine was prepared, but in insufficient quantity for the preparation and study of 9-fluorenylnitrones.

Grammaticakis,[3] Martynoff, and Cope and Haven all regarded the production of hydroxylamine in the acid hydrolysis of the *N*-derivative of an oxime as good evidence of rearrangement to the *O*-derivative, followed by hydrolysis:

$$R{\cdot}\overset{+}{N}(\overset{-}{O}){:}CR_2' \longrightarrow R{\cdot}O{\cdot}N{:}CR_2' \longrightarrow R{\cdot}O{\cdot}NH_2 + COR_2'$$
$$\downarrow$$
$$HO{\cdot}NH_2$$

This conclusion is not always valid, for *N*-diphenylmethylhydroxylamine is hydrolysed under relatively mild conditions to hydroxylamine and bisdiphenylmethyl ether.

Experimental.—N-*Phenylbenzaldoxime.*[4] This nitrone (0·762 g.) was heated at 200° for 1 hr. Steam distillation then gave benzaldehyde which yielded the 2 : 4-dinitrophenylhydrazone (1·007 g.), m. p. and mixed m. p. 235°; the residue afforded benzanilide (mixed m. p.) (46 mg.).

N-*Benzylbenzaldoxime.*[5] This was prepared by oxidising *NN*-dibenzylhydroxylamine (50 g.) in chloroform (450 ml.) with yellow mercuric oxide (60 g.) with shaking and cooling. The product (46·5 g.) was crystallised from ethanol–ligroin (b. p. 60—80°). *NN*-Dibenzylhydroxylamine [6] was obtained from hydroxylamine hydrochloride (42 g.), benzyl chloride (144 g.), and sodium carbonate (110 g.), in refluxing water (200 ml.)–ethanol (1000 ml.) for 6 hr. Ethanol was distilled off, water added, and the precipitate crystallised twice from ethanol to give large crystals. The small crystals of tribenzylamine (mixed m. p.) were washed out with ether and the product was again crystallised from ethanol; it had m. p. 123°.

In three experiments, *N*-benzylbenzaldoxime was heated at 150° for 8 hr., at 190° for 3 hr., and distilled under 15 mm. pressure. In each case the product was heated with phenylhydrazine at 107—110° for 8 hr. to liberate *N*- and possibly *O*-benzylhydroxylamine; after *N*-benzylhydroxylamine and unchanged phenylhydrazine had been destroyed by Fehling's solution, no *O*-benzylhydroxylamine could be recognised. When 10% of *O*-benzylbenzaldoxime [7] was added to this initial material in parallel experiments *O*-benzylhydroxylamine was easily recognised and characterised as *O*-benzyl-*p*-nitrobenzaldoxime [8] (mixed m. p.) (Found: N, 11·0. Calc. for $C_{14}H_{12}O_3N_2$: N, 10·9%).

N-*Diphenylmethylbenzaldoxime.* *N*-Diphenylmethylhydroxylamine oxalate [9] (6·1 g.), m. p. 185° (decomp.), benzaldehyde (2·65 g.), and hydrated sodium acetate (3·4 g.) in ethanol (100 ml.) were refluxed for 2 hr., affording *N*-diphenylmethylbenzaldoxime (6·3 g.), as needles, m. p. 159—160°,[5] from ethanol. The nitrone (6 g.) was heated at 170° for 3 hr. From the melt, acid extracted diphenylmethylamine (1·22 g.), identified as hydrochloride and as *p*-nitrobenzylidene derivative (mixed m. p.s); no *O*-diphenylmethylhydroxylamine could be recognised by the procedure reported above. Distillation of *N*-diphenylmethylbenzaldoxime (6 g.) at 17 mm.

[2] Cope and Haven, *J. Amer. Chem. Soc.*, 1950, **72**, 4896.
[3] Grammaticakis, *Compt. rend.*, 1937, **205**, 60.
[4] Bamberger, *Ber.*, 1894, **27**, 1556.
[5] Angeli, Alessandri, and Aiazzi-Mancini, *Atti reale Accad. Lincei*, 1911, **20**, I, 546.
[6] Behrend and Leuchs, *Annalen*, 1890, **257**, 216.
[7] Beckmann, *Ber.*, 1889, **22**, 514.
[8] Behrend and König, *Annalen*, 1891, **263**, 353.
[9] Platner, *ibid.*, 1894, **278**, 364.

pressure gave *sym.*-tetraphenylethane (mixed m. p.; 1·3 g.) and diphenylmethylamine (0·6 g.); this was identified as before. N-*Diphenylmethyl*-p-*nitrobenzylideneamine*, needles (m. p. 135°) from ethanol, was also prepared from diphenylmethylamine hydrochloride and *p*-nitrobenzaldehyde with sodium acetate in boiling alcohol (3 hr.) (Found: C, 76·0; H, 5·2; N, 8·7. $C_{20}H_{16}O_2N_2$ requires C, 76·0; H, 5·1; N, 8·7%).

N-*Cinnamylbenzaldoxime*. Cinnamyl bromide (22·5 g.), acetoxime (12·5 g.), acetic acid (25 ml.), and water (8 ml.) were boiled for 30 min. and then evaporated quickly to half the bulk (cf. ref. 9). After addition of water, the mixture was extracted thoroughly with ether and the aqueous layer treated with ammonium oxalate. The precipitated N-*cinnamylhydroxylamine oxalate* (8 g.) crystallised from 90% ethanol in plates, m. p. 177—178° (decomp.) (Found: C, 61·75; H, 5·9; N, 7·4. $C_{20}H_{24}O_6N_2$ requires C, 61·9; H, 6·2; N, 7·2%). The oxalate (6 g.), benzaldehyde (3·4 g.), and hydrated sodium acetate (4·25 g.) in ethanol (100 ml.) were refluxed for 3 hr., affording N-*cinnamylbenzaldoxime* as needles, m. p. 73°, from ether–ligroin (b. p. 40—60°) (Found: C, 80·8; H, 6·4; N, 5·4. $C_{16}H_{15}ON$ requires C, 81·1; H, 6·3; N, 5·9%). When the nitrone was heated at 138° for 2 hr., or distilled at 19—20 mm. pressure, it decomposed extensively, the only definable product being benzaldehyde.

9-Bromofluorene (5 g.), treated with acetoxime (1·49 g.) in acetic acid (75%; 20 ml.) as in the previous instance, gave variable yields (⩾20%) of N-9-*fluorenylhydroxylamine oxalate*, as plates, m. p. 205° (decomp.), from ethanol (Found: C, 70·0; H, 5·0; N, 5·6. $C_{28}H_{24}O_6N_2$ requires C, 69·5; H, 5·0; N, 5·8%).

Hydrolysis of N-*diphenylmethylhydroxylamine*. The base (2·4 g.) in 12% hydrochloric acid (50 ml.) was heated on a boiling-water bath for 4 hr. Ether then extracted bis(diphenylmethyl) ether (mixed m. p.). Evaporation of the acid solution gave a solid, part of which dissolved in chloroform and was the hydrochloride of the unchanged base. The insoluble portion (0·48 g.) was recognised as hydroxylamine hydrochloride (Found: Cl, 50·6. Calc. for NH_4OCl: Cl, 51·0%) by the spot test with salicylaldehyde and copper acetate [10] and by conversion into benzophenoneoxime (mixed m. p.).

The authors thank the Sheffield Town Trustees for a Scholarship (to A. H. W.).

THE UNIVERSITY, SHEFFIELD, 10. [*Received, June 10th*, 1958.]

[10] Feigl, *Rec. Trav. chim.*, 1939, **58**, 475.

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87. *Steric Effects and Hydrogen Isotope Exchange in* 1 : 2 : 3-*Trimethoxybenzene.*

By D. P. N. SATCHELL.

WHILE investigating [1] the rate of aromatic hydrogen isotope exchange between [4 : 6-^{3}H]1 : 2 : 3-trimethoxybenzene and aqueous solutions of weak acids, we wished to show that the exchange rate for this compound in aqueous solutions of strong mineral acids was determined by Hammett's acidity function, as it is for all neutral aromatic compounds so far studied.[2] The rate of exchange was examined at three acidities in aqueous sulphuric acid. This strong acid was chosen because the behaviour of anisole has been studied quantitatively in it; [2] this study, coupled with that of Melander and Olsson [3] on the isotope effect in aromatic hydrogen exchange, makes possible a moderately quantitative prediction of the exchange rate of 1 : 2 : 3-trimethoxybenzene, it being assumed that the activating effects of substituents in the ring are independent and additive.[4]

The measured exchange-rate constants, λ, and the H_0 data are in the Table. log λ

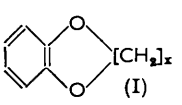
[1] Satchell, *J.*, 1958, 3904.
[2] Satchell, *J.*, 1956, 3911 and references therein.
[3] Melander and Olsson, *Acta. Chem. Scand.*, 1956, **10**, 879.
[4] (*a*) Bradfield, *Trans. Faraday Soc.*, 1941, **37**, 726; (*b*) Jones, *J.*, 1942, 418, 1676; (*c*) Condon, *J. Amer. Chem. Soc.*, 1948, **70**, 1963; (*d*) de la Mare and Vernon, *J.*, 1951, 1764; (*e*) de la Mare and Hassan, *J.*, 1958, 1519.

is linearly related to H_0, with a slope close to unity, as expected. However, the observed exchange rate at, say, 4·7M, is about sixty-fold slower than that predicted. The prediction admittedly involves some assumptions apart from that of the methoxyl substituents' contributing independently and additively to the activation energy.

First-order exchange rate in aqueous sulphuric acid at 25°.

