359. *Fatty Acids of the Seed Fat of* Pongamia glabra.

By S. P. Pathak and L. M. Dey.

The seed fat of *Pongamia glabra* (family Papilionaceae, order Leguminosae) contains about 40% of oil. This has been examined by Desai *et al.*,[1] by Gupta and Mitra,[2] and again by us. The contents of various component fatty acids are shown in the Table. Our results

	Whole fat			Excluding unesterifiable matter			
Acid	Group *A* (% w/w)	Group *B* (% w/w)	Total (% w/w)	Total (mol. %)	Total (% w/w)	Ref. 1 (% w/w)	Ref. 2 (% w/w)
Myristic	—	—	—	—	—	—	1·6
Palmitic	6·2	0·1	6·3	7·1	6·3	6·6	7·9
Stearic	8·0	0·9	8·9	9·1	8·9	2·4	3·7
Arachidic	2·2	—	2·2	2·0	2·2	4·7	2·5
Behenic	5·3	—	5·3	4·5	5·3	—	4·2
Lignoceric	2·0	—	2·0	1·5	2·0	3·5	1·1
Hexadecanoic	0·4	0·2	0·6	0·7	0·6	—	—
Oleic	1·3	44·9	46·2	47·3	46·5	71·3	6·2·1
Linoleic	—	18·1	18·1	18·6	18·2	10·8	11·9
Linolenic	—	—	—	—	—	—	5·0
Eicosenoic	0·3	9·2	9·5	8·9	9·6	—	—
C_{22} (− 2H)	0·2	—	0·2	0·2	0·2	—	—
C_{24} (− 2H)	0·2	—	0·2	0·1	0·2	—	—
Unsaponifiable	0·1	0·4	0·5	—	—	—	—
Total saturated					17·9	24·7	21·0
Total unsaturated					82·1	75·3	79·0

are in broad agreement with those already reported [1,2] of the saturated acids; behenic acid was not found by Desai *et al.*, but Gupta and Mitra, like us, have found it, and it was also isolated by Manjunath and Rao.[3] Among the unsaturated acids, linolenic acid was reported by Gupta and Mitra, but not by Desai *et al.* or us, and eicosenoic, docosenoic, and tetracosenoic acids, which were not found by the previous authors, were found by us.

The results are in line with those from other members of the Family. Eicosenoic acid has been reported (2—9%) in fats from *Macadamia ternifolia*,[4] *Nephelium lappaccum*,[5] *Corchorus capsularis*,[6] and *Erythrina christogalli*.[7]

Experimental. The oil was extracted from the kernels, of which it formed 39·4%, with hot acetone. Its acid value was 2·1, saponification equivalent 289·3, and iodine value 79·4. It was esterified, unsaponifiable matter was removed, and the acids recovered as usual. The mixed acids were resolved by the modified Twitchell lead-salt method [8] into two groups: *A* (26·2%), mainly solid (iodine value 8·2), and *B* (73·8%), mainly liquid (iodine value 109·6).

Each group was separately converted into the methyl esters, and fractionated in an efficient electrically heated column at 0·1 mm., the saponification equivalent and iodine value of each fraction being determined. The composition of the fat was determined by Hilditch's method.[9] The absence of linolenic acid was established by the hexabromide test. The results are contained in the Table.

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[*Received, January 4th*, 1955.]

[1] Desai, Sudborough, and Watson, *J. Indian Inst. Sci.*, 1923, **6**, 93.
[2] Gupta and Mitra, *J. Indian Chem. Soc.*, 1953, **30**, 781.
[3] Manjunath and Rao, *ibid.*, 1938, **15**, 653.
[4] Bridge and Hilditch, *J.*, 1950, 2396.
[5] Hilditch and Stainsby, *J. Soc. Chem. Ind.*, 1934, **53**, 197 T.
[6] Meara and Sen, *J. Sci. Food Agric.*, 1952, **5**, 237.
[7] Cataneo, *Anal. Asoc. quím. argentina*, 1945, **33**, 5.
[8] Hilditch, "The chemical composition of natural fats," Chapman and Hall, London, 2nd edn., 1947, p. 468.
[9] Hilditch, ref. 8, pp. 505—510.

360. *Preparation of Glycol Monoesters of Fatty Acids with the Use of Boron Intermediates.*

By L. HARTMAN.

THE preparation of ethylene glycol monoesters of fatty acids has recently received renewed attention owing to a disagreement on the best method of avoiding diester formation. Verkade and his co-workers [1] prepared pure monoesters by protecting one hydroxyl group of the glycol with the triphenylmethyl group which was removed after acylation. Baer [2] suggested, however, that direct acylation of the glycol in an appropriate solvent mixture is preferable since the triphenylmethyl compound tends to contaminate the final product, which was denied by van Gijzen and Verkade.[3] In view of this controversy Bevan, Malkin, and Smith [4] worked out a procedure based on the acylation of ethylene iodohydrin followed by refluxing of the iodoethyl ester with alcoholic silver nitrite, whereby iodine is replaced by hydroxyl.

All these methods require thorough purification of reagents and anhydrous conditions owing to the use of acid chlorides. In comparison, Hilditch and Rigg's method [5] of direct esterification of fatty acids with a large excess of glycol (up to 10 mol.) in phenol solution is much simpler. Unfortunately phenol apparently enters into the reaction, which would explain the low melting points recorded by Hilditch and Rigg for their products. The search for an alternative method led to the selection of tri-(2-hydroxyethyl) orthoborate $B(O\cdot CH_2\cdot CH_2\cdot OH)_3$ as an intermediate in the synthesis of monoesters. The preparation of this orthoborate from ethylene glycol and boron trichloride [6] is inconvenient, but it was found that heating boric acid with 3 mols of the glycol *in vacuo* at 80—90° gave a product of sufficient purity. Fatty acids were soluble in, and reacted readily with, this borate at 100° in the presence of toluene-*p*-sulphonic acid. The resulting mixed ester yielded, on hydrolysis with water, the 2-hydroxyethyl ester of the fatty acid. Although some free glycol was probably present in the product of the reaction between boric acid and ethylene glycol, very little fatty-acid diester was formed, owing to the preferential esterification of the orthoborate. It was even found that despite the use of a large excess (3·3 mols.) of borate, the esterification led almost exclusively to $B(O\cdot CH_2\cdot CH_2\cdot O\cdot OC\cdot R)_3$ instead of the expected mixture of mono-, di-, and tri-esters. An excess of borate was needed to reduce the time and temperature of the reaction. Temperatures above 100° resulted in appreciable formation of the diester.

A similar procedure was tried for the preparation of monoglycerides, but proved unsuccessful owing to the complexity of the reaction between glycerol and boric acid.

Experimental.—Materials. Commercial decanoic, lauric, myristic, palmitic, and stearic acid were purified by fractional distillation of their methyl esters and crystallisation. Good-quality ethylene glycol and boric acid of analytical-reagent grade were used.

Tri-(2-hydroxyethyl) orthoborate. Ethylene glycol (12·4 g., 0·2 mole) and boric acid (4·1 g., 0·066 mole) were heated on a water-bath *in vacuo* at 80—90° until evolution of water ceased (10 min.; loss of wt., 3·7 g.; calc., 3·6 g.). The product was a viscous liquid which solidified overnight; it was soluble after melting in chloroform but insoluble in ethyl ether and hydrocarbons. Its boron content was determined by boiling a sample with water under reflux for a few minutes and titrating the boric acid with 0·1N-sodium hydroxide in the presence of mannitol (phenolphthalein) (Found: B, 5·5. Calc. for $C_6H_{15}O_6B$: B, 5·6%). However, the product was not pure. Extraction with a mixture of anhydrous ethyl ether and methyl acetate yielded a liquid fraction containing 0·94% of boron whereas digestion with absolute

[1] Verkade, Tollenaar, and Posthumus, *Rec. Trav. chim.*, 1942, **61**, 373.
[2] Baer, *J. Amer. Chem. Soc.*, 1953, **75**, 5533.
[3] Van Gijzen and Verkade, *Rec. Trav. chim.*, 1954, **73**, 496.
[4] Bevan, Malkin, and Smith, *J.*, 1955, 1043.
[5] Hilditch and Rigg, *J.*, 1935, 1774.
[6] Councler, *Ber.*, 1878, **11**, 1106.

ethanol gave a solid residue containing 10·3% of boron. On the other hand, the infrared absorption spectra of the product and of tri-(2-hydroxyethyl) borate prepared from the glycol and an excess of boron trichloride [6] agreed fairly well and there was no indication of absorption characteristic of free boric acid. (The absorption spectra were scanned over the region 4000—650 cm.$^{-1}$ with a Perkin-Elmer model 21 infrared spectrophotometer.) Thus it could be assumed that the product was essentially the borate $B(O{\cdot}CH_2{\cdot}CH_2{\cdot}OH)_3$ containing some free glycol and diborate $B(O{\cdot}CH_2{\cdot}CH_2{\cdot}O)_3B$ (calc. for $C_6H_{12}O_6B_2$: B, 10·7%).

Glycol monopalmitate and other monoesters. Palmitic acid (5·1 g, 0·02 mole) and toluene-*p*-sulphonic acid (0·2 g.) were dissolved in warm tri-(2-hydroxyethyl) borate (12·8 g., 0·066 mole; freshly prepared) and heated on a boiling-water bath for 1 hr. *in vacuo*. The product was swirled with water (50 ml.) to hydrolyse the palmito-boric ester, and the monopalmitate extracted with warm light petroleum (b. p. 40—60°). On cooling, the petroleum extract gave colourless plates of 2-hydroxyethyl palmitate (5 g., 80%), m. p. 52—53° (lit., 52—53°) (Found : C, 72·0; H, 11·9. Calc. for $C_{18}H_{36}O_3$: C, 71·9; H, 12·0%).