	(*a*) [4 : 6-^{3}H]1 : 2 : 3-Trimethoxybenzene			(*b*) [4 : 6-^{3}H]2-Hydroxy-1 : 3-dimethoxybenzene	
H_2SO_4 (M)	3·51	4·70	5·22	4·70	5·22
$-H_0$	1·62	2·15	2·37	2·15	2·37
$10^4\lambda$ (sec.$^{-1}$)	0·52	1·75	2·91	3·00	5·06

It is first assumed that the exchange data for benzene in aqueous sulphuric acid [2] may be extrapolated to 4·7M (*ca.* 3 H_0 units), so that the appropriate *ortho*- and *para*-partial rate factors for anisole can be calculated. This extrapolation seems unlikely to lead to great error.[2] Secondly, the previous data apply to deuterium exchange whereas the present rates concern tritium. An isotope rate ratio has, therefore, to be assumed. Melander and Olsson found this ratio, λ_T/λ_D, for exchange in toluene to be *ca.* 0·5. No great error is likely to be introduced by assuming the value for 1 : 2 : 3-trimethoxybenzene to be about the same. Thirdly, a value for the *meta*-partial rate factor of anisole has to be assumed. It is *ca.* 0·25 in strong perchloric acid, and probably much the same in strong sulphuric acid.[2] However, the trends of the graphs in ref. 2 imply that, if anything, the deactivation will decrease as the acidity decreases. (Results for other types of reaction with dimethoxybenzenes indicate *activation* of the *meta*-position.[2]) Hence the assumption of a value of 0·2 seems well on the safe side. It is considered that the above assumptions, which lead to an expected rate of *ca.* $1{\cdot}0 \times 10^{-2}$ sec.$^{-1}$ for the 4- and the 6-position of [4 : 6-^{3}H]1 : 2 : 3-trimethoxybenzene, are not likely to involve a greater total error than a factor of 3 or 4. The observed exchange rate is, in fact, 57-fold slower than predicted. It seems clear that the three methoxyl groups are *not* activating the ring independently and additively, and some form of steric interaction seems probable.[4e]



(I)

Neighbouring methoxyl groups, and methoxyl groups flanked by other substituents, have been studied before from the steric viewpoint.[5] The general conclusions are as follows. First, for the methoxyl group to exert its maximum accelerative effect on electrophilic aromatic substitution, both its oxygen and carbon atoms should lie in the plane of the ring. Secondly, comparisons between the reactivity of veratrole and compounds of type (I) indicate that the most favoured disposition of the oxygen–carbon bonds is *trans–trans*. It has been suggested [5b] that in this position the lone pair of electrons on one oxygen atom can interact electrostatically with the positive charge developed on the other on assuming its quinonoid form. It is possible that this extra stabilisation, available in veratrole but not in anisole, explains the seeming discrepancy between partial rate factors deduced for the latter from experiments with the former, and the directly determined partial rate factors.[2] Thirdly, there is evidence that when both positions *ortho* to a methoxyl group are occupied, the group has difficulty in assuming the most favourable, planar configuration.

The above considerations apply to the influence of steric requirements on the methoxyl group's mesomeric activation of the ring. The plane of the carbon–oxygen–carbon bond is probably less important in determining the (deactivating) inductive effect of the group.

The 4- and the 6-position are the reactive sites in 1 : 2 : 3-trimethoxybenzene. Their powerful activation is provided by the 1- and the 3-methoxyl group and is (perhaps) moderated by the 2-substituent. Steric considerations lead to the conclusion that, for three adjacent methoxyl groups, only the 1- and the 3-substituent can lie easily and

[5] (*a*) Brown, Wilzbach, and Urry, *Canad. J. Res.*, 1949, **27**, *B*, 398; (*b*) Baddeley, Holt, Smith, and Whittaker, *Nature*, 1951, **168**, 386; (*c*) Baddeley and Smith, *ibid.*, 1949, **164**, 1014; (*d*) Baddeley, Smith, and Vickars, *J.*, 1956, 2455; (*e*) Horton and Rossiter, *J. Org. Chem.*, 1958, **23**, 488.

simultaneously in the plane of the ring, *i.e.*, in their positions most favourable mesomerically for reactivity. To do so they must take up the *trans–trans* position, interaction with the neighbouring oxygen atom discouraging the *cis–trans* or *cis–cis* configuration. The 2-substituent cannot easily lie in the plane of the ring.

These points being borne in mind, there seem two possible reasons for the unexpectedly low reactivity of the 4- and the 6-position. (1) The net effect of the 2-substituent on the reaction centres *meta* to it is doubtless due to a balance between its $-I$ effect and any second-order relay of its $+T$ effect.[6] The loss of conjugation by this group must reduce the latter, and thus deactivate the 4- and the 6-position if the inductive effect is unaffected, as it may be. This influence is, however, even by description, a second-order effect, and likely to be small. This is supported by experiments with 2-hydroxy-1 : 3-dimethoxybenzene described below. (2) The presumed *trans–trans* orientation of the 1- and the 3-substituent, at least at the moment of reaction, will shield the 4- and the 6-position, and to some extent hinder the approach of the reagent. Possibly this effect is appreciable, and it is considered that it probably accounts for most of the loss of reactivity. Thus, for 1 : 2 : 3-trimethoxybenzene, it is concluded that direct steric shielding of the reaction centres is more important than any sterically induced loss of mesomerism.

The rate of tritium exchange at the 4- and the 6-position of 2-hydroxy-1 : 3-dimethoxybenzene was also measured in aqueous sulphuric acid, and is included in the Table. The rate is faster than for trimethoxybenzene by a factor of *ca.* 1·7. For the 2-hydroxy-compound steric considerations indicate that all the substituents can lie in the plane of the ring, though the factor which chiefly influences the orientation of the 4- and the 6-substituent, namely the adjacent oxygen atom, remains unchanged, so that little change in steric hindrance due to these groups is to be expected—and if anything a reduction.

The hydroxyl group possesses inductive and mesomeric effects similar in magnitude to those of a methoxyl group.[7] The $+T$ effect seems a little more,[2] and the $-I$ effect a little less,[8] powerful than for the latter group. The absence of any steric inhibition of mesomerism for the hydroxyl group will therefore produce a second-order relay, at the 4- and the 6-position, comparable to that which the 2-methoxyl group of 1 : 2 : 3-trimethoxybenzene would produce if it could assume coplanarity. The inductive deactivation will be comparable, if a little less. Hence an increase in reactivity for the 2-hydroxy-compound is to be expected from three sources, all of which are likely to be small. The fact that they *are* small is proved by the rate factor of only 1·7. It seems clear (as was assumed above) that the steric reduction of second-order relay can play only a minor part in determining the reactivity of the 4- and the 6-position in trimethoxybenzene.

Experimental.—Tritiated compounds. The preparation of the [4 : 6-^{3}H]1 : 2 : 3-trimethoxybenzene has been described.[1] The labelled 2-hydroxy-1 : 3-dimethoxybenzene was prepared by solution of the light compound in 24·4 moles % ethanol–THO, containing hydrogen chloride, and of known [9] H_0. After a period based on the expected exchange rate for the 4- and the 6-position (the 5-position must be *ca.* 10^4 times less active) at 25°, the solution was partly neutralised with sodium hydroxide, diluted with water, and extracted with ether. Evaporation of the ether, followed by recrystallisation, gave a product of m. p. 36°. The hydroxyl group of the main product was not rigorously freed from significant tritium, since in the kinetic experiments the large excess of solvent automatically accomplished this. A small portion was so freed for use as the sample representing zero exchange time. Its activity showed that exchange equilibrium had not been reached for the 4- and the 6-position, and therefore the 5-position was doubtless free from tritium.

Exchange experiments. These were conducted under homogeneous conditions at 25°. Samples (~0·08 g.) were dissolved in 100 ml. samples of acid mixture in flasks fitted with ground

[6] Baker, Barrett, and Tweed, *J.*, 1952, 2833.
[7] Rosenwald, *J. Amer. Chem. Soc.*, 1952, **74**, 4602.
[8] Badger, " Structures and Reactions of the Aromatic Compounds," Cambridge Univ. Press, 1954, p. 190.
[9] Satchell, *J.*, 1957, 3524.

glass stoppers, and immersed in a thermostat bath. Flasks were removed after known intervals, and their contents diluted with water and extracted with ether. Evaporation of the ether left crystalline material of good m. p., the activity of which was determined as previously described.[1]

The methoxyl groups of both the 1 : 2 : 3-trimethoxy- and the 1 : 2-dimethoxy-compounds should be stable in the acid mixtures used.[10]

H_0 data are taken from Paul and Long.[11] Those in ref. 2 were not.

This work was performed under the auspices of the U.S. Atomic Energy Commission.

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[10] Burwell, *Chem. Rev.*, 1954, **54**, 615.
[11] Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

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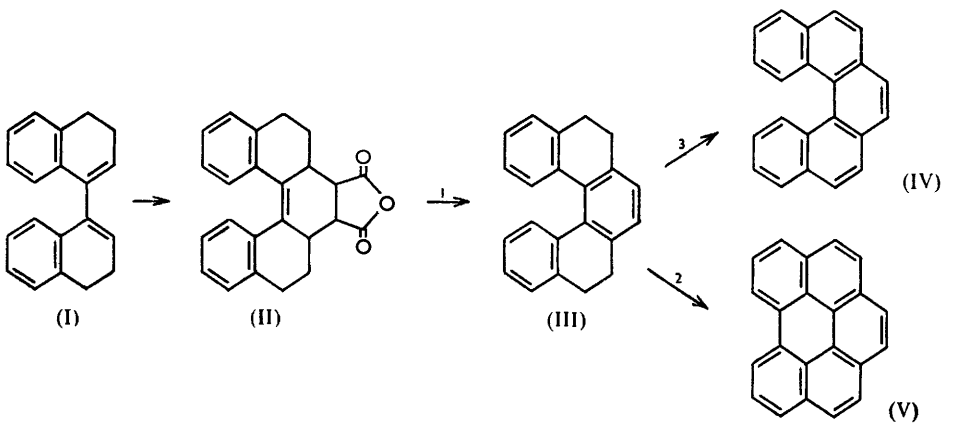
88. *Alicyclic Studies. Part XIV.*[1] *An Improved Synthesis of 3 : 4-5 : 6-Dibenzophenanthrene and 1 : 12-Benzoperylene.*

By YANINA ALTMAN and DAVID GINSBURG.

IT appeared from our work on symmetrical alicyclic dienes [1] that the existing syntheses of 3 : 4-5 : 6-dibenzophenanthrene [2-4] could be improved. This compound has been synthesised in 23% overall yield based on α-tetralone as starting material, the lead dioxide oxidative–decarboxylation procedure [5, 6] being employed on the intermediate (II). Bromination-dehydrobromination of the product (III) afforded the required hydrocarbon (IV).



Reagents: 1, PbO_2. 2, Pd–C. 3, *N*-Bromosuccinimide, then NaOAc.

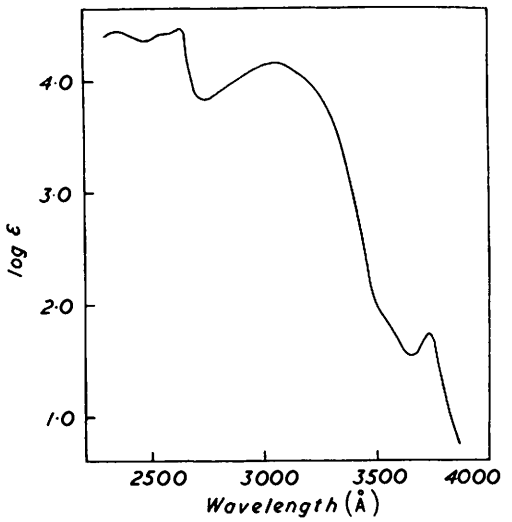
Alternatively, dehydrogenation of compound (III) with palladised carbon afforded 1 : 12-benzoperylene (V) in 95% yield, an improvement over previous syntheses of this hydrocarbon.[7, 8]

[1] Part XIII, Greidinger and Ginsburg, *J. Org. Chem.*, 1957, **22**, 1406.
[2] Weidlich, *Ber.*, 1938, **71**, 1203.
[3] Cook, *J.*, 1933, 1592.
[4] E. D. Bergmann and Szmuszkovicz, *J. Amer. Chem. Soc.*, 1951, **73**, 5153.
[5] Doering and Farber, *ibid.*, 1952, **74**, 4370.
[6] Doering and Finkelstein, *J. Org. Chem.*, 1958, **23**, 141.
[7] Clar, *Ber.*, 1932, **65**, 846.
[8] Hewett, *J.*, 1938, 1286.

The ultraviolet absorption spectrum of compound (III) is reproduced in the Figure. The spectra of compounds (IV) and (V) were superimposable, respectively, upon those already published.[4, 7]

Experimental.—3 : 4 : 3′ : 4′-*Tetrahydro*-1 : 1′-*dinaphthyl* (I). A mixture of freshly scraped aluminium foil (6 g.; 0·005 in. thickness, 1 sq. cm. squares), α-tetralone (21 g.), dry ethanol (150 ml.), dry benzene (100 ml.), and mercuric chloride (0·5 g.) was heated on the steam-bath for 14 hr. After cooling, the excess of aluminium was dissolved in cold 10% hydrochloric acid. The aqueous phase was extracted with benzene–ether (1 : 1), and the combined organic phases were washed once with dilute hydrochloric acid. The solvents were removed and a mixture of acetic acid (45 ml.) and acetic anhydride (45 ml.) was added to the residue and dehydration of the pinacol was completed by boiling for 2 hr. Concentration of the solution to a small volume afforded the diene (15 g., 81%), m. p. 138—140°, which was sufficiently pure for the next step. It had m. p. 141° (from ethanol) (lit.,[2, 9] m. p. 141°).

Spectrum of 1 : 2 : 7 : 8-*tetrahydro*-3 : 4-5 : 6-*dibenzophenanthrene in* cyclo*hexane.*



1 : 2 : 7 : 8 : 8a : 9 : 10 : 10a-*Octahydro*-3 : 4-5 : 6-*dibenzophenanthrene*-9 : 10-*dicarboxylic anhydride* (II). On the steam-bath maleic anhydride (24 g.) and the above diene (6 g.) gave a melt which began depositing crystals after 30 min. After 4 hours' heating, the solid formed was dissolved in hot acetic acid. Concentration and cooling gave the *anhydride* (6·2 g., 75%), m. p. 252—254°. Recrystallisation from toluene raised the m. p. to 256° (lit.,[2, 9] m. p. 254°, 256°). A 95% yield of crude adduct has been reported.[9]

1 : 2 : 7 : 8-*Tetrahydro*-3 : 4-5 : 6-*dibenzophenanthrene* (III). A finely powdered mixture of the anhydride (500 mg.) and lead dioxide (1·34 g.; Fisher, technical grade) and freshly distilled decalin (4 ml.) were placed in a 25 ml. flask equipped with gas-inlet tube leading to the surface of the reaction mixture and an outlet tube leading into a solution of barium hydroxide. The temperature was gradually raised to 190—200° and the mixture was kept in an inert atmosphere. Carbon dioxide was evolved during *ca.* 3 hr. The mixture was cooled to 100°, 2 : 2 : 4-trimethylpentane was added, and reflux was maintained for 10 min. The liquid was decanted and this procedure was repeated twice. Finally the solid was removed and washed with ether. All of the extracts were united and the solvents were removed in a vacuum. The residual oil was triturated with pentane, giving brown prisms (165 mg., 41%). Sublimation at 140—150°/0·05 mm. gave the colourless hydrocarbon (160 mg.), m. p. 144—146°. Recrystallisation from ethanol gave prismatic rosettes, m. p. 148—149° (lit.,[2] 142°). 43% of the theoretical quantity of carbon dioxide was isolated as barium carbonate.

[9] F. Bergmann, Eschinazi, and Neeman, *J. Org. Chem.*, 1943, **8**, 179.

With specially prepared lead dioxide [6] the yield fell to 15%. When powdered Pyrex glass was used instead of decalin, together with double the quantity of lead dioxide,[6] the yield was 30—32%.

3 : 4-5 : 6-*Dibenzophenanthrene* (IV). A mixture of the above hydrocarbon (227 mg.), *N*-bromosuccinimide (284 mg.), dibenzoyl peroxide (14 mg.), and dry carbon tetrachloride (10 ml.) was refluxed for 30 min. Much hydrogen bromide was evolved. Acetic acid (4 ml.) and sodium acetate (0·82 g.) were added and heating was continued for 1 hr. After cooling, water was added and the organic layer was separated and washed with water, sodium hydrogen carbonate solution, and again water. After drying (Na_2SO_4) and removal of the solvent, the yellow residue was dissolved in benzene (2 ml.)–hexane (1 ml.), and the solution was filtered through a column of basic alumina (15 g.) and eluted with benzene–hexane (2 : 1). Removal of solvents from the eluate afforded the light yellow aromatic hydrocarbon (220 mg.), m. p. 176°. Crystallisation from ethanol (charcoal) gave colourless material, m. p. 178° (204 mg., 92%). Crystallisation from ethanol with rapid cooling gave glistening platelets. Slow crystallisation from hexane gave yellowish prisms whilst slow crystallisation from ethanol gave both needles and rosette-shaped feathers (lit.,[2-4] m. p. 177°, 177—178°).

1 : 12-*Benzoperylene* (V). A mixture of the hydrocarbon (III) (60 mg.), 30% palladised carbon (40 mg.), and *p*-cymene (5 ml.) was heated under reflux for 5 hr. in an inert atmosphere. Cooling and removal of the catalyst and the solvent afforded a yellow residue of 1 : 12-benzoperylene (57 mg.), m. p. 273° (from propan-1-ol) (lit.,[7, 8] m. p. 273°, 269—270°).

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89. *The Extractives of* Dysoxylum spectabile, *Hook.*

By R. C. Cambie.

Dysoxylum spectabile Hook. (New Zealand "Kohekohe"; family, Meliaceae) is the only species of the genus found in New Zealand and is endemic, the tree being restricted to the coastal and semi-coastal forests of North Island and the northern part of South Island. The aim of the investigation was to isolate the (possibly crystalline) pigments which were responsible for the strong reddish colour of the heartwood. Extraction of the heartwood and the bark with light petroleum, followed by chromatography on alumina, gave β-sitosterol as the principal sterol present, in 0·014% and 0·017% yield respectively. As mixed-melting-point determinations are unreliable for sitosterols,[1] characterisation was by means of the acetate. Other sterols probably present in the heartwood extract, as indicated by positive Liebermann–Burchard and Nath [2] tests, were not present in sufficient quantity for purification.

Extraction of the bark with ether gave a non-phenolic oil, chromatography of which on alumina gave no useful results. Saponification, followed by chromatography of the unsaponifiable fraction, however, gave an impure but crystalline ketone in a yield (0·002%) that was insufficient to permit further examination. Preliminary examination showed that ether gave a negligible extract from the heartwood.