Similarly were obtained the *decanoate*, m. p. 16—17° (Found : C, 66·4; H, 11·1. $C_{12}H_{24}O_3$ requires C, 66·7; H, 11·2%), laurate, m. p. 32—32·5° (lit., 31—32°) (Found : C, 68·7; H, 11·4. Calc. for $C_{14}H_{28}O_3$: C, 68·8; H, 11·5%), myristate, m. p. 42·5—43·5° (lit., 43—43·5°) (Found : C, 70·6; H, 11·8. Calc. for $C_{16}H_{32}O_3$: C, 70·5; H, 11·8%), and stearate, m. p. 60—61° (lit., 60—61°) (Found : C, 73·2; H, 12·0. Calc. for $C_{20}H_{40}O_3$: C, 73·1; H, 12·3%).

These monoesters can be also prepared in a single-stage process by heating all the ingredients *in vacuo* for 1 hr. at 90—100°. The danger of diester formation is not great since fatty acids and the glycol are not miscible at 100°, and the glycol reacts at this temperature much faster with boric acid than with fatty acids. However, the removal of water proceeds more smoothly in a two-stage reaction.

The mixed ester of boric and palmitic acid was isolated in a separate sample by extracting the mixture with light petroleum (b. p. 40—60°) in which the glycol and the borate are practically insoluble. From the petroleum solution a white semicrystalline substance was recovered which melted at 49—50° (3·15 g. from 2·56 g. of palmitic acid). This substance was dissolved in ethyl ether and washed three times with small portions of water to effect hydrolysis. Boric acid was determined in the aqueous extract by titration as above (Found : B, 1·3. Calc. for $B(O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}OC{\cdot}C_{15}H_{31})_3$: B, 1·2%). The yield calculated on this basis (3·02 g.) also agreed well with that obtained (3·15 g.). From the ethereal solution 2-hydroxyethyl palmitate, m. p. 52—53°, was recovered.

It was found that triglycol orthoborate can also be esterified with fatty acid chlorides in chloroform at room temperature by using pyridine or quinoline as catalyst. This procedure, however, has no advantage over esterification with fatty acids and is much more time-consuming. It could be used for steam-volatile fatty acids to avoid losses which would occur during heating *in vacuo*.

The infrared absorption spectra of the borates and boric acid were measured by Dr. B. Cleverley, of Dominion Laboratory, Department of Scientific and Industrial Research.

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361. *The Isolation of* 5-O-α-L-*Arabopyranosyl*-L-*arabinose from Partly Degraded Gums of* Virgilia *Species.*

By A. M. STEPHEN.

WHILE studying the acid hydrolysis of the polysaccharide gums obtained as exudates from the bark of *Virgilia oroboides* and of *V. divaricata* Adamson (the South African "Keurboom"; family, Leguminosae), it was observed that within a few hours of commencing hydrolysis of either gum with 0·01N-sulphuric acid at 95° there was produced, in addition to much arabinose and traces of rhamnose, galactose, and a number of oligosaccharides, a disaccharide whose rate of movement on paper chromatograms was just

slower than that of galactose. This substance showed a pink spot when the chromatogram was sprayed with aniline hydrogen oxalate or *p*-anisidine hydrochloride, and, on isolation and hydrolysis, gave L-arabinose only. There was maximum production of the disaccharide after about 5 hr., hydrolysis to arabinose occurring during the following 20 hr.

The disaccharide was isolated as a hygroscopic white powder,* $[\alpha]_D$ −14°, from *V. oroboides* gum after hydrolysis for 6 hr., followed by column chromatography on cellulose [1] (aqueous butanol as solvent) and elution from charcoal–Celite [2] (with 5% aqueous ethanol), a yield of about 4% being obtained. A phenylosazone (m. p. 200°; *M* 472, by its absorption [3] at 394 mμ) was prepared, and its oxidation with periodate by the method of Hough, Powell, and Woods [4] gave the 1 : 2-bisphenylhydrazone of mesoxalic dialdehyde, but no formaldehyde (result published by courtesy of Dr. L. Hough). The relatively slow hydrolysis of the disaccharide indicating a pyranosyl structure for the non-reducing unit, the compound appeared to be 5-*O*-α-L-arabopyranosyl-L-arabinose : the anomeric configuration follows from consideration of Hudson's rules.[5] Methylation of the disaccharide afforded a hexa-*O*-methyl derivative, $[\alpha]_D$ −16°, which on acid hydrolysis gave the expected equimolecular mixture of 2 : 3 : 4-tri-*O*-methyl-L-arabinose and 2 : 3-di-*O*-methyl-L-arabinose.

The new disaccharide is the third L-arabopyranosyl-L-arabinose to be reported : the β : 3-linked compound has been isolated after hydrolysis of a number of natural products [6-10] and after acid reversion of L-arabinose,[11] while more recently the β : 4-linked isomer has been shown (tentatively) to be a minor acid reversion product of L-arabinose.[12] In addition, 5-*O*-β-D-xylopyranosyl-L-arabinose has been detected among the hydrolysis products of peach and cholla gums,[7] and this differs from the disaccharide now reported only in the configuration of $C_{(4)}$ of the non-reducing end of the molecule.

It is improbable that the disaccharide produced from these two gums obtained from *Virgilia* spp. should be a reversion product, since the behaviour on acid hydrolysis of the gums, involving rapid splitting of a furanoside bond followed by gradual hydrolysis of the arabopyranosyl moiety of the resulting disaccharide, is fully consistent with a linkage in the gum through $C_{(5)}$ of an arabinose residue. Acid reversion of 5-*O*-α-L-arabopyranosyl-L-arabinose has in fact been brought about by evaporating a concentrated solution in the presence of acid : there was produced a polymer (*ca.* 6 arabinose residues; $[\alpha]_D$ −8°; immobile in the acid and basic chromatographic tanks), which when heated during 6 hr. with 0·01N-sulphuric acid released the disaccharide and no other product in observable quantity, apart from a trace of arabinose. Nevertheless, the gums must be hydrolysed after methylation to establish the mode of bonding of the arabinose residues.

Experimental.—Specific rotations were measured in water. The chromatographic tanks contained butan-1-ol–ethanol–water (4 : 1 : 5, upper layer), ethyl acetate–acetic acid–formic acid–water (18 : 3 : 1 : 4), and butan-1-ol–pyridine–water (9 : 2 : 2). R_{gal} and R_G values are relative to D-galactose and 2 : 3 : 4 : 6-tetra-*O*-methyl-D-glucose, respectively. Paper ionophoresis was carried out for 5 hr. at 700 V and 18 mA, in alkaline borate buffer; [13] the M_G value is relative to D-glucose.

* On being stored, the solid absorbed moisture and crystallised in elongated prisms with blunt ends.

[1] Hough, Jones, and Wadman, *J.*, 1949, 2511.
[2] Whistler and Durso, *J. Amer. Chem. Soc.*, 1950, **72**, 677.
[3] Barry, McCormick, and Mitchell, *J.*, 1955, 222.
[4] Hough, Powell, and Woods, *J.*, 1956, 4799.
[5] Hudson, *J. Amer. Chem. Soc.*, 1909, **31**, 66; 1916, **38**, 1566.
[6] Jones, *J.*, 1953, 1672.
[7] Andrews, Ball, and Jones, *J.*, 1953, 4090.
[8] Andrews and Jones, *J.*, 1954, 4134.
[9] *Idem*, *J.*, 1955, 583.
[10] Charlson, Nunn, and Stephen, *J.*, 1955, 1428.
[11] Ball, Jones, and Nicholson, Amer. Chem. Soc. Meeting, Minneapolis, Sept. 1955, Abs. Papers, 7*D*.
[12] Ball, Jones, Nicholson, and Painter, TAPPI, 1956, **39**, 438.
[13] Foster, *J.*, 1953, 982.

Isolation. *Virgilia oroboides* gum, collected at Kirstenbosch Botanical Gardens, Cape Town, in late summer (through the courtesy of Professor H. B. Rycroft), was dissolved in water and precipitated in the acid form by pouring an aqueous solution into 0·1N-ethanolic hydrochloric acid, then washed with ethanol and acetone, and dried. A portion of the mother liquors was neutralised and evaporated, yielding a negligible quantity of carbohydrate material which included galactose, arabinose, and numerous oligosaccharides. The gum acid (75 g.) was heated with 0·01N-sulphuric acid (1 l.) at 95° for 6 hr., the solution was cooled, neutralised ($BaCO_3$), and centrifuged, and then concentrated at 45° *in vacuo*. On pouring the clear liquid into excess of methanol, there was obtained the partly-degraded polysaccharide (as barium salt) together with a mixture of sugars in solution. The latter, after concentration to a syrup, was de-ionised with Amberlite resins IR-120(H) and IR-4B(OH) to give a syrup from which chromatographically pure L-arabinose (5·5 g.) crystallised rapidly (after one recrystallisation this had m. p. and mixed m. p. 155—156°, $[\alpha]_D^{20}$ +100°; benzoylhydrazone, m. p. 209°). The syrupy mixture, after removal of the arabinose, was passed through a succession of cellulose and charcoal–Celite columns, whereby more arabinose (9·4 g.), a number of oligosaccharides (1·0 g.), traces of rhamnose and galactose, and a disaccharide (3·3 g.) were separated. This disaccharide had $[\alpha]_D^{20}$ −14° (*c* 1·5); R_{gal} 0·85 (acid tank), 0·90 (basic tank), 0·92 (neutral tank); M_G 0·7; reducing power towards hypoiodite,[14] 0·5 of that of L-arabinose.