Alcoholic extracts of both the heartwood and the bark were deep red but were mainly composed of condensed tannins, as indicated by a variety of reagents.[3] The tannin fractions which were responsible for the colour did not melt and had zero R_F in all chromatographic systems tried. They were not readily purified and were not investigated further. Paper chromatography of the heartwood extract showed the presence of a single further phenolic compound which was isolated by chromatography of an ethyl acetate extract on a

[1] Fieser and Fieser, "Natural Products Related to Phenanthrene," Reinhold Publ. Corpn., New York, 1949, p. 286.
[2] Nath, *Ann. Biochem. Exp. Med.*, 1942, **2**, 83; *Chem. Abs.*, 1943, **37**, 3701.
[3] Russell, *Chem. Rev.*, 1935, **17**, 165; Michaluk, *Acta Polon. Pharm.*, 1954, II, 362; *Chem. Abs.*, 1955, **49**, 9948.

cellulose column. It was identified as (+)-catechin by comparison with an authentic sample. It was not detected in the bark by paper chromatography. Tests indicated absence of flavonoids,[4] anthocyanins,[4] *leuco*anthocyanins,[5] and alkaloids from extracts of both the bark and the heartwood.

Experimental.—Microanalyses were by Dr. A. D. Campbell, University of Otago, N.Z. Infrared spectra were measured on potassium bromide discs and ultraviolet spectra were measured for ethanolic solutions.

(a) *The heartwood*; β-*sitosterol.* Finely milled heartwood (720 g.) was extracted (Soxhlet) with light petroleum (b. p. 56—62°) for 90 hr. Chromatography of the waxy concentrate (170 mg.) in benzene on neutralised alumina and recrystallisation of the major product as plates from aqueous methanol gave β-sitosterol, m. p. and mixed m. p. 134—135° [Found: for sample dried at room temperature: C, 80·3, 80·4; H, 12·7, 12·3%; *M* (Rast), 436. Calc. for $C_{29}H_{50}O,H_2O$: C, 80·5; H, 12·1%; *M*, 433. Found, for sample dried at 100°: C, 84·1; H, 12·6. Calc. for $C_{29}H_{50}O$: C, 84·0; H, 12·2%], $\lambda_{max.}$ 207 mμ (log ε 3·61) [Wheeler and Mateos [6] record 207 mμ (ε 4200)], $\nu_{max.}$ 3436 (bonded OH), 2950 (C–H), 2857 (C–H), 1684 (Δ^5-ethylenic bond) cm.$^{-1}$. The acetate, prepared by the use of pyridine and acetic anhydride (1 hr.; 90°), formed plates (from methanol), m. p. and mixed m. p. 127—128° (Found: C, 81·9; H, 11·6. Calc. for $C_{31}H_{52}O_2$: C, 81·5; H, 11·5%).

(+)-*Catechin.* The air-dried heartwood was further extracted with ethanol for 9 hr. and tannins (50 g.) were precipitated from the syrupy concentrate by the addition of ether. The filtrate was extracted with saturated sodium hydrogen carbonate, and the extract acidified. Chromatography of an ethyl acetate extract of the precipitate, on a cellulose column, gave a discoloured fraction (261 mg.), circular R_F 0·41 in phenol–water (9 : 1), 0·73 in 40% acetic acid. Repeated crystallisation from hot water (charcoal) gave colourless needles of (+)-catechin, m. p. and mixed m. p. 175—176° with sintering at 149—150° (Found, for sample dried at 100°: C, 61·7; H, 4·9. Calc. for $C_{15}H_{14}O_6$: C, 62·1; H, 4·9%), $[\alpha]_D^{25}$ +17° [*c* 0·8 in Me_2CO–H_2O (1 : 1)], $\lambda_{max.}$ 280 mμ (log ε 3·62), $\nu_{max.}$ 3401 (OH), 3322 (OH), 2985 (C–H), 1626 (H_2O), 1618 (aromatic) cm.$^{-1}$. The penta-acetate, prepared by the use of pyridine and acetic anhydride, formed elongated prismatic rods (from methanol), m. p. 131—132° (Found: C, 59·8; H, 4·8; Ac, 41·8. Calc. for $C_{25}H_{24}O_{11}$: C, 60·0; H, 4·8; 5Ac, 42·3%).

Chromatography of the ether solution remaining after extraction with sodium hydrogen carbonate, on alumina, gave further β-sitosterol (10 mg.).

(b) *The bark.* Finely milled bark (1·025 kg.) was extracted (Soxhlet) with light petroleum for 24 hr. and the waxy concentrate chromatographed in benzene or alumina (Brockmann II). Recrystallisation, from methanol, of the fractions eluted with benzene–ether gave needles of β-sitosterol, m. p. and mixed m. p. 137—138° (Found: C, 84·2; H, 11·8%) (identical infrared spectrum). The acetate had m. p. and mixed m. p. 127—128° (Found: C, 81·4; H, 11·4%).

The bark was re-extracted with ether for 24 hr. and the brown oily concentrate (9·8 g.) hydrolysed with 2N-ethanolic potassium hydroxide for 6 hr. The unsaponifiable fraction was chromatographed in benzene on alumina (Brockmann II). Elution with benzene, benzene–ether, and ether gave yellow oils. From the fractions eluted with ethyl acetate a colourless fraction was obtained which separated from ethyl acetate as granular crystals (25 mg.), m. p. 89—90° (Found: C, 74·2; H, 12·2%), $\lambda_{max.}$ 273 mμ, $\nu_{max.}$ 2959 (CH_2), 2899 (CH_2), 1712 (C:O) cm.$^{-1}$. The substance gave positive tests for the carbonyl group but a negative Fehling's test.

A methanol extract of the bark (24 hr.) gave condensed tannins (10 g.), insoluble in ethyl acetate or water.

The author thanks Professor L. H. Briggs for suggesting this investigation and for interest in the work.

Department of Chemistry,
University of Auckland, New Zealand. [*Received, July 14th*, 1958.]

[4] Geissman in "Modern Methods of Plant Analysis," Springer-Verlag, Berlin, 1955, Vol. III, pp. 450—498.
[5] Bate-Smith and Lerner, *Biochem. J.*, 1954, **58**, 126.
[6] Wheeler and Mateos, *J. Org. Chem.*, 1956, **29**, 1110.

90. *Chemistry of the* Coprosma *Genus. Part XI.* The Colouring Matters from* Coprosma foetidissima.

By E. G. Brooker.

Coprosma foetidissima [1] is a widely occurring, small shrub or tree endemic to New Zealand. All portions of the plant give a strong fœtid odour when bruised and methanethiol has been identified in a steam-distillate of the leaves.[2] The inner aerial bark is bright yellow and contains asperuloside.[3] Examination of a light petroleum extract of the aerial bark indicated the presence of three anthraquinones in insufficient amounts for identification. Further extraction with benzene gave a brown gum containing traces of anthraquinones, and an ether-extract contained traces of anthraquinones, rutin, and quercetin. Extraction with methanol yielded a brown gum from which rutin was obtained in 9·6% yield. Hydrolysis of the rutin mother-liquors indicated the presence of asperuloside but attempted isolation of asperuloside from unhydrolysed mother-liquors by Trim and Hill's procedure [4] did not yield sufficient material for identification. Rutin has been isolated from the root-bark of *Coprosma rhamnoides*.[5]

Experimental.—The analysis was carried out by Dr. A. D. Campbell, University of Otago. Anthraquinones were chromatographed in acetone over magnesium oxide. Paper chromatography of rutin and quercetin was carried out on Whatman No. 1 discs with aqueous acetic acid (1 : 13 v/v and 1 : 4 v/v, respectively) as developing solvents and ammonia vapour to locate the spots.

Air-dried aerial bark of *Coprosma foetidissima*, collected at Tongariro National Park in January, was extracted (Soxhlet) successively with light petroleum (b. p. 50—65°), benzene, ether, and methanol. The bright orange gum extracted by light petroleum gave colour reactions with concentrated sulphuric acid and aqueous alkali indicating the presence of anthraquinones. Chromatography over magnesium oxide gave three bands (upper band blue, middle band pink, and lower band yellow), but there were insufficient amounts of the pigments for identification. Chromatography of the benzene and the ether extracts indicated traces of anthraquinones. Paper chromatography of the ether extract showed the presence of rutin and quercetin.

The considerable amount of brown gum extracted by methanol crystallised on treatment with hot water, to give light yellow needles, m. p. *ca.* 170°, decomp. >189°. Repeated recrystallisation from 50% aqueous ethanol afforded yellow needles of rutin, m. p. and mixed m. p. 195° (decomp.) (Found: C, 52·7; H, 5·1. Calc. for $C_{27}H_{30}O_{16}$: C, 53·0; H, 5·0%), $\lambda_{max.}$ 212, 260, 305, and 362 mμ in EtOH (log ε 4·42, 4·26, 3·95, and 4·24) (cf. ref. [6]).

The glycoside was hydrolysed with 10% hydrochloric acid at 100° for 2 hr. The insoluble aglycone on repeated recrystallisation from 60% acetic acid gave quercetin as stout yellow rods, m. p. and mixed m. p. 316—316·5°. Paper chromatography of the aqueous hydrolysate (ethyl acetate–acetic acid–water, 3 : 1 : 3 v/v, followed by spraying with aniline–trichloroacetic acid) revealed glucose and rhamnose.

Hydrolysis of the rutin mother-liquors with aqueous hydrochloric acid gave a blue-green solution; later there was precipitation of considerable black solid. Similar changes are observed when asperuloside is hydrolysed.

The author is indebted to Professor L. H. Briggs for his continued interest and encouragement, to Mr. T. A. Turney, of this Department, for the collection of bark, and to Dr. R. C. Cooper, Auckland Institute and Museum, for its botanical identification.

University of Auckland, Auckland, New Zealand. [*Received, August 5th*, 1958.]

* Part X, *J.*, 1955, 3298.

[1] Oliver, "The Genus *Coprosma*," Bernice P. Bishop Museum Bull., 1935, p. 132.
[2] Sutherland, *New Zealand J. Sci. Technol.*, 1947, **29**, *B*, 94.
[3] Briggs and Nicholls, *J.*, 1954, 3940.
[4] Trim and Hill, *Biochem. J.*, 1952, **50**, 310.
[5] Briggs and Taylor, *J.*, 1955, 3298.
[6] Geissman, "Modern Methods of Plant Analysis," Springer-Verlag, Berlin, 1955, Vol. III, p. 487.

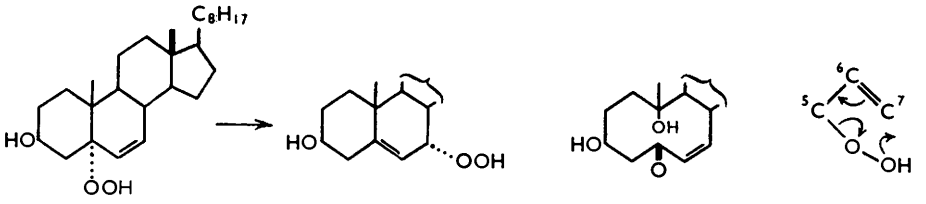
91. *Allylic Rearrangement of an αβ-Unsaturated Hydroperoxide.*

By B. Lythgoe and S. Trippett.

During their studies on the photo-induced reactions of organic compounds and oxygen, Schenck and his co-workers [1] showed that olefins can be converted into αβ-unsaturated hydroperoxides; thus cholesterol gives the 5α-hydroperoxide (I), the hydroperoxyl group becoming attached to one of the termini of the original double bond, whilst the latter migrates to the adjacent position. They also observed [1] that the peroxide (I) in chloroform slowly underwent mutarotation, which, it was suggested, might be due to a rearrangement [2] to the hydroxy-ketone (II) or its internal hemiacetal.

An interest in compounds of type (II) prompted us to examine the rearrangement of the hydroperoxide (I); it was effectively complete at room temperature in chloroform after 12 hr., and the product was then obtained crystalline in very high yield. That the product was a hydroperoxide was shown by its rapid liberation of iodine from potassium iodide in acetic acid; its high negative optical rotation suggested that it contained a 5 : 6-double bond. Controlled catalytic reduction gave in high yield crystalline 7α-hydroxycholesterol; the product is therefore not the hydroxy-ketone (II), but 7α-hydroperoxycholesterol (III).

We believe this rearrangement to be the first example of an allylic rearrangement of an αβ-unsaturated hydroperoxide, and the nature of the change, together with the apparently complete retention of the α-configuration during it, suggests that it takes place through a cyclic 5-membered transition state (IV). This mechanism does not, however, explain the function of the solvent in the reaction. The chloroform used was free from hydrogen chloride, and the reaction did not take place in benzene, methanol, pyridine, or tetrahydrofuran, nor in the latter solvent containing toluene-*p*-sulphonic acid.



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

Professor Schenck has kindly informed us that similar results have also been obtained in his laboratory, and that the allylic rearrangement of (I) has been shown to be an example of a general phenomenon. His results will be published elsewhere.

Experimental.—*7α-Hydroperoxycholesterol.* A suspension of 5α-hydroperoxycholest-6-en-3β-ol [3] (4·6 g.) in chloroform (100 c.c.) was set aside at room temperature for 24 hr. with occasional shaking. Evaporation of the clear solution and crystallisation of the residue from ethyl acetate–light petroleum (b. p. 40—60°) gave *7α-hydroperoxycholesterol* (3·9 g.) as needles, m. p. 154—155° (decomp.), $[\alpha]_D^{17}$ −131° (*c*, 0·8 in pyridine) (Found: C, 77·3; H, 10·9. $C_{27}H_{46}O_3$ requires C, 77·5; H, 11·1%).

7α-Hydroxycholesterol. A solution of 7α-hydroperoxycholesterol (1 g.) in ethanol (60 c.c.) was shaken with palladium–charcoal and hydrogen at room temperature and pressure until 1·0 mol. of hydrogen had been absorbed. Filtration, evaporation of the filtrate, and crystallisation of the residue from aqueous methanol gave 7α-hydroxycholesterol (0·9 g.) as needles, m. p. 183—184°, $[\alpha]_D^{17}$ −86° (*c*, 1·1 in chloroform) (lit. values,[4] m. p. 184—185°, $[\alpha]_D$ −86·4°).

[1] Schenck, *Angew. Chem.*, 1957, **69**, 579.
[2] Hock and Lang, *Ber.*, 1944, **77**, 259.
[3] Schenck, Gollnick, and Neumüller, *Annalen*, 1957, **603**, 46.
[4] Barr, Heilbron, Parry, and Spring, *J.*, 1936, 1437. For proof of the α-configuration see Heymann and Fieser, *Helv. Chim. Acta*, 1952, **35**, 631.

Acetylation with pyridine–acetic anhydride gave the diacetate, m. p. (from ethanol) 121·5—122·5°, $[\alpha]_D^{17}$ −174° (*c*, 0·9 in chloroform) (lit. values,[4] m. p. 121—122°, $[\alpha]_D$ −174·6°) (Found: C, 76·4; H, 10·2. Calc. for $C_{31}H_{50}O_4$: C, 76·5; H, 10·3%).

THE UNIVERSITY, LEEDS 2. [*Received, July 24th*, 1958.]

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92 *Thermodynamics of the Hydrogen- and Hydroxy-complexes of Aluminium with Ethylenediaminetetra-acetic Acid.*

By T. RANDALL and L. A. K. STAVELEY.

IN a systematic study of the thermodynamics of the complexes of ethylenediaminetetra-acetic acid (EDTA) with tervalent metals, it was thought worthwhile to extend the measurements with aluminium to give information about the hydrogen complex $Al(H_2O)HY$ present at lower pH values and the hydroxy-complex $Al(OH)Y^{2-}$ present at higher pH values. We have therefore measured ΔH at 20° for the reactions:

$$Al(H_2O)HY \rightleftharpoons Al(H_2O)Y^- + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$Al(H_2O)Y^- \rightleftharpoons Al(OH)Y^{2-} + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where Y is the anion of EDTA. There seems little doubt that, in the normal complex, at least one water molecule is closely associated with the aluminium.[1]

The calorimeter used has already been described.[2] The thermal quantities measured were the following. (*a*) The heat change on addition of about a 10% excess of EDTA (approximately in the form of the tetrapotassium salt) to about one litre of a solution of aluminium nitrate (~0·01M) containing sufficient nitric acid to give the final solution of the complex the desired pH and sufficient potassium nitrate to make the final ionic strength 0·1. The pH of the aluminium nitrate solution before complex-formation never exceeded 3. In this way, complications due to hydrolysis of the aluminium ion were avoided. (*b*) The heat change on addition of the same amount of EDTA to a solution of the same volume as in (*a*) containing the same amount of nitric acid but lacking the aluminium nitrate. Sufficient potassium nitrate was again present to make the final ionic strength 0·1. The pH's of the final solutions in (*a*) and (*b*) were measured. Three sets of experiments were carried out, involving different amounts of nitric acid, such that the pH values of the final solution were 3·26, 4·93, and 7·44. Saito and Terrey [1] determined the equilibrium constants at 15° for reactions (1) and (2). Values at 20° (and hence also the derived ΔG values at this temperature) were estimated by using approximate figures for the associated changes in heat content. It was then possible to evaluate the amounts of the complexes $Al(H_2O)HY$, $Al(H_2O)Y^-$, and $Al(OH)Y^{2-}$ present in the final solutions at the different pH values, and so to estimate, not only the heat of formation of the normal complex, but also the changes in heat content for reactions (1) and (2).

The results were as follows: For reaction (1) at 20°, $\Delta H = +3{\cdot}9°$ kcal./mole, whence, since $\Delta G = +3{\cdot}97$ kcal./mole, $\Delta S = \sim 0$ e.u. For reaction (2) at 20°, $\Delta H = +5{\cdot}0$ kcal./mole, whence, since $\Delta G = +8{\cdot}21$ kcal./mole, $\Delta S = -10{\cdot}9$ e.u. The simplest view of the nature of the hydrogen complex is that in the normal complex one $\cdot CH_2 \cdot CO_2^-$ group is free and that the hydrogen complex is formed by the addition of a proton to this group. Reaction (1) above is then essentially the ionization of a carboxylic acid. Usually for the ionization of such an acid ΔH is between 0 and −1 kcal./mole and ΔS is about −20 e.u. That both ΔH and ΔS for reaction (1) are larger than these values may be because the

[1] Saito and Terrey, *J.*, 1956, 4701.
[2] Davies, Singer, and Staveley, *J.*, 1954, 2304; Care and Staveley, *J.*, 1956, 4571.

$\cdot CH_2 \cdot CO_2^-$ group in the normal complex is to some extent prevented by the rest of the complex from interacting as strongly with the water molecules as a simple carboxylate ion does. Another possibility for the hydrogen complex is that the proton is attached to a nitrogen atom. The high positive charge on the nearby aluminium ion could then account for the large drop from, say, the pK_2 of 9·78 for glycine to the value of 2·96 for the aluminium–hydrogen–EDTA complex. The ionization of a proton from a substituted ammonium ion is usually accompanied by a much larger increase in both heat content and entropy than is the ionization of a carboxylic acid, so that this possibility, although perhaps the less likely of the two, is also qualitatively consistent with the observed values of the thermodynamic parameters for the ionization.

For the normal ionization [3] of water at 25°, $\Delta G = 19{\cdot}1$ kcal./mole, $\Delta H = 13{\cdot}5$ kcal./mole and $\Delta S = -18{\cdot}7$ e.u. The much greater acidity of the water molecule in the EDTA complex is hence due partly to a decreased ΔH on ionization and to an increased ΔS. It would naturally be expected that the large charge on the aluminium ion would reduce the energy required for the expulsion of a proton from the adjacent water molecule, while the increased entropy change may arise primarily because the hydroxyl ion produced remains bound in the complex so that it cannot exert the ordering influence which it would have on surrounding water molecules if it were free.