Phenylosazone of the disaccharide. On treatment in aqueous solution with phenylhydrazine and acetic acid for 3 hr. at 75°, the disaccharide formed a *phenylosazone* (bright-yellow, elongated prisms from aqueous ethanol), m. p. 198—200° (Kofler block) (Found: C, 55·1; H, 6·1. $C_{22}H_{28}O_7N_4,H_2O$ requires C, 55·2; H, 6·3%); $\lambda_{max.}$ in 95% ethanol: 256 (ε 19,150), 308 (ε 10,580), and 394 mμ (ε 19,840). No trace of L-arabinosazone, which might have been formed by cleavage, could be detected by circular paper chromatography.[15]

Methylation and hydrolysis. The disaccharide (1·04 g.) was methylated by Haworth's method, isolated by chloroform extraction, and then treated twice with Purdie's reagents; distillation of the *product* at 170°(bath)/0·05 mm. yielded a syrup (0·97 g.), n_D^{20} 1·4615, $[\alpha]_D^{20}$ −16° (*c* 4·6) (Found: OMe, 49·0. $C_{16}H_{30}O_9$ requires OMe, 50·8%). A portion (0·91 g.) was hydrolysed with N-hydrochloric acid (20 c.c.) on the boiling-water bath for 2 hr., during which time $[\alpha]_D$ rose rapidly to a final value of +104°. Neutralisation with silver carbonate, followed by removal of silver ion from the filtrate by hydrogen sulphide, filtration, and evaporation, yielded a mixture (0·88 g.) of two methylated sugars which were separated by cellulose-column chromatography, water-saturated butan-1-ol (3 parts) and light petroleum (b. p. 100—120°; 7 parts) being used. There were produced: (i) 2 : 3 : 4-tri-*O*-methyl-L-arabinose (0·43 g.), $[\alpha]_D^{20}$ +120° (*c* 0·86), R_G 0·75 (neutral tank) (Found: OMe, 47·0. Calc. for $C_8H_{16}O_5$: OMe, 48·4%), identified by conversion, after bromine oxidation, into the phenylhydrazide of 2 : 3 : 4-tri-*O*-methyl-L-arabonic acid, m. p. 158° (lit., m. p. 156°); and (ii) 2 : 3-di-*O*-methyl-L-arabinose (0·41 g.), $[\alpha]_D^{20}$ +107° (*c* 1·09), R_G 0·66 (neutral tank) (Found: OMe, 35·0. Calc. for $C_7H_{14}O_5$: OMe, 34·8%), which gave formaldehyde (dimedone derivative, m. p. and mixed m. p. 187—188°) in good yield on oxidation with periodate, and which after oxidation with bromine water was converted into the characteristic lactone, m. p. 36°, $[\alpha]_D^{20}$ −26° (*c* 2·44), and amide, m. p. and mixed m. p. 158—159°, of 2 : 3-di-*O*-methyl-L-arabonic acid (specimen kindly given by Dr. L. Hough).

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CHEMISTRY DEPARTMENT, UNIVERSITY OF EDINBURGH. [*Received, November 2nd,* 1956.]

[14] Hirst, Hough, and Jones, *J.*, 1949, 928.
[15] Barry and Mitchell, *J.*, 1954, 4020.

362. *A Simplified Preparation of 4-Benzoyloxycyclohexanol.*

By D. A. V. Dendy and D. A. H. Taylor.

4-Benzoyloxy*cyclo*hexanol is useful for the synthesis of alicyclic compounds. The best recorded preparation is that of Owen and Robins as modified by Jones and Sondheimer: [1] treating quinitol with benzoyl chloride under carefully controlled conditions gives a yield of about 60%, with much quinitol dibenzoate. In our hands this has proved cumbersome and sensitive to conditions, in some runs only the dibenzoate being obtained. Since a reaction under equilibrating conditions is the most suitable for this preparation, base-catalysed ester interchanges were investigated. Heating either ethyl benzoate and quinitol, or quinitol dibenzoate and ethanol, in the presence of sodium ethoxide gave mixtures containing 50—60% of quinitol monobenzoate. Although this yield is no higher than Jones and Sondheimer's, the method is quick and simple, and quinitol and its dibenzoate are readily recovered and recycled.

Experimental.—(*a*) Quinitol (189 g.; crude *cis–trans* mixture) and ethyl benzoate (240 g.), both dried by distillation, were added to a solution of sodium (100 mg.) in ethanol (50 ml.). The solution was then heated for ½ hr. (to distil out ethanol), during which the internal temperature was raised to 250°, then acidified with acetic acid and distilled in a vacuum. After a fore-run (mainly quinitol), 4-benzoyloxy*cyclo*hexanol (210 g., 53%) was collected at 180°/0·2 mm. The residue was quinitol dibenzoate.

The ethyl benzoate may be replaced by an equivalent amount of quinitol dibenzoate.

(*b*) Quinitol dibenzoate (165 g.) was added to a solution of sodium (100 mg.) in ethanol (31 ml.) and the whole refluxed for ½ hr., neutralised with acetic acid, and distilled in a vacuum. After a fore-run (quinitol and ethyl benzoate), 4-benzoyloxy*cyclo*hexanol (56 g., 48%) was collected.

University of Liverpool. [*Received, November 9th*, 1956.]

[1] Owen and Robins, *J.*, 1949, 320; Jones and Sondheimer, *J.*, 1949, 615.

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363. *Reactivity of the Carbonyl Group in Xanthones.*

By Neil Campbell, (Miss) Sheila R. McCallum, and Donald J. Mackenzie.

The reactions of γ-pyrones, chromones, etc., with hydroxylamine are sluggish although isolated examples of formation of oxime, and *p*-nitro- and 2 : 4-dinitro-phenylhydrazone are recorded.[1] Xanthone is stated not to form an oxime, phenylhydrazone, or semicarbazone,[2] but we have prepared an oxime and a 2 : 4-dinitrophenylhydrazone, the former by heating xanthone with hydroxylamine in pyridine.[3] Xanthone could not be converted directly into the phenylhydrazone, hydrazone, or semicarbazone, but the phenylhydrazone was obtained from the oxime. The oxime and the phenylhydrazone resembled the derivatives obtained from xanthione.[4]

We have confirmed that 2-chloro-7-methylxanthone-1-carboxylic acid reacts readily with phenylhydrazine to give a pyridazone (I; R = Cl, R′ = Me).[5] 2 : 3 : 4-Trichloro-7-methylxanthone-1-carboxylic acid under the same conditions, however, gives a product believed to be the phenylhydrazono-phenylhydrazone (II). Xanthone-1-carboxylic acid itself rapidly gives a pyridazone (I; R = R′ = H).

The carbonyl reactivity of xanthone is therefore enhanced when reaction is accompanied

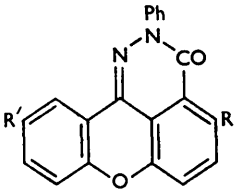
[1] Simonis and Rosenberg, *Ber.*, 1914, **47**, 1232; Bedeker *et al.*, *J. Indian Chem. Soc.*, 1935, **12**, 465; Wittig and Bangert, *Ber.*, 1925, **58**, 2636; Mozingo and Adkins, *J. Amer. Chem. Soc.*, 1938, **60**, 669; Baker, Marborne, and Ollis, *J.*, 1952, 1294.

[2] Speigler, *Ber.*, 1884, **17**, 807; Fosse, *Ann. Chim.*, 1916, **6**, 13.

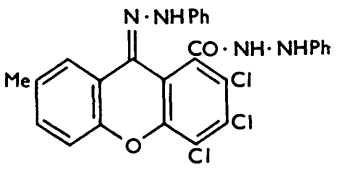
[3] Cf. Meisenheimer and Mahler, *Annalen*, 1934, **508**, 191.

[4] Graebe and Röder, *Ber.*, 1899, **32**, 1688; Mann and Turnbull, *J.*, 1951, 757.

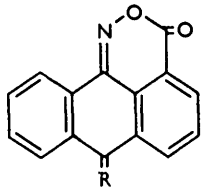
by ring-formation. In the anthraquinones also reaction with phenylhydrazine, etc., occurs readily only when a chloro-,[6] carboxyl-,[7] benzoyl-,[8] or amino-group[9] occupies the 1-position; a heterocyclic product is obtained in each case and attack occurs almost exclusively at the 9-carbonyl group. We find that merely heating (½ hr.) anthraquinone-1-carboxylic acid with phenylhydrazine and pyridine gives 2 : 3-dihydro-2-phenyl-3-oxo-1 : 2-diaza*meso*benzanthrone;[7] anthraquinone under these conditions is unchanged. The



(I)



(II)



(III)

acid is reported to react with hydroxylamine to give the oxazone (III; R = O);[7] if it is heated (4 hr.) with hydroxylamine and pyridine, the oxime (III; R = NOH) is obtained.

1-Chloro-4-methyl- and 4-chloro-1-methyl-thiaxanthone do not react with hydroxylamine in pyridine, but 2-methylthiaxanthone dioxide forms an oxime.

Experimental.—Xanthone derivatives. Xanthone (5 g.), hydroxylamine hydrochloride (25 g.), and pyridine (50 ml.) were boiled (24 hr.); pyridine (25 ml.) was then distilled off and the residue poured into water. The oxime was obtained in needles (from benzene), m. p. 161° (lit., 161°) (Found: C, 73·7; H, 4·3; N, 6·5. Calc. for $C_{13}H_9O_2N$: C, 73·9; H, 4·3; N, 6·6%). In sulphuric acid it gives a yellow solution with a blue fluorescence and when heated with hydrochloric acid yields xanthone. The oxime (1 g.) and phenylhydrazine (1 g.) were boiled (12 hr.) and then poured into water. The precipitate was washed with warm dilute hydrochloric acid and then with water, and was finally boiled in methanol. Xanthone phenylhydrazone remained as insoluble yellow needles (from acetic acid), m. p. 149—150° (lit., 152°) (Found: N, 10·1. Calc. for $C_{19}H_{14}ON_2$: N, 10·4%). The phenylhydrazone in concentrated sulphuric acid gives a dark green solution with a pale green fluorescence. Xanthone (2 g.), 2 : 4-dinitrophenylhydrazine (2 g.), concentrated sulphuric acid (4 ml.), and ethanol (30 ml.) were boiled (4 hr.). *Xanthone 2 : 4-dinitrophenylhydrazone* formed red crystals (from tetralin), m. p. 278° (Found: N, 15·2. $C_{19}H_{12}O_5N_4$ requires N, 14·9%).

2 : 3 : 4-Trichloro-7-methylxanthone-1-carboxylic acid (0·25 g.) and phenylhydrazine (2 ml.) were boiled (5 min.) and diluted with ethanol. The cold solution deposited the *phenylhydrazono-phenylhydrazone* (II), orange needles (from acetic acid), m. p. 316—319° (Found: C, 59·8; H, 3·0; N, 10·0; Cl, 20·0. $C_{27}H_{19}O_2N_4Cl_3$ requires C, 60·3; H, 3·5; N, 10·4; Cl, 19·7%).