We thank Imperial Chemical Industries Limited for financial assistance.

THE INORGANIC CHEMISTRY LABORATORY, OXFORD. [*Received, July 24th*, 1958.]

[3] Harned and Owen, " The Physical Chemistry of Electrolytic Solutions," 3rd edn., Reinhold Publ. Corp., New York, 1958, p. 667.

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93. *Synthesis of 5-Bromotryptophan and Some Derivatives.*

By D. G. HARVEY.

THE importance of *NN*-diethylbromolysergamide as an active antagonist to serotonin *in vivo* has stimulated interest in bromoindole derivatives. As Shaw and Woolley [1] have recognised the harman type of nucleus in serotonin antagonists it was desirable to prepare the 2-methyl-β-carbolinecarboxylic acid and corresponding carboline base derived from

Compound	Yield, %	Form	M. p.	Formula	Found, % C	Found, % H	Found, % N	Required, % C	Required, % H	Required, % N
5-Bromoindole	75—80	Plates	83°	C_8H_6NBr	49·5	3·2	6·7	48·9	3·1	7·1
5-Bromo-3-dimethylaminomethylindole (5-bromogramine)	65	Leaflets	162	$C_{11}H_{13}N_2Br$	55·5	5·3	10·7	52·1	5·1	11·1
Diethyl (5-bromo-3-indolylmethyl)formamidomalonate	90	Cubes or rhombs	141	$C_{17}H_{19}O_5N_2Br$	49·4	4·7	6·4	49·4	4·6	6·8
5-Bromotryptophan	66	Leaflets	251	$C_{11}H_{11}O_2N_2Br,2H_2O$	42·5	4·9	8·5	41·4	4·7	8·7
8-Bromo-2 : 3 : 4 : 5-tetrahydro-2-methyl-β-carboline-4-carboxylic acid	66	Needles	268	$C_{13}H_{13}O_2N_2Br,2H_2O$	45·4	4·6	7·7	45·2	4·9	7·9
8-Bromo-2-methyl-β-carboline	52	Needles	246	$C_{11}H_9N_2Br$	55·2	3·6	10·5	55·0	3·4	10·7

5-bromotryptophan and acetaldehyde. The syntheses of 5-bromotryptophan, 8-bromo-2 : 3 : 4 : 5-tetrahydro-2-methyl-β-carbolinecarboxylic acid, and 8-bromo-2-methyl-β-carbolin are now reported.

[1] Shaw and Woolley, *J. Biol. Chem.*, 1953, **203**, 69, 979.

Ethyl 5-bromoindole-2-carboxylate was prepared by cyclisation of ethyl pyruvate *p*-bromophenylhydrazone in polyphosphoric acid (cf. Rydon and Tweddle [2]). The indolecarboxylic acid itself, freed from traces of sulphate, was decarboxylated in good yield to 5-bromoindole by boiling quinoline and copper chromite.

Subsequent steps in the synthesis of the amino-acid and of the carbolines were identical with those used for the synthesis of 5-iodotryptophan; relevant details are summarised in the Table.

Experimental.—All m. p.s are uncorrected.

Ethyl pyruvate p-*bromophenylhydrazone.* This was prepared by esterification of pyruvic acid *p*-bromophenylhydrazone and by the Japp–Klingemann reaction of diazotised *p*-bromoaniline with ethyl α-acetylpropionate. The ester crystallised in very pale brown needles, m. p. 144° (Found: N, 10·0. Calc. for $C_{11}H_{13}O_2N_2Br$: N, 9·8%).

Ethyl 5-bromoindole-2-carboxylate. Ethyl pyruvate *p*-bromophenylhydrazone (35 g.) was well mixed with polyphosphoric acid (65 g. of phosphoric oxide and 40 g. of phosphoric acid). The mixture was warmed to 110—120°; the internal temperature rose sharply to 170° and was kept there for 5 min. It was then cooled to 70°, treated with water, and filtered. The *product* (28 g., 92%) formed needles, m. p. 162°, from ethanol (Found: C, 49·4; H, 3·8; N, 5·3. $C_{11}H_{10}O_2NBr$ requires C, 49·1; H, 3·7; N, 5·2%).

5-Bromoindole-2-carboxylic acid. The ester (28 g.) was hydrolysed [sodium hydroxide (28 g.), ethanol (280 ml.), and water (280 ml.)] for 1·5 hr. under reflux and then kept at room temperature overnight, then acidified. The *acid* formed rhombs (17 g., 68%), m. p. 248°, from alcohol (Found: C, 46·0; H, 2·7; N, 5·8. $C_9H_6O_2NBr$ requires C, 45·0; H, 2·5; N, 5·8%).

I am indebted to Miss L. Butula for valuable assistance.

DEPARTMENT OF PATHOLOGY, ROYAL VETERINARY COLLEGE,
LONDON, N.W.1. [*Received, July 31st,* 1958.]

[2] Rydon and Tweddle, *J.* (1955), 3499.
[3] Harvey, *J.*, 1958, 3760.

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94. *Nuclear Magnetic Resonance of* cis-trans-β-*Methylmuconic Acid.*

By J. A. ELVIDGE.

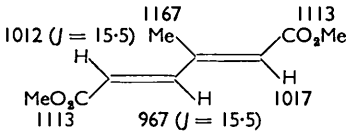
PREVIOUS work [1,2] established that the several routes to β-methylmuconic acid of m. p. *ca.* 170° gave the same material. This, on balance of evidence, was assigned the *cis-trans*-configuration. Reasons were given for rejecting the *cis-cis*-configuration which otherwise was suggested by the preparations from aromatic precursors [1] and particularly from β-methylmuconic anhydride.[2,3] A consequence [2] was that Karrer's first criticism [3] of the Pauling–Zechmeister theory of stereoisomerism in the carotenoids lost its basis. Nevertheless, this criticism was later upheld by the preparation of genuine examples of hindered *cis*-polyenes (*e.g.*, refs. 4, 5). Because of this, Gabers, Eugster, and Karrer wrote: [6] " Eine andere Ausnahme glaubten wir früher in der *cis-cis*-β-methylmuconsäure gefunden zu haben. Diese Substanz wurde dann aber von J. A. Elvidge, R. P. Linstead, and P. Sims als *cis-trans*-Verbindung gedeutet. Die Versuche von Linstead *et al.* sollen überprüft werden."

Reinvestigation of the β-methylmuconic acid in question has now unambiguously confirmed the *cis-trans*-configuration.

[1] Elvidge, Linstead, and Sims, *J.*, 1951, 3386.
[2] *Idem, ibid.*, p. 3398.
[3] Karrer, Schwyzer, and Neuwirth, *Helv. Chim. Acta*, 1948, **31**, 1210.
[4] Gabers, Eugster, and Karrer, *ibid.*, 1952, **35**, 1850.
[5] Oroshnik, Karmas, and Mebane, *J. Amer. Chem. Soc.*, 1952, **74**, 295.
[6] Ref. 4, p. 1858.

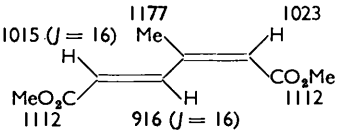
Jackman and Wiley [7] have found that nuclear magnetic resonance spectroscopy readily distinguishes between the *cis*- and *trans*-forms of trisubstituted olefins of the type $RR'C{:}CH{\cdot}CO_2Me$. Further, the method shows with certainty whether such an olefin is a mixture of the two geometrical isomers, provided one of the pure forms is available. Their method has now been extended.

There is no disagreement about an all *trans*-configuration for the high-melting β-methylmuconic acid, m. p. *ca.* 235° (decomp.). This can safely be taken as a reference compound. Its dimethyl ester gave a spectrum in carbon disulphide which showed the expected seven proton resonance lines. There were three singlets at 1167 (C–Me), 1113 (O–Me) and 1017 c./sec. $\left(=C\!<^{H}\right)$ and two doublets with weighted-mean positions at 1012 and 967 c./sec. The large splitting observed for the doublets (J = 15·5 c./sec.) identifies the two hydrogen atoms responsible as those arranged *trans* about an ethylenic link.[8] The interpretation of the resonance spectrum is unique; it is in agreement with the *trans-trans*-configuration and must be as shown in (I).



±1·0 c./sec.

(I)



±2·5 c./sec.

(II)

The results summarised earlier [1,2] showed that the lower-melting β-methylmuconic acid (m. p. *ca.* 170°) had at least one *cis*-arrangement. The possibilities were that it was the *cis-trans*- or less probably the *cis-cis*-isomer. That it might have been a molecular compound of two geometrical forms was not considered. Its dimethyl ester gave a spectrum in carbon disulphide which again showed only three singlets and two doublets. This proves that the compound is a single isomer and not a mixture or molecular compound. The singlet proton resonance lines were at 1177 (C–Me), 1112 (O–Me), and 1023 c./sec. $\left(=C\!<^{H}\right)$. The doublets had weighted-mean positions at 1015 and 916 c./sec. with J = 16 c./sec. so that the two hydrogen atoms responsible are again identified as those *trans* about a double bond. The large drop in weighted-mean frequency for one of the doublets, from 967 in the all-*trans*-isomer to 916 c./sec., indicates that the hydrogen atom responsible is now in a hindered position in the second isomer. Moreover, the C–Me proton resonance, occurring at 10 c./sec. *higher* frequency (1177) than in the all-*trans*-compound (1167 c./sec.) must now be *trans* to methoxycarbonyl, rather than *cis* as in (I).

Again, the interpretation is unique and indicates the *cis-trans*-geometrical form (II) for the lower-melting β-methylmuconate and so for the acid. Karrer's contention that this β-methylmuconic acid, derivable from β-methylmuconic anhydride, has the all-*cis*-configuration [3,4] is therefore incorrect.