Xanthone-1-carboxylic acid (0·1 g.) was boiled (5 min.) with phenylhydrazine (1 c.c.) and pyridine (5 c.c.), the mixture poured into water, and the resulting *pyridazone* crystallised from ethanol; it formed needles, m. p. 240° (decomp.) (Found: C, 76·4; H, 3·8; N, 9·1. $C_{20}H_{12}O_2N_2$ requires C, 76·9; H, 3·9; N, 9·0%). In the absence of pyridine, only nitrogen-free products were obtained.

Anthraquinone-1-carboxylic acid derivatives. Anthraquinone-1-carboxylic acid (0·5 g.), phenylhydrazine (3 c.c.), and pyridine (10 c.c.) were boiled (½ hr.) and cooled. The oxodiaza-*meso*benzanthrone crystallised from acetic acid in yellow needles, m. p. 298—299° (lit., 292°) (Found: C, 77·7; H, 3·8; N, 8·3. Calc. for $C_{21}H_{12}O_2N_2$: C, 77·8; H, 3·7; N, 8·6%).

The acid (1 g.), hydroxylamine hydrochloride (5 g.), and pyridine (25 c.c.) were boiled (4 hr.), the mixture poured into water, and the product crystallised from acetone–ethanol. The *hydroxyimino-oxazone* (III; R = NOH) separated in needles, m. p. 228—230° (decomp.) (Found: C, 68·1; H, 3·4; N, 11·0. $C_{15}H_8O_3N_2$ requires C, 68·2; H, 3·1; N, 10·6%).

[5] Knesebeck and Ullmann, *Ber.*, 1922, **55**, 306.
[6] Freund and Achenbach, *Ber.*, 1910, **43**, 3251.
[7] Ullmann and van der Schalk, *Annalen*, 1912, **388**, 212.
[8] Schaarschmidt, *Ber.*, 1915, **48**, 831; Waldmann and Oblath, *Ber.*, 1938, **71**, 366.
[9] Beilstein, "Handbuch der organischen Chemie," 1931, Vol. 14, 178.

2-Methylthiaxanthone dioxide oxime. The dioxide (2 g.), hydroxylamine hydrochloride (10 g.), and pyridine (25 c.c.) were boiled (4 hr.) and then poured into water. The oxime crystallised from aqueous acetone in yellow needles, m. p. 199—200° (Found: C, 61·9; H, 4·3; N, 5·4; S, 11·7. $C_{14}H_{11}O_3SN$ requires C, 61·5; H, 4·1; N, 5·1; S, 11·7%).

Thanks are expressed to Dr. O. Kruber for a sample of xanthone-1-carboxylic acid, Dr. T. M. Sharp for supplying thiaxanthones, Dr. S. Coffey for samples of thiaxanthone dioxides, and the British Petroleum Oil Co. Ltd. for a grant.

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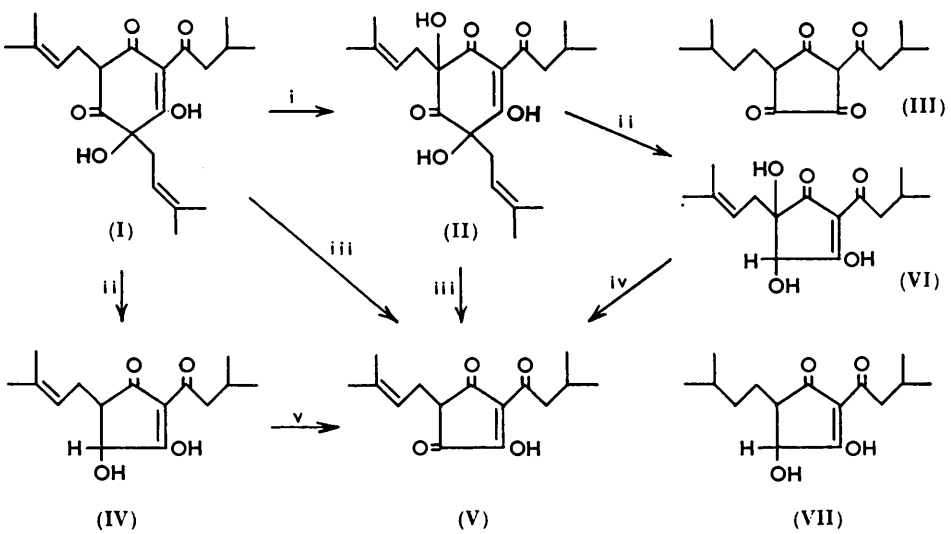
364. *The Chemistry of Hop Constituents. Part X.* Structure of a Degradation Product of Humulinone.*

By G. A. HOWARD and C. A. SLATER.

PREVIOUS work led to structure (II) being suggested [1] for humulinone, compared with the formulation (I) for its precursor, humulone. The latter is isomerised by alkali, and in particular its behaviour towards methanolic potassium hydroxide has been extensively investigated.[2,3] The effect of this reagent on humulinone was therefore studied.

A crystalline product was obtained which proved however, not to be isomeric with humulinone but had the empirical formula $C_{15}H_{20}O_4$. The compound resembled *iso*-humulinic acid (III) [4] in its yellow colour, its ultraviolet absorption spectrum, and the purple colour given with methanolic ferric chloride. It contained one double-bond and thus was possibly the enolised *cyclo*pentanetrione (V). As dihydrohumulinic acid (VII) is



i, O. ii, NaOH—H_2O. iii, KOH—MeOH. iv, $KHSO_4$. v, Bi_2O_3.

oxidised by bismuth trioxide to *iso*humulinic acid (III),[5] humulinic acid (IV) was accordingly oxidised similarly. The reaction was smooth and gave the same compound as was obtained from humulinone (m. p., reactions, and infrared spectra).

* Part IX, *J. Inst. Brewing*, 1956, 220.

[1] Cook, Howard, and Slater, *J. Inst. Brewing*, 1955, 321.
[2] Carson, *J. Amer. Chem. Soc.*, 1932, **74**, 4615.
[3] Howard, Slater, and Tatchell, *J. Inst. Brewing*, in the press.
[4] Harris, Howard, and Pollock, *J.*, 1952, 1906.
[5] Howard, Pollock, and Tatchell, *J.*, 1955, 174.

Humulinone is degraded by aqueous alkali principally to oxyhumulinic acid [1] (VI). As this compound is stable to methanolic potash, it cannot be an intermediate in the formation of the enolised trione (V) from humulinone. Nevertheless it is readily dehydrated by potassium hydrogen sulphate to the trione (V).

Humulone itself with alcoholic potassium hydroxide gives,[2,3] among other products, a compound, $C_{15}H_{20}O_4$, whose known properties leave no doubt [2] that it is the trione (V). It is suggested that its formation from humulone (I) proceeds *via* humulinone, and it is significant in this connection that Carson [2] made no attempt to exclude oxygen when he treated humulone with methanolic potash.[2]

Experimental.—Humulinone. Humulone (15·7 g.) in ether (30 ml.), underlayered with saturated aqueous sodium hydrogen carbonate (150 ml.), was oxidised with cumene hydroperoxide (10 ml.). After 5 days at room temperature the sodium salt (14·5 g.) of humulinone was filtered off; after a further 3 days an additional 1 g. separated, giving an overall yield of 89%.

Preparation of 5-(3-*methylbut*-2-*enyl*)-3-iso*valeryl*cyclo*pentane*-1 : 2 : 4-*trione from humulinone.* Humulinone (14·5 g.) was heated under reflux with methanolic potassium hydroxide (0·75 g. in 164 ml.) in nitrogen for 3 hr. The solution was cooled and poured into 2N-hydrochloric acid (200 ml.) containing crushed ice (100 g.). Extraction with light petroleum gave a syrup (5·6 g.) which partially crystallised. Crystallisation from light petroleum and then from aqueous ethanol gave the enolised cyclo*pentanetrione* as lemon-yellow prisms (0·25 g.), m. p. 136° (Found: C, 68·1, 68·0; H, 7·8, 7·8%; equiv., 264; I value, 94. $C_{15}H_{20}O_4$ requires C, 68·2; H, 7·6%; equiv., 264; I value for 1 double-bond, 96). Light absorption: in ethanol, $\lambda_{max.}$ 255 and 280 mμ ($E^{1\%}_{1\,cm.}$ 818 and 681); in alkaline ethanol, $\lambda_{max.}$ 275 and 303 mμ ($E^{1\%}_{1\,cm.}$ 978 and 982). This material, which gave a purple colour with methanolic ferric chloride, did not depress the m. p. of *iso*humulinic acid (m. p. 142°; I value, 0).

Evaporation of the mother-liquors yielded an intensely bitter syrup which failed to give any acyl*cyclo*pentanetrione (V) when boiled with methanolic potassium hydroxide for a further 6 hr. Neither was it possible to obtain this compound by heating oxyhumulinic acid with methanolic potassium hydroxide for 3 hr.

Preparation of the cyclo*pentanetrione* (V) *from humulinic acid.* Humulinic acid [4] (0·6 g.) was heated under reflux with bismuth trioxide (1 g.) in glacial acetic acid (25 ml.) for 5 hr. The resulting solution was poured into 2N-hydrochloric acid (50 ml.). The yellow crystals were recrystallised from aqueous ethanol (charcoal) giving a compound (0·2 g.), m. p. 135° alone or on admixture with the material described above. The infrared absorption spectrum of this compound was identical with that of the product described above.

Preparation of the cyclo*pentanetrione* (V) *from oxyhumulinic acid.* Oxyhumulinic acid [1] (0·5 g.) was mixed with finely powdered anhydrous potassium hydrogen sulphate (0·5 g.), and the mixture was gently heated. A vigorous reaction set in and the heating was stopped. The resulting orange mass was extracted with methanol (2 × 5 ml.), and the extract was treated with charcoal, filtered, and diluted with water. The crystals which separated gave, on recrystallisation from aqueous ethanol, pale yellow prisms (0·05 g.), m. p. 132—133° alone or on admixture with the acyl*cyclo*pentanetrione described above.

We are indebted to Mr. M. F. Carroll for infrared data.

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365. *Preparation of the Di-*p*-toluoyl Derivative of (−)-Tartaric Acid.*

By J. H. Hunt.