The opportunity is taken to correct the ultraviolet absorption data previously given [1] for the two β-methylmuconic acids and ten derivatives. Each of these compounds has a single, rather broad maximum at 264—266 mμ so that the subsidiary inflexions and peaks (on p. 3389, ref. 1) should be deleted. The reason for such mis-readings has been discussed.[9]

[7] Jackman and Wiley, *Proc. Chem. Soc.*, 1958, 196; in last line, 2nd para., for "*cis*" read "*trans*".
[8] Pople, "Applications of Electron and Nuclear Resonance in Chemistry," *Chem. Soc. Special Publ.*, No. 12, 1958, p. 211.
[9] Allan, Jones, and Whiting, *J.*, 1955, 1862.

Experimental.—*trans-trans*-β-Methylmuconic acid was prepared from 4-methyl*cyclo*hexanol as before [1] except that the crude dark product was extracted with dry ether in a Soxhlet apparatus. The acid then formed tiny colourless crystals, m. p. 235° (decomp.). This was converted by brief treatment with ethereal diazomethane, filtration, and evaporation into the dimethyl ester which crystallised from light petroleum (b. p. 40—60°) as needles, m. p. 57° (Found: C, 58·7; H, 6·5. Calc. for $C_9H_{12}O_4$: C, 58·7; H, 6·6%).

cis-trans-β-Methylmuconic acid,[1,2] m. p. 171° (decomp.), was similarly esterified to give in near-quantitative yield the dimethyl ester which formed needles, m. p. 38°, from light petroleum (b. p. 40—60°) or carbon tetrachloride at 0° (Found: C, 58·6; H, 6·6%).

The proton magnetic resonance data were obtained with a Varian Associates nuclear magnetic resonance spectrometer with a 40 megacycle oscillator. The spectra were calibrated against tetramethylsilane as an internal reference.[10] Tetramethylsilane at infinite dilution in carbon tetrachloride gives a signal at 1257 cycles per second relative to the aromatic C–H line of external toluene, which is given the arbitrary value of 1000 c./sec.

I am very grateful to Dr. L. M. Jackman of this Department for his help with the nuclear magnetic resonance spectra.

Chemistry Department, Imperial College of Science and Technology,
London, S.W.7. [*Received, September 8th*, 1958.]

[10] Van Dyke Tiers, "Proton Nuclear Spin Resonance Spectroscopy; Reliable Shielding Values by Internal Referencing with Tetramethylsilane," read at 133rd National Meeting of the Amer. Chem. Soc., San Francisco, April 13—18th, 1958; *J. Phys. Chem.*, 1958, **62**, 1151.

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95. *Preparation of Symmetrically Substituted Deoxybenzoins.*

By P. H. Carter, J. Cymerman Craig, (Miss) Ruth E. Lack, and M. Moyle.

The synthesis of deoxybenzoins from phenylacetyl chloride and benzene has been described;[1] however, direct reduction of the readily accessible benzoin provides a more convenient preparation of symmetrically substituted deoxybenzoins. Reduction of benzoin by zinc dust and acetic acid has been reported,[2] and other procedures employed hydrochloric acid and granulated tin [3] (the only detailed instance [4] affording 48·5% of deoxypiperoin), or amalgamated powdered tin [5] (giving 70% of deoxybenzoin, raised to 88% by distillation of the mother-liquors). We record the following observations on this reduction:

Best results were obtained by using powdered tin of 100—200 mesh size. Tin coarser than this left unchanged benzoin, while finer metal tended to conglomerate and give lower yields. The use of amalgamated tin did not enhance yields. A reflux period of 24 hours was optimal. Reduction in the amounts of either tin or acid lowered the yields. Under the conditions defined above, yields of 93·5% of deoxyanisoin, 89% of deoxypiperoin, and 84% of deoxybenzoin were obtained in one step, without the need for distillation of the product.

Experimental.—*Deoxyanisoin.* Anisoin (52 g., 0·19 mole) and 10N-hydrochloric acid (52 c.c.) were added to powdered tin (40 g., 0·33 mole; 100—200 mesh) and 95% ethanol (60 c.c.), and the mixture was refluxed for 24 hr. The boiling solution was decanted from undissolved tin, cooled to 0°, and filtered. The boiling filtrate was used to wash the tin, and

[1] Allen and Barker, *Org. Synth.*, 1943, Coll. Vol. II, p. 156.
[2] Kohler and Nygaard, *J. Amer. Chem. Soc.*, 1930, **52**, 4133.
[3] Buck and Jenkins, *ibid.*, 1929, **51**, 2163.
[4] Allen and Buck, *ibid.*, 1930, **52**, 310.
[5] Ballard and Dehn, *ibid.*, 1932, **54**, 3970.

the washings were cooled to 0° and filtered. Recrystallisation of the combined solids from 95% ethanol (450 c.c.) gave deoxyanisoin (46 g., 93·5%), m. p. and mixed m. p. 109—110°. A mixed m. p. with anisoin was 92—95°.

Deoxybenzoin. Benzoin (53 g., 0·25 mole), 10N-hydrochloric acid (53 c.c.), tin (53 g., 0·445 mole), and 95% ethanol (50 c.c.) gave deoxybenzoin (84%), m. p. and mixed m. p. 56—58°.

Deoxypiperoin. Piperoin (14·25 g., 0·048 mole), 10N-hydrochloric acid (13 c.c.), tin (10 g., 0·082 mole), and 95% ethanol (30 c.c.) afforded deoxypiperoin (89%), m. p. and mixed m. p. 112—114°. A mixed m. p. with piperoin was 90—95°.

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N.S.W., AUSTRALIA. [*Received, September 15th*, 1958.]

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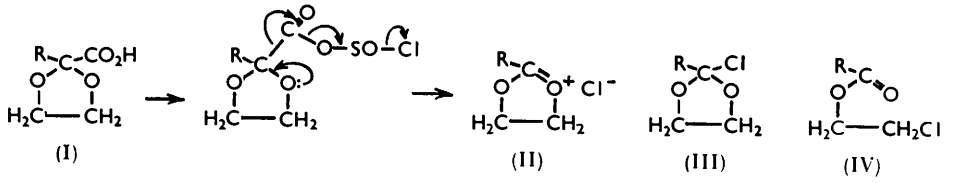
96. *The Action of Thionyl Chloride on 2-Methyl- and 2-Ethyl-1 : 3-dioxolan-2-carboxylic Acid.**

By R. P. A. SNEEDEN.

SCHINZ and VOGEL [1] recorded the isolation of a compound $C_5H_9O_2Cl$ after reaction of thionyl chloride with 2-ethyl-1 : 3-dioxolan-2-carboxylic acid (I; R = Et), and from its conversion by boiling water into propionic acid and its other reactions suggested that it was 2-chloro-2-ethyl-1 : 3-dioxolan (III; R = Et); they comment that its reactivity is between that of an acid chloride and an alkyl halide.



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

Because of the many potential uses of this type of substance an attempt was made to prepare the analogous compound from the 2-methyl-acid (I; R = Me). This gave a chloro-compound, whose homogeneity was established by distillation and a comparison of the infrared spectra of arbitrary fractions: bands at 1740, 1075, 1040, and 660 cm.$^{-1}$ indicated the presence of an ester and a C–Cl group. Consideration of the probable reaction sequence indicates that the initial product would be the oxonium chloride (II). The formation of compound (III; R = Me) (as indicated by Schinz and Vogel's work [1]) would involve formation, without rearrangement, of a C–Cl bond from (II). However, in accordance with the reactions of keten ketals [2] the oxonium ion of (II) should undergo rearrangement to 2-chloroethyl acetate (IV; R = Me). Indeed the reaction product was this compound.

Re-investigation of the action of thionyl chloride on 2-ethyl-1 : 3-dioxolan-2-carboxylic acid (I; R = Et) then showed that the product was the expected 2-chloroethyl propionate (IV; R = Et).

* Submitted in part to the XVIth Internat. Congress Pure Appl. Chem., Paris, 1957.

[1] Schinz and Vogel, *Helv. Chim. Acta*, 1950, **33**, 116.
[2] McElvain and Aldridge, *J. Amer. Chem. Soc.*, 1953, **75**, 3993.

Experimental.—*2-Methyl-1 : 3-dioxolan-2-carboxylic acid.* The ethylene ketal [3] of ethyl pyruvate (7·65 g.; b. p. 84—89°/17 mm., n_D^{17} 1·4250) was added with cooling to potassium hydroxide (4·05 g.) in water (5·05 c.c.). Concentrated hydrochloric acid (7·0 g.) was added and the product isolated by continuous extraction with ether (15 hr.). Fractional distillation of the dried extract gave *2-methyl-1 : 3-dioxolan-2-carboxylic acid*, b. p. 127—130°/14 mm., n_D^{19} 1·4440 (Found: C, 45·6; H, 6·25. $C_5H_8O_4$ requires C, 45·45; H, 6·1%).

Action of thionyl chloride on the above acid. The acid (12·8 g.) was kept in pure thionyl chloride (7·5 c.c.) overnight. Fractional distillation then gave unchanged thionyl chloride and 2-chloroethyl acetate, b. p. 143°, n_D^{18} 1·4250 (lit., b. p. 143°, n_D^{18} 1·4252). The infrared spectra of this and an authentic specimen were superposable.

2-Ethyl-1 : 3-dioxolan-2-carboxylic acid. The ethylene ketal of ethyl α-oxobutyrate [3] (7·4 g.; b. p. 150—160°/32 mm., n_D^{17} 1·4275) was hydrolysed as described above. The product, on distillation, gave 2-ethyl-1 : 3-dioxolan-2-carboxylic acid, b. p. 160—165°/34 mm., $n_D^{17\cdot5}$ 1·4530.