Stoll and Hofmann [1] have described the preparation of both optical antipodes of di-*p*-toluoyltartaric acid, which are useful resolving agents, by the acylation of (+)- and (−)-tartaric acid with *p*-toluoyl chloride. When the (−)-isomer is required, this method suffers from the disadvantage that the isolation in good yield of (−)-tartaric acid by resolution of racemic acid with cinchonine [2] is somewhat tiresome because the acid is water-soluble and isolation through the lead salt is necessary.

It has now been found that (±)-di-*p*-toluoyltartaric acid is readily resolved by cinchonine, giving a good yield of the cinchonine salt of the (−)-acid from which the free diacylated acid can easily be obtained having an optical rotation identical with that recorded previously.[1]

Some samples prepared by both methods have shown evidence of polymorphism, melting at 148°, resolidifying, and finally melting at 168° (uncorr.) [Stoll and Hofmann [1] give 172° (corr.)]. This is especially apparent in these samples on rapid heating. After recovery of cinchonine, the residue from the mother-liquors may be worked up to give a smaller yield of the (+)-isomer or can conveniently be hydrolysed to recover *p*-toluic acid.

Experimental.—(±)-OO-*Di*-p-*toluoyltartaric anhydride* was prepared from racemic acid (35·6 g.) [3] and *p*-toluoyl chloride (117 g.) by Stoll and Hofmann's method.[1] Recrystallised from xylene, it had m. p. 162—163° (Found: C, 64·8; H, 4·45. $C_{20}H_{16}O_7$ requires C, 65·2; H, 4·4%).

(±)-OO-*Di*-p-*toluoyltartaric acid*. The anhydride (32 g.) was refluxed for 2 hr. with acetone (75 ml.) and water (7·5 ml.), and the mixture evaporated. The solid residue was boiled with xylene to remove unchanged anhydride and filtered hot. The air-dried insoluble *product* (25 g.) had m. p. 183—184° and was sufficiently pure for the next stage. A sample recrystallised from nitrobenzene had m. p. 188° (Found: C, 62·2; H, 4·6. $C_{20}H_{18}O_8$ requires C, 62·3; H, 4·7%).

Resolution. The racemic acid (25 g.) was added to a suspension of cinchonine (19 g.) in boiling alcohol (500 ml.). The components dissolved completely and the solution on cooling deposited crystals which after 1 hr. were filtered off. The crude salt was refluxed with alcohol (60 ml.) for 15 min., filtered off, and dried at 100°. The *cinchonine* (−)-OO-*di*-p-*toluoyltartrate* so obtained (20 g.) melted at 201° and could be used without further purification. It recrystallised when treated in dimethylformamide with an equal volume of alcohol; it then melted at 208°, $[\alpha]_D^{26}$ +79·4° (*c* 0·4 in dimethylformamide) (Found: C, 68·3; H, 5·9; N, 4·2. $C_{39}H_{40}O_9N_2$ requires C, 68·8; H, 5·9; N, 4·1%).

(−)-OO-*Di*-p-*toluoyltartaric acid*. The cinchonine salt (156 g.) was suspended in water (1 l.), ether (200 ml.) added, and the whole stirred while concentrated hydrochloric acid (75 ml.) was added. The ether was separated, the mixture was extracted with a further portion of ether (200 ml.), and the combined extracts were dried ($MgSO_4$). Evaporation gave a gum which was refluxed for 1 hr. with benzene (600 ml.), during which a few crystals of the racemic compound were added to induce crystallisation of any traces remaining. The solution was filtered hot and allowed to cool slowly. Next morning the acid was filtered off, washed with benzene, and dried at 60° (81 g.). It had m. p. 148°, resolidified, and remelted 168°; $[\alpha]_D^{20}$ +138° (*c* 1 in alcohol). After recrystallisation from benzene the m. p. was unchanged, and $[\alpha]_D^{25}$ was +140° (Found: C, 62·3; H, 4·7%). Stoll and Hofmann [1] report m. p. 172° (corr.), $[\alpha]_D$ +140°.

The pure acid is slowly soluble in about 70 parts of boiling benzene. Its solubility is, however, greatly increased by the addition of small amounts of acetone or ether and in the

[1] Stoll and Hofmann, *Helv. Chim. Acta*, 1943, **26**, 922.
[2] Marckwald, *Ber.*, 1896, **29**, 42.
[3] Church and Blumberg, *Ind. Eng. Chem.*, 1951, **43**, 1780.

above procedure, the gummy product retains sufficient ether for complete solution in the quantity of benzene stated.

The author thanks Miss P. Schaay for technical assistance and the Directors of Allen & Hanburys Ltd. for permission to publish these results.

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WARE, HERTS. [*Received, November 13th*, 1956.]

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366. *The Reduction of Ruthenium Tetroxide in Hydrofluoric Acid.*

By M. L. HAIR, M. A. HEPWORTH, and P. L. ROBINSON.

RUFF [1] found that aqueous hydrofluoric acid, in contrast to the other halogen acids, is without action on ruthenium tetroxide. The tetroxide can be reduced electrolytically [2] in perchloric acid to give a solution containing Ru^{IV} and Ru^{III}, these valency states being characterised by their absorption spectra. A Ru^{IV} solution in nitric acid [3] was obtained from the reaction between ruthenium tetroxide and hydrogen peroxide in the aqueous acid. The use of hydrogen peroxide as a reducing agent has now been extended to solutions in aqueous hydrofluoric acid.

Solutions of Ru^{IV} in nitric acid contain [3] the cationic species $[Ru(H_2O)_5OH]^{3+}$ and it is probable that a similar ion is present in perchloric acid solutions. In common with perchlorate and nitrate, the fluoride ion is a poor complexing ligand for noble metals compared with chloride, cyanide, or nitrite. This gives grounds for expecting it to be present in the corresponding solutions of Ru^{IV} in hydrofluoric acid, as has now been realised, for their evaporation at room temperature permits the isolation of solid $[Ru(H_2O)_5OH]F_3$ which, however, is largely decomposed with loss of hydrogen fluoride and water when heated to 100°. The corresponding nitrate has previously been isolated.[3] The deep colour of solutions with the ruthenium in the cation is in marked contrast with those containing the $[RuF_6]^{2-}$ anion,[5] which are almost colourless.

Experimental.—Ruthenium metal sponge was converted into the tetroxide by Martin's [4] method. The tetroxide (0·5 g.) was washed into a platinum dish; suspended in " AnalaR " 40% hydrofluoric acid (15 ml.) and treated, dropwise, with pure 30% hydrogen peroxide solution. Oxygen was copiously evolved and the tetroxide dissolved to a deep red solution; when the reaction was complete the temperature was raised on a steam-bath to 100° to decompose excess of hydrogen peroxide.

After dilution, the absorption spectrum of the solution was measured in a Unicam ultra-violet spectrophotometer with 1 cm. matched Perspex cells. This was identical with that found for a Ru^{IV} solution in perchloric acid.[2] That the ruthenium was present in the cation was shown by the solution's losing its colour by exchange with hydrogen ion when passed through a Polythene column containing Zeo-Karb 225 resin in the hydrogen form.

Evaporation of the Ru^{IV} solution in a vacuum desiccator (KOH) left a vitreous, black solid {Found: Ru, 39·9; F, 21·1. $[Ru(H_2O)_5OH]F_3$ requires Ru, 38·3; F, 21·5%}. This solid dissolves readily in water to re-form the original red solution. When evaporated to dryness on a steam-bath it left a black solid which was virtually insoluble in both water and hydrofluoric acid (Found: Ru, 47·3; F, 11·4%). These evaporations must be carried out as soon as possible. On allowing the original solution to stand overnight further reduction takes place and spectroscopic evidence shows the presence of the hydrated Ru^{III} ion.

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KING'S COLLEGE, NEWCASTLE UPON TYNE, 1. [*Received, November 14th*, 1956].

[1] Ruff and Vidic, *Z. anorg. Chem.*, 1924, **136**, 52.
[2] Wehner and Hindman, *J. Amer. Chem. Soc.*, 1950, **72**, 3911.
[3] Fletcher, Jenkins, Lever, Martin, Powell, and Todd, *J. Inorg. Nuclear Chem.*, 1955, **1**, 378.
[4] Martin, *J.*, 1952, 3055.
[5] Hepworth, Peacock, and Robinson, *J.*, 1954, 1197.

367. 3-*Methyl*-3-*phenyloxindole.*

By (Miss) E. F. M. Stephenson.

3-Methyl-3-phenyloxindole has been prepared in good yield by cyclisation of (±)-atrolactanilide with polyphosphoric acid. With the same reagent (±)-mandelanilide gave 3-phenyloxindole.[1] (±)-Atrolactanilide was obtained from methyl (±)-atrolactate by Bodroux's method.[2]

Experimental.—M. p.s marked • were determined on a Kofler hot-stage microapparatus. Microanalyses were made by the C.S.I.R.O. Microanalytical Service. Temperatures quoted for sublimations refer to the heating-bath. The phosphoric acid had *d* 1·75.

Methyl (±)-*atrolactate.* A mixture of anhydrous (±)-atrolactic acid (33·2 g.), absolute methanol (120 ml.), and concentrated sulphuric acid (6 ml.) was refluxed for 6 hr. and methanol (85 ml.) then removed by distillation. The residue was poured into ice-water and extracted with benzene, the benzene distilled off, and the *ester* distilled under reduced pressure; it had b. p. 83—85°/1·3 mm., n_D^{20} 1·5154 (Found: C, 66·9; H, 6·8. $C_{10}H_{12}O_3$ requires C, 66·7; H, 6·7%).

(±)-*Atrolactanilide.* A solution of ethylmagnesium bromide [from magnesium (1·31 g.), ethyl bromide (4·5 ml.), and ether (40 ml.)] was cooled in ice, and aniline (5·15 ml.) in ether (10 ml.) added with shaking during 8—10 min. The mixture was kept for 0·5 hr. at room temperature, then again cooled in ice, methyl (±)-atrolactate (2·7 g.) in ether (30 ml.) was added with shaking during 3 min., and the mixture refluxed for 0·5 hr. and decomposed with ice and dilute sulphuric acid. The ether layer gave an oil which was freed from aniline by being stirred with dilute sulphuric acid. The *anilide* (2·28 g.) formed plates, m. p.* 136·5—137·5°, from aqueous ethanol (Found: C, 74·4; H, 6·4; H, 5·7. $C_{15}H_{15}O_2N$ requires C, 74·7; H, 6·3; N, 5·8%).

3-*Methyl*-3-*phenyloxindole.* To a solution of phosphoric oxide (5·3 g.) in phosphoric acid (3 ml.) at 107° (±)-atrolactanilide (0·3 g.) was added rapidly, and the internal temperatures of the stirred mixture was raised from 110° to 116° during 55 min. The hot solution was poured on ice and after several hours crystallisation of the product was complete. After sublimation at 160°/0·7 mm. and crystallisation from aqueous ethanol, the *oxindole* (215 mg.) formed prisms, m. p.* 155—156 (Found: C, 80·8; H, 5·9; N, 6·3; O, 7·5. $C_{15}H_{13}ON$ requires C, 80·7; H, 5·9; N, 6·3; O, 7·2%). Attempts to cyclise atrolactanilide with sulphuric acid did not give useful results. 3-Methyl-3-phenyloxindole dissolves rapidly in warm dilute aqueous sodium hydroxide and is reprecipitated on acidification.

3-*Phenyloxindole.* To a solution of phosphoric oxide (5·3 g.) in phosphoric acid (3 ml.) at 106° (±)-mandelanilide (0·23 g.) was added rapidly, and the internal temperature of the stirred mixture was raised from 106° to 120° in 95 min. As the anilide dissolved the solution became rose-pink but the colour faded as cyclisation proceeded. The hot, pale brown solution was poured on ice and after 2 hr. crystallisation of the product was complete. After sublimation at 155°/0·3 mm. and crystallisation from aqueous ethanol, the oxindole (80 mg.) had m. p.* 184—185° (Found: C, 80·4; H, 5·3; N, 6·7. Calc. for $C_{14}H_{11}ON$: C, 80·4; H, 5·3; N, 6·7%). 3-Phenyloxindole has been prepared by Meisenheimer and Meis and by Palazzo and Rosnati [1] in unspecified yield by cyclisation of (±)-mandelanilide with concentrated sulphuric acid.

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Carlton, N.3, Victoria, Australia. [*Received, November 19th*, 1956.]

[1] Meisenheimer and Meis, *Ber.*, 1924, **57**, 297; Palazzo and Rosnati, *Gazzetta*, 1953, **83**, 211.
[2] Bodroux, *Compt. rend.*, 1904, **138**, 1427; 1906, **142**, 401; *Bull. Soc. chim. France*, 1905, **33**, 832; cf. Hardy, *J.*, 1936, 398.

368. *The Synthesis of* (±)-*Felinine.*

By S. Trippett.

Westall [1] isolated from cat's urine a non-crystalline sulphur-containing amino-acid, felinine, which gave no crystalline derivatives and was optically active. Desulphurisation with Raney nickel gave alanine and *iso*pentyl alcohol, and on this basis Westall suggested structure (I) for felinine. The racemic compound (I) has now been synthesised and shown to be (±)-felinine.

$HO{\cdot}CH_2{\cdot}CH_2{\cdot}CMe_2{\cdot}S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$ (I)

$HO_2C{\cdot}CH(NH_2){\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}CMe_2{\cdot}S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$ (II)

The addition of toluene-ω-thiol to β-methylcrotonaldehyde gave β-(benzylthio)*iso*valeraldehyde [2] which, on reduction with lithium aluminium hydride, gave 2-(benzylthio)-*iso*pentyl alcohol. Treatment of this with sodium in liquid ammonia gave the sodium salt of the thiol which was coupled *in situ* with α-amino-β-chloropropionic acid to give in good yield *S*-(3-hydroxy-1 : 1-dimethylpropyl)cysteine (I).

This was shown to be (±)-felinine by the following evidence. (i) The synthetic material behaved on paper chromatography exactly as did natural (−)-felinine in the five solvent systems examined. (ii) Oxidation with hydrogen peroxide at the origin of a paper chromatogram led to the disappearance of the original spot and to the appearance of a new spot in the same position as that from a similar oxidation of natural felinine. (iii) Treatment of the synthetic material with 5N-hydrochloric acid at 105° gave a mixture of unchanged amino-acid and of free cystine together with a new amino-acid, $C_{11}H_{22}O_4N_2S_2$ [probably (II)], which ran on paper in the alanine region; natural felinine behaved in exactly the same way.[1] (iv) Final proof was obtained by the preparation from the synthetic racemate of a crystalline *N*-2 : 4-dinitrophenyl derivative which had the same infrared spectrum as the non-crystalline *N*-2 : 4-dinitrophenyl derivative prepared from natural (−)-felinine and purified by chromatography.

Experimental.—2-(*Benzylthio*)iso*pentyl alcohol.* A solution of β-(benzylthio)*iso*valeraldehyde (10 g.) in ether (100 ml.) was added slowly to a solution of lithium aluminium hydride (0·7 g.) in ether (50 ml.), and the resulting suspension was refluxed for 15 min., cooled in ice, and decomposed by dilute sulphuric acid. Ether extraction gave 2-(*benzylthio*)iso*pentyl alcohol*, b. p. 120—122°/0·3 mm. (Found : C, 68·3; H, 8·8. $C_{12}H_{18}OS$ requires C, 68·5; H, 8·6%).

(±)-*Felinine.* To a stirred solution of 2-(benzylthio)*iso*pentyl alcohol (1·05 g.) in liquid ammonia (100 ml.), sodium was added in small pieces until a permanent blue colour was obtained. α-Amino-β-chloropropionic acid (0·46 g.) was then added and the ammonia allowed to evaporate. The residue was taken up in water (50 ml.) and placed on a column of Dowex 50 (acid form; 2 × 10 cm.) which was then washed with water till the eluate was neutral. The amino-acid was then eluted with 0·5N-ammonia. Evaporation of the eluate and crystallisation from aqueous ethanol gave S-(3-*hydroxy*-1 : 1-*dimethylpropyl*)*cysteine*, m. p. 181° (decomp.) (Found : C, 45·9; H, 8·1; N, 6·7. $C_8H_{17}O_3NS$ requires C, 46·4; H, 8·2; N, 6·8%). This material ran on paper exactly as did a sample of natural (−)-felinine in the following solvent systems, the approximate R_f values being given in parentheses : butan-1-ol–acetic acid–water (5 : 1 : 4) (0·4), butan-1-ol–ethanol–water (7 : 2 : 3) (0·38), *tert.*-amyl alcohol (0·28), collidine (0·46), and phenol (0·88).

Treatment with 2 : 4-dinitrofluorobenzene gave the N-2 : 4-*dinitrophenyl derivative*, m. p. (from aqueous ethanol) 120—122° (Found : C, 45·1; H, 5·4; N, 11·6. $C_{14}H_{19}O_7N_3S$ requires C, 45·0; H, 5·1; N, 11·3%). The infrared spectrum of a solution in acetonitrile–chloroform (2 : 5 v/v), showed the expected features and was identical with that of the amorphous N-2 : 4-*dinitrophenyl derivative* of (−)-felinine, purified by chromatography in ethyl acetate on Hyflo Supercel (Found : N, 11·35%), taken in the same solvent mixture.

[1] Westall, *Biochem. J.*, 1953, **55**, 244.
[2] Catch, Cook, Graham, and Heilbron, *J.*, 1947, 1609.

Action of 5N-*hydrochloric acid on* (±)-*felinine.* (±)-Felinine (0·2 g.) was heated with 5N-hydrochloric acid (4 ml.) in a sealed tube under nitrogen for 36 hr. A small quantity of a brown oil separated and was removed. The solution was evaporated under reduced pressure and the residue, in water (20 ml.), placed on a column of Dowex 50 (acid form; 1 × 15 cm.) which was then washed with water. Elution with 0·5N-ammonia gave an amino-acid fraction which was evaporated to 3 ml. and set aside at 0° overnight. Filtration gave a *product*, m. p. 244—245° (decomp.) (Found: C, 42·2; H, 7·0; N, 8·6. $C_{11}H_{22}O_4N_2S_2$ requires C, 42·5; H, 7·1; N, 9·0%).

I thank Dr. R. G. Westall for a supply of natural felinine and Dr. J. Holgate for arranging a supply of cat's urine.

THE UNIVERSITY, LEEDS, 2. [*Received, November 19th,* 1956.]

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369. *Activity Coefficients and Transport Numbers for Hydrochloric Acid at 0°.*

By A. K. COVINGTON and J. E. PRUE.

RECENTLY it was shown [1] that an analysis of the freezing-point data [2] for hydrochloric acid gives values for the activity coefficient which differ by more than the apparent experimental accuracies from the values obtained from e.m.f. measurements.[3] In connection with other work [4,5] we have obtained values of the activity coefficient at 0° by combining e.m.f. measurements on cells with transport-number data.

Experimental.—The e.m.f. measurements were made with silver–silver chloride electrodes and the transport numbers t^+ obtained by the moving-boundary technique.[4,5] The temperature of the thermostat, which contained a 20% alcohol–water mixture, was adjusted to 0·00° ± 0·01° by comparison with the temperature of crushed ice made from distilled water and maintained with the aid of a commercial refrigerator unit.

Results.—The results are shown in Tables 1 and 2. The value adopted for the e.m.f. constant (RT/F) ln 10 was $(2{\cdot}27115 \times 10^3)(2{\cdot}30259 \times 10^3)/(0{\cdot}964877 \times 10^5) = 54{\cdot}199$ mv,

TABLE 1.

c (mole l.$^{-1}$)	$c^{\frac{1}{2}}$ (mole$^{\frac{1}{2}}$ l.$^{-\frac{1}{2}}$)	t^+_{obs}	Vol. corr.	$t^+_{corr.}$
$0{\cdot}02151_1$	0·1468	0·8491	0·0002	0·8493
$0{\cdot}03970_2$	0·1993	0·8501	0·0004	0·8505
$0{\cdot}05787_9$	0·2404	0·8511	0·0006	0·8517
$0{\cdot}07995_9$	0·2828	0·8524	0·0007	0·8531
$0{\cdot}09739_7$	0·3121	0·8527	0·0009	0·8536
0·09928	0·3151	0·8529	0·0009	0·8538

TABLE 2.