This acid (1 g.), treated with thionyl chloride as described, gave 2-chloroethyl propionate, b. p. 80—85°/60 mm., n_D^{14} 1·4320 (lit., b. p. 80—85°/60 mm., n_D^{14} 1·4322). The infrared spectra of this and an authentic specimen were superposable.

THE UNIVERSITY, GLASGOW. [*Received, September 19th*, 1958.]

[3] Kuhn, *J. prakt. Chem.*, 1940, **156**, 143.

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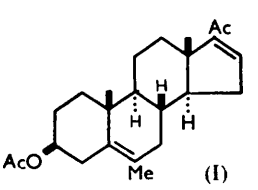
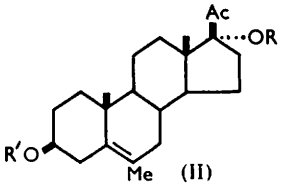
97. *Preparation of 17α-Acetoxy-6α-methylprogesterone.*

By (MISS) S. P. BARTON, B. ELLIS, and V. PETROW.

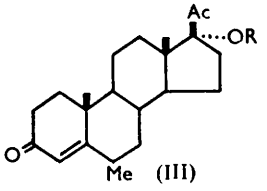
TREATMENT of 3β-acetoxy-6-methylpregna-5 : 16-dien-20-one [1] (I) with alkaline hydrogen peroxide gave 16α : 17α-epoxy-3β-hydroxy-6-methylpregn-5-en-20-one, converted by hydrogen iodide and subsequent dehalogenation into 3β : 17α-dihydroxy-6-methylpregn-5-en-20-one (II; R = R′ = H). Drastic acetylation [2] furnished the 3β : 17α-diacetate (II;



(I)



(II)



(III)

R = R′ = Ac), which passed into 17α-acetoxy-3β-hydroxy-6-methylpregn-5-en-20-one (II; R = Ac, R′ = H) with alcoholic hydrochloric acid. Oppenauer oxidation then gave 17α-acetoxy-6α-methylprogesterone (III; R = Ac), a highly active progestational agent independently prepared by Babcock *et al.*[3]. Careful alkaline hydrolysis [4] of the monoacetate gave 17α-hydroxy-6α-methylprogesterone (III; R = H). Other 17α-acyl derivatives can be similarly prepared.

Experimental—Optical rotations were measured in chloroform solutions in a 1-dm. tube. The ultraviolet absorption spectrum (in ethyl alcohol) was kindly determined by Mr. M. T. Davies, B.Sc.

[1] Burn, Ellis, Petrow, (Mrs.) Stuart-Webb, and Williamson, *J.*, 1957, 4092.
[2] Cf. Turner, *J. Amer. Chem. Soc.*, 1953, **75**, 3489.
[3] Babcock, Gutsell, Herr, Hogg, Stuki, Barnes, and Dulin, *J. Amer. Chem. Soc.*, 1958, **80**, 2904; cf. Cooley, Ellis, Kirk, and Petrow, *J.*, 1957, 4112.
[4] Ringold, Löken, Rosenkranz, and Sondheimer, *J. Amer. Chem. Soc.*, 1956, **78**, 816.

16 : 17α-*Epoxy*-3β-*hydroxy*-6-*methylpregn*-5-*en*-20-*one*. 3β-Acetoxy-6-methylpregna-5 : 16-dien-20-one [1] (20 g.) in boiling methanol (250 ml.) was treated with aqueous sodium hydroxide (40%; 40 ml.), followed immediately by hydrogen peroxide (30%; 40 ml.) added dropwise during 5 min. The mixture was refluxed for 20 min. and then poured into water, and the solids were collected and purified from aqueous ethanol. The *epoxide hydrate* formed plates, m. p. 180—182°, $[\alpha]_D^{23}$ −8° (*c* 0·94) (Found: C, 72·8, 72·8; H, 9·4, 9·3. $C_{22}H_{32}O_3,H_2O$ requires C, 72·9; H, 9·45%). The *anhydrous compound* (Found: C, 76·2; H, 9·2. $C_{22}H_{32}O_3$ requires C, 76·7; H, 9·4%) was obtained by heating the hydrate *in vacuo* at 150°. The 3β-*acetate* separated in needles (from acetone–hexane), m. p. 136—137°, $[\alpha]_D^{24}$ −18° (*c* 0·25) (Found: C, 74·1; H, 8·8. $C_{24}H_{34}O_4$ requires C, 74·6; H, 8·8%).

3β : 17α-*Dihydroxy*-6-*methylpregn*-5-*en*-20-*one* (II; R = R′ = H). The 3β-hydroxy-steroid (12 g.) in dioxan (400 ml.) was treated for 30 min. with aqueous hydrogen iodide (55%; 84 ml.). The mixture was poured into water (3 l.), and the precipitate collected and washed until neutral. Its solution in ethanol (500 ml.) was mechanically shaken for 30 min. with Raney nickel (120 g. of sludge), the nickel filtered off and the filtrate taken to dryness under reduced pressure. Trituration of the residue with ether gave a solid which was purified from acetone–hexane. 3β : 17α-*Dihydroxy*-6-*methylpregn*-5-*en*-20-*one hydrate* separated in needles, m. p. 221—222°, $[\alpha]_D^{22}$ −85° (*c* 0·95) (Found: C, 72·8; H, 10·0. $C_{22}H_{34}O_3,H_2O$ requires C, 72·5; H, 10·0%). The *anhydrous compound* (Found: C, 76·1; H, 9·7. $C_{22}H_{34}O_3$ requires C, 76·3; H, 9·9%) was obtained from the hydrate *in vacuo* at 150°.

3β : 17α-*Diacetoxy*-6-*methylpregn*-5-*en*-20-*one* (II; R = R′ = Ac), formed by treating the foregoing compound (5 g.) with acetic anhydride (50 ml.) and toluene-*p*-sulphonic acid (1 g.) for 24 hr. at room temperature, crystallised from aqueous methanol in needles, m. p. 187—188°, $[\alpha]_D^{26}$ −76° (*c* 1·14) (Found: C, 72·4; H, 9·1. $C_{26}H_{38}O_5$ requires C, 72·5; H, 8·9%).

17α-*Acetoxy*-3β-*hydroxy*-6-*methylpregn*-5-*en*-20-*one* (II; R = Ac, R′ = H), formed by heating the diacetate (10 g.) under reflux with methanol (300 ml.) and concentrated hydrochloric acid (2 ml.) for 1½ hr., crystallised from acetone–hexane in needles, m. p. 219—222°, $[\alpha]_D^{22}$ −72° (*c* 0·92) (Found: C, 74·6; H, 9·3. $C_{24}H_{36}O_4$ requires C, 74·2; H, 9·3%).

17α-*Acetoxy*-6α-*methylprogesterone* (III; R = Ac). A solution of the foregoing compound (7·5 g.) in toluene (300 ml.) and *cyclo*hexanone (70 ml.) was distilled until 75 ml. of distillate had collected. After the addition of aluminium *iso*propoxide (3·5 g.) in toluene (100 ml.), the mixture was refluxed for 1 hr., cooled, and treated with excess of aqueous Rochelle salt. The solvents were removed by steam-distillation, and the solid obtained was crystallised from aqueous acetone. 17α-Acetoxy-6α-methylprogesterone formed needles, m. p. 205—208°, $[\alpha]_D^{21}$ +51° (*c* 1·2), $\lambda_{max.}$ 239 mμ (log ε 4·19) (Found: C, 74·3; H, 9·0. Calc. for $C_{24}H_{34}O_4$: C, 74·6; H, 8·9%). Babcock *et al.*[3] give m. p. 205—209°, $[\alpha]_D$ +56°, $\lambda_{max.}$ 240 mμ (log ε 4·20).

17α-*Hydroxy*-6α-*methylprogesterone* (III; R = H). To a refluxing solution of the acetate (3·7 g.) in methanol (100 ml.), there was added, under nitrogen, potassium hydroxide (700 mg.) in methanol (15 ml.) and water (3 ml.), introduced dropwise during 45 min. The mixture was refluxed for a further 2 hr. and then acidified with acetic acid, and water was added to the point of crystallisation. The product was purified from acetone–hexane, giving 17α-hydroxy-6α-methylprogesterone as needles, m. p. 220—223°, $[\alpha]_D^{22}$ +78° (*c* 1·04) (Found: C, 76·7; H, 9·4. Calc. for $C_{22}H_{32}O_3$: C, 76·7; H, 9·4%). The compound occasionally separated in a second form, m. p. *ca.* 264°, which, however, reverted to the lower-melting variety on storage for several days at room temperature. Babcock *et al.*[3] give m. p. 220—223·5°, $[\alpha]_D$ +75°.

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98. 11-*Ethoxy*-1 : 2 : 3 : 4 : 10 : 11-*hexahydrofluoren*-1-*one. A Correction.*

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Some time ago we described the cyclisation of γ-1-(or -3)-indenylbutyronitrile [1] by means of sulphuric acid in ethanol to a compound to which we assigned the structure 11-ethoxy-1 : 2 : 3 : 4 : 10 : 11-hexahydrofluoren-1-one. The evidence for this was the analysis of the compound for carbon and hydrogen, and the fact that it gave 1 : 2 : 3 : 4-tetrahydrofluoren-1-one dinitrophenylhydrazone. We now find that the compound contains nitrogen. The analysis corresponds to that expected for 1 : 2 : 3 : 4 : 10 : 11-*hexahydro*-10-(or -11)-*hydroxy*-1-*iminofluorene*, possible products from the internal attack of the protonated cyano-group on the indenyl double bond, followed by the addition of hydroxyl ion (Found: C, 77·4, 78·1; H, 7·5, 7·8; N, 7·0. $C_{13}H_{15}ON$ requires C, 77·6; H, 7·5; N, 7·0%).

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[1] Howell and Taylor, *J.*, 1957, 3011.