$m_1 = 0{\cdot}10930$ mole kg.$^{-1}$ $t_1 = 0{\cdot}8538$

$10^3 m_2$ (mole kg.$^{-1}$)	E (mv)	t^+	$-\Delta \log \gamma$	$\Delta \log \gamma - \Delta \log \gamma^{st}$	Δm (mole kg.$^{-1}$)
5·825	111·59	0·8466	0·06186	0·02479	0·1035
11·35	86·02	0·8478	0·05064	0·02362	0·09795
21·25	62·16	0·8491	0·03768	0·02098	0·08805
30·25	48·73	0·8500	0·03001	0·01894	0·07905
44·34	34·26	0·8510	0·02101	0·01536	0·06496
72·55	5·62	0·8526	0·00908	0·00862	0·03675

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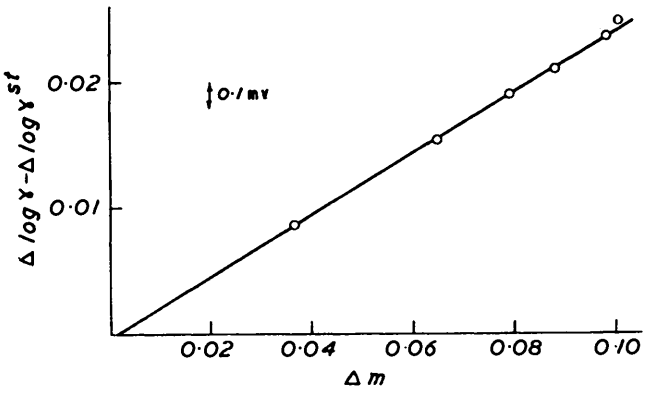
[1] Guggenheim and Prue, "Physicochemical Calculations," North-Holland Publ. Co., Amsterdam, 1955, p. 226.
[2] Randall and Vanselow, *J. Amer. Chem. Soc.*, 1924, **46**, 2418.
[3] Harned and Ehlers, *J. Amer. Chem. Soc.*, 1932, **54**, 1350.
[4] Covington and Prue, *J.*, 1955, 3701.
[5] Covington and Prue, *J.*, 1957, 1567.

for the Debye–Hückel constant (A) 0·488 (mole^{-1} kg.)$^{\frac{1}{2}}$, and for the faraday 96·488 c mole^{-1}. The volume corrections were estimated from partial molal volumes calculated from density data in the International Critical Tables.

The plot of $\Delta \log \gamma - \Delta \log \gamma^{st}$ against Δm (m = molality) gives an excellent straight line (Figure), the slope of which corresponds to

$$\log \gamma = -Am^{\frac{1}{2}}/(1 + m^{\frac{1}{2}}) + 0{\cdot}240m \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The value of the coefficient of the linear term (0·240) is in excellent agreement with that obtained from e.m.f. measurements (0·241) rather than from the freezing-point measurements (0·216). The discrepancy corresponds to a difference of slightly more than ½% in γ at a molality of 0·1. The freezing-point measurements were analysed [1] by using the value $\lambda = 1{\cdot}860$ deg. mole^{-1} kg. for the cryoscopic constant of water based on the best modern measurements. If the older value $\lambda = 1{\cdot}858$ deg. mole^{-1} kg. had been used the discrepancy in γ at 0·1m would be reduced to about 0·3%.



Transport numbers and activity coefficients at rounded concentrations are given in Table 3. The transport numbers were smoothed by use of Shedlovsky's equation [6] modified by replacing the term $c^{\frac{1}{2}}$ by $c^{\frac{1}{2}}/(1 + c^{\frac{1}{2}})$; this in general we find gives linear plots with a smaller slope than does the original equation. In using this equation the

TABLE 3.

c	0	0·01	0·02	0·05	0·10
t^+	0·8441	0·8476	0·8490	0·8514	0·8538
m	—	0·01	0·02	0·05	0·10
γ	—	0·9079	0·8798	0·8372	0·8068

value of the equivalent conductivity at infinite dilution, Λ_0(HCl) = 265·2 int. ohm^{-1} mole^{-1} cm.^{2}, was taken from Randall and Vanselow's paper. The activity coefficient values were obtained from eqn. 1.

We are grateful to the Department of Scientific and Industrial Research for a grant to one of us (A. K. C.).

READING UNIVERSITY. [*Received, November 20th*, 1956.]

[6] Shedlovsky, *J. Chem. Phys.*, 1938, **6**, 845.

370. *Ultraviolet Absorption Spectra of Some Condensed Thiophen Derivatives.*

By W. CARRUTHERS and J. R. CROWDER.

THE ultraviolet absorption spectra of polycyclic compounds derived from five-membered heterocyclic systems have recently been described by Badger and Christie,[1] who concluded that there is a fundamental similarity between the spectra of the heterocyclic compounds and those of the related benzenoid hydrocarbons. In the Table we record the spectra of some other condensed thiophen derivatives which support this conclusion.

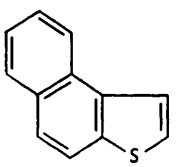
Ultraviolet absorption maxima (mμ) *with* log ε *in parentheses.**

Compound	Group I	Group II	Group III
4 : 5-Benzothio-naphthen †	245 255 (4·70) (4·44)	281 292 304 (3·95) (4·10) (4·06)	316 {323} 330·5 (329) {(2·88)} (3·22)
6 : 7-Benzothio-naphthen	255 261 264 (4·55) (4·68) (4·66)	281 292 304 (3·92) (3·84) (3·53)	{317} 325 334 341 {(2·66)} (2·84) (2·60) (2·80)
Thiophanthren	232 251—255 (4·51) (4·84)	{300} 313 328 336 352 {(3·37)} (3·61) (3·72) (3·76) (3·84)	
Thiophanthren dioxide	257 (4·79)	278 288 299 (4·03) (4·01) (3·99)	333 348 364 (3·16) (3·41) (3·46)
2-Methyl-5 : 6-benzo-thiophanthren	277 285 (4·74) (4·60)	302 309 320 336 (3·88) (3·92) (4·04) (4·10)	350 {360} 368 (3·20) {(2·64)} (2·64)
2-Methyl-7 : 8-benzo-thiophanthren	246 265 274 285 (4·26) (4·23) (4·54) (4·68)	303 315 330 (4·02) (4·00) (3·90)	{345} 353 362 372 {(2·88)} (3·10) (2·73) (2·94)

* Figures with braces { } indicate inflexions. † Cf. Campaigne and Cline, *J. Org. Chem.*, 1956, **21**, 39.

4 : 5- and 6 : 7-Benzothionaphthen (I and II) show three well defined groups of absorption bands, and the similarity with the spectrum of phenanthrene is even closer than was observed in the case of dibenzothiophen.[1] Displacement of the maxima to shorter wavelengths is much less pronounced than in dibenzothiophen. The increased intensity of the long-wavelength absorption, noted by Badger and Christie, is again evident.

A similar relation is found with thiophanthren (III) whose spectrum is very similar to that of anthracene. Like the hydrocarbon it shows only two regions of absorption, but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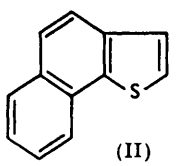
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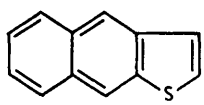
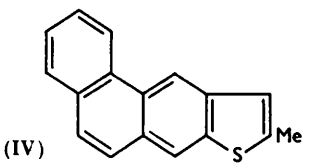

(III)

the long-wavelength maxima are displaced 20—25 mμ towards the violet, and the short-wavelength maxima are of somewhat lower intensity than in anthracene. The spectrum of the dioxide is more complicated and shows three groups of bands indicating a contribution of the SO_2 group to the conjugation. The similarity in the spectra of anthracene and thiophanthren suggests some correspondence in chemical properties, and this is being investigated.

In the tetracyclic series, the spectra of 2-methyl-5 : 6-benzothiophanthren (IV) and

[1] Badger and Christie, *J.*, 1956, 3438.

2-methyl-7 : 8-benzothiophanthren (V) are again very similar to those of their hydrocarbon analogues 7- and 6-methyl-1 : 2-benzanthracene.[2] The Group II and Group III



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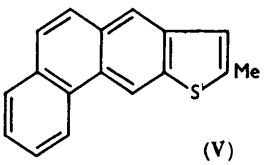


(V)

bands occur at shorter wavelengths, but the increased intensity of the Group III maxima, noted in other cases,[1] is not observed with these compounds.

Experimental.—Absorption spectra. These were determined with a " Unicam " spectrophotometer with *cyclo*hexane solutions, except in the case of thiophanthren dioxide where the solvent was 95% ethanol.

Materials. 4 : 5- and 6 : 7-Benzothionaphthen were obtained as described previously.[3]

2-Methyl-5 : 6- and 2-methyl-7 : 8-benzothiophanthren were prepared by the method of Buu-Hoï and Nguyen-Hoan.[4] The m. p. of the latter compound was found to be 112—114°, not 189° as reported by them (Found : C, 82·5; H, 4·8. Calc. for $C_{17}H_{12}S$: C, 82·2; H, 4·8%). The *picrate* formed orange-red needles, m. p. 155°, from benzene–ethanol (Found : C, 57·7; H, 3·3; N, 9·0. $C_{17}H_{12}S,C_6H_3O_7N_3$ requires C, 57·9; H, 3·2; N, 8·8%). Desulphurisation of the compound with Raney nickel in boiling ethanol [5] gave 2-*n*-propylphenanthrene as plates, m. p. 35—36° alone or mixed with an authentic specimen.

Thiophanthren was obtained in very poor yield by reduction of thiophanthraquinone [6] by boiling a suspension (2 g.) for 2 days with zinc dust (7 g.) in concentrated aqueous ammonia (25 c.c.), further portions of zinc and ammonia being added at intervals. The mixture was filtered hot, and the residue washed with water and with alkaline sodium dithionite to remove excess of quinone. The product was extracted from the insoluble portion with boiling benzene. After purification by chromatography on alumina and by sublimation, thiophanthren was obtained as colourless plates (20 mg.), m. p. 186—189°, from benzene–ethanol (lit.,[7] 189°) (Found : C, 78·4; H, 4·3. Calc. for $C_{12}H_8S$: C, 78·2; H, 4·4%). The *dioxide*, obtained when thiophanthren (10 mg.) and hydrogen peroxide (0·05 c.c., 30%) in acetic acid (1 c.c.) were heated on the water-bath for 2 hr., formed straw-coloured prisms, m. p. 177—179° (Kofler block), from benzene–methanol (Found : C, 66·5; H, 3·9. $C_{12}H_8O_2S$ requires C, 66·7; H, 3·7%).

Microanalyses were by Mr. J. M. L. Cameron and Miss M. Christie. One of us (W. C.) was supported by the Medical Research Council.

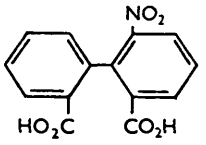
UNIVERSITY OF GLASGOW. [*Received, November 21st*, 1956.]

[2] Friedel and Orchin, " Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, 1951, Spectra nos. 505 and 506.
[3] Carruthers, *J.*, 1953, 4186.
[4] Buu-Hoï and Nguyen-Hoan, *Rec. Trav. chim.*, 1948, **67**, 309.
[5] Blicke and Sheets, *J. Amer. Chem. Soc.*, 1948, **70**, 3768.
[6] Etienne, *Bull. Soc. chim. France*, 1947, 634.
[7] von Meyer, *Annalen*, 1931, **488**, 259.

371. *A Redetermination of the Racemisation Velocities of 6-Nitro-, 4 : 6′-Dinitro-, and 4 : 6 : 4′-Trinitro-diphenic Acid in Alkaline Solution.*

By JEAN W. BROOKS, MARGARET M. HARRIS, and K. E. HOWLETT.

THE mode of operation of the nitro-group in influencing the optical stability of substituted diphenic acids is at present a matter of speculation.[1,2,3] Attempts to explain the effect of substituting further nitro-groups in the 4- and 4′-position in 6-nitrodiphenic acid (I) have so far been based upon the experimental work of Kuhn and Albrecht;[4] these authors



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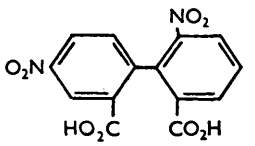

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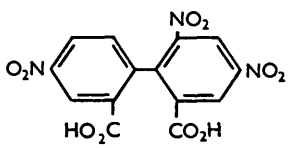

(III)

were the first to show that the decrease in optical activity of diphenyls obeys the first-order kinetic law. Their results are given in Table 1, together with the enthalpies ($\Delta H^{\ddagger}$)

TABLE 1.

Acid	$\frac{1}{2{\cdot}303}k$ (min.$^{-1}$) in 2N-Na_2CO_3 [4]	E (kcal. mole^{-1}) [4]	$\Delta H^{\ddagger}$ [1]	$\Delta S^{\ddagger}$ [1]
(II)	0·018 at 98·2°; 0·0014 at 73·5°	26	25·7	−4·2
(III)	0·0060 at 98·6°; 0·00074 at 74·6°	22·4	21·2	−18·5

and entropies ($\Delta S^{\ddagger}$) of activation calculated by Cagle and Eyring [1] using Kuhn and Albrecht's data.

The racemisation of 6-nitrodiphenic acid (I) in 0·1N-sodium hydroxide was investigated by Adams and Hale [5] at one temperature only, presumably the boiling point of the solution. A half-life of 4·6 minutes was recorded.

We have now repeated the observation of the racemisation of these acids, in greater detail, in 2N-sodium carbonate (not sodium hydroxide [1,5]) solution. Table 2 shows the

TABLE 2.

Acid	Temp.	10^4k (sec.$^{-1}$)	E (kcal. mole^{-1})	A (sec.$^{-1}$)	$\Delta S^{\ddagger}$ (e.u.)
(I)	87·6°	8·05	22·6	$10^{10\cdot6}$	−12·2
	80·6	4·24			
	67·55	1·26			
	57·0	0·435			
(II)	91·0	3·42	22·6	$10^{10\cdot1}$	−14·7
	83·4	1·69			
	74·4	0·769			
	70·4	0·515			
(III)	94·0	1·90	22·6	$10^{9\cdot7}$	−16·3
	84·6	0·85			
	82·0	0·66			
	72·4	0·275			

first-order racemisation velocity constants and the parameters for the corresponding rate equations.

[1] Cagle and Eyring, *J. Amer. Chem. Soc.*, 1951, **73**, 5628.
[2] de la Mare, "Progress in Stereochemistry," Ed. Klyne, Butterworths, London, Vol. I, 1954, p. 120.
[3] Westheimer, "Steric Effects in Organic Chemistry," Ed. Newman, John Wiley, New York, 1956, p. 553.
[4] Kuhn and Albrecht, *Annalen*, 1927, **455**, 272; **458**, 221.
[5] Adams and Hale, *J. Amer. Chem. Soc.*, 1939, **61**, 2825.

In calculating $\Delta S^{\ddagger}$ from the formula $k = \kappa e \frac{kT}{h} \exp(\Delta S^{\ddagger}/R - E/RT)$ the value of the transmission coefficient κ is taken as unity in each case.

The marked increase in optical stability on addition of a further nitro-group in a *para*-position (where it can exercise neither a blocking nor a buttressing effect) is here shown to reside in the entropy-of-activation factor rather than in the activation energy of the racemisation process.

The authors are indebted to the Department of Scientific and Industrial Research for a maintenance grant (to J. W. B.).

BEDFORD COLLEGE, LONDON, N.W.1. [*Received, December 6th*, 1956.]

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372. *The Interaction of Phenacyl Chloride and Aqueous Alkali.*

By C. EABORN.

THE reaction between phenacyl halides and alcoholic alkalis has been much studied,[1] and high yields of " α- and β-diphenacyl halides " (2-benzoyl-3-halogenomethyl-3-phenyloxirans) have been obtained. Thus phenacyl chloride with potassium hydroxide in methanol gives the " diphenacyl chlorides " in 95% yield,[2] and phenacyl bromide with sodium ethoxide in ethanol gives " diphenacyl bromide " in 83% yield.[1] There appear to be no reports, however, of the interaction of phenacyl halides and aqueous alkali, and when we examined this we were surprised to obtain mandelic acid in *ca.* 45% yield. When as little as 30% of methanol was added to the aqueous system mandelic acid was no longer formed. At first sight the acid might seem to result from an unusual rearrangement, but since we find that phenacyl alcohol, which is known to be readily oxidized,[3] is converted into mandelic acid under the reaction conditions we believe that this alcohol is first formed and is then oxidized, presumably by atmospheric oxygen. In agreement with this suggestion, much less mandelic acid was obtained when the reaction was carried out in a nitrogen atmosphere, and the small quantity obtained was probably formed during the working-up. Probably the very low solubility of phenacyl chloride in water reduces the chance of the self-condensation to give the " diphenacyl chlorides," and simple substitution at the C–Cl bond is allowed to proceed.

Experimental.—Phenacyl chloride and aqueous alkali. Phenacyl chloride (5 g.) was added in small portions during 1 hr. to a stirred solution of sodium hydroxide (10 g.) in water (100 ml.) kept at 65—70°, and the mixture was stirred at this temperature for ½ hr. longer. The orange solution was cooled and decanted from a red solid (2·2 g., after drying) and then extracted with ether, the extract being discarded. Acidification of the solution followed by extraction with large volumes of ether and removal of the solvent from the extracts gave (±)-mandelic acid (2·1 g., 43%), m. p. and mixed m. p. 118—120° after recrystallization from ether–light petroleum. The m. p. was depressed on admixture with benzoic acid.

When the reaction was carried out under nitrogen, but with exposure of the system to the air during extraction processes, only 0·3 g. of mandelic acid was obtained. Acidification of the alkaline solution [after decantation from the red solid (2·5 g.) and extraction with ether] liberated a yellow oil which was taken up in a little ether before the mandelic acid was extracted with large volumes of ether. The oil (1·6 g.) was recovered and found to contain no material readily soluble in water.

Phenacyl chloride and aqueous methanolic alkali. The halide (5 g.) was added during 20 min.

[1] Wasserman, Aubrey, and Zimmerman, *J. Amer. Chem. Soc.*, 1953, **75**, 96, and refs. therein.
[2] Stevens, Church, and Traynelis, *J. Org. Chem.*, 1954, **19**, 522.
[3] Evans, *Amer. Chem. J.*, 1903, **35**, 115.

to a stirred, refluxing solution of sodium hydroxide (2 g.) in water (60 ml.) and methanol (25 ml.). The halide quickly disappeared and the solution became deep orange-red. The methanol was boiled off quickly, and the aqueous system was treated as above, to give a very small quantity of solid from which no pure compound was isolated.

Phenacyl alcohol and aqueous alkali. The alcohol [3] (5 g., m. p. 87·5°) was added during 1 hr. to a stirred solution of sodium hydroxide (5 g.) in water (100 ml.) kept at 65—70° in a vessel open to the atmosphere. The solution became orange in the first few min. and a solid separated. Stirring and heating were continued for an additional 1 hr., and the solution was extracted several times with ether (these extracts being discarded), and then acidified. The green oil which separated was discarded and the aqueous solution was extracted several times with ether. Evaporation of these extracts gave crude mandelic acid (2·1 g.), which on recrystallisation gave material (1·5 g.) of m. p. and mixed m. p. 119—120° (depressed on admixture with benzoic acid).

In a separate experiment the alcohol (5 g.) was shaken for 1 min. at room temperature with water (100 ml.) containing sodium hydroxide (10 g.), and the mixture was quickly cooled in ice. The liquid was decanted from the red solid (1·9 g.) which had been formed and was extracted several times with ether and then acidified. The yellow oil (1·9 g.) which separated was taken up in a little ether and the remaining liquid was extracted several times with large volumes of ether to give (±)-mandelic acid (0·3 g.), m. p. 116—118°, mixed m. p. 118—120°, on evaporation.

UNIVERSITY COLLEGE, LEICESTER. [*Received, July 31st*, 1956.]