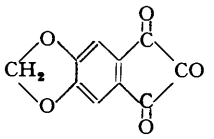
NOTES.

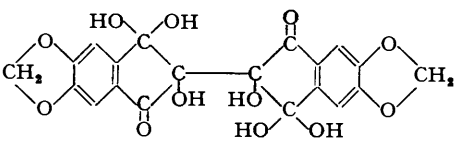
Studies on Indene Derivatives. Part VIII. *Methylenedioxyindanetrione.* By RADWAN MOUBASHER.

5 : 6-METHYLENEDIOXYINDANE-1 : 2 : 3-TRIONE (I) is obtained when the corresponding hydrate is heated in a vacuum at 250° or treated with thionyl chloride or oxalyl chloride (cf. Ruhemann, *J.*, 1912, **101**, 780). When suspended in *iso*propyl alcohol and exposed to sunlight, or treated with the Gomberg–Bachmann reagent (*J. Amer. Chem. Soc.*, 1927, **49**, 236), (I) was reduced to the colourless hydrindantin (II). Prolonged treatment of (I) with hydrogen sulphide gave the substance (III; R = H). Since (II) behaved similarly it probably represents an intermediate stage in the reduction. Substance (III) gave the dimethyl ether (III; R = Me) on treatment with diazomethane. With α-amino-acids, the hydrate of (I) gave a mixture of (II) and (III; R = H) (cf. Moubasher and Ibrahim, *J.*, 1949, 702), and with dilute ammonia the benzoylglyoxalinoindenone (IV). As shown by Ruhemann (*loc. cit.*), heating (IV) alone or in acetic acid or acetic anhydride gave a red compound formulated as (V) or (VI) (cf. Moubasher, *J.*, 1949, 1038).

Photo-chemical Reaction between 5 : 6-*Methylenedioxyindane*-1 : 2 : 3-*trione and* iso*Propyl Alcohol.*—Freshly prepared triketone (0·5 g.) suspended in freshly distilled *iso*propyl alcohol (10 g.; dried with calcium carbide) in a closed Monax tube filled with carbon dioxide was exposed to sunlight for 15 days (March). The red substance gradually disappeared and a colourless solid was formed. The excess of *iso*propyl alcohol was removed in a vacuum, and the residue (0·3 g.) crystallised from aqueous acetone. The photo-product showed the properties of *di*-(5 : 6-*methylenedioxy*)*hydrindantin* (II); it turned red at about 120° and decomposed at 278° with evolution of gas; it formed an intense blue solution in sodium hydroxide solution. It crystallises from acetone–alcohol (Found: C, 53·5; H, 3·0. $C_{20}H_{14}O_{12}$ requires C, 53·8; H, 3·1%).

Action of Gomberg–Bachmann's Reagent.—To powdered magnesium (4 g.) in a mixture of dry ether (50 c.c.) and dry benzene (50 c.c.; thiophen-free) iodine was added until its colour persisted. Dry magnesium powder (4 g.) was then added, followed by the anhydrous triketone (I) (0·3 g.), and the mixture was shaken at room temperature for ½ hour and then refluxed for another ½ hour. The product was added to ice-cold dilute hydrochloric acid and left overnight in an open vessel. The deposit was then filtered off and crystallised from acetone–alcohol, the hydrindantin (II) (0·2 g.) being obtained as colourless crystals (identified by m. p., mixed m. p., and properties).

(I.) 



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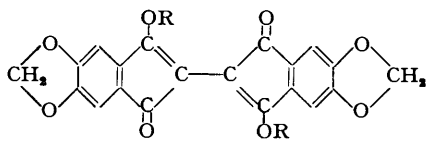

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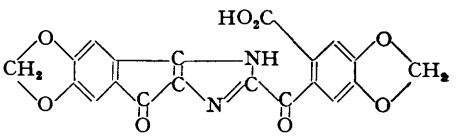

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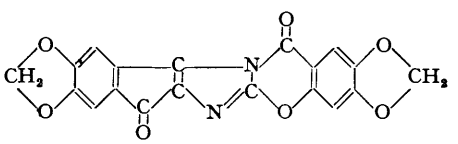
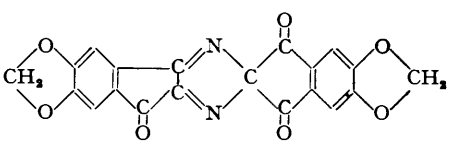


(V.)



(VI.)

Action of Oxalyl Chloride on Di-(5 : 6-*methylenedioxy*)*hydrindantin Hydrate.*—0·2 G. of (II) was refluxed with 10 c.c. of oxalyl chloride for ½ hour, and the excess of oxalyl chloride removed by distilling under a vacuum; the colourless residue recrystallised from much dry benzene in colourless needles of di-(2-dihydroxy-1 : 3-diketo-5 : 6-methylenedioxyindan-2-yl), m. p. 288° (Found : C, 58·1; H, 2·6. Calc. for $C_{20}H_{10}O_{10}$: C, 58·5; H, 2·4%).

Formation of Di-(2-*hydroxy*-3-*keto*-5 : 6-*methylenedioxyinden*-2-*yl*) (III; R = H).—(a) *From the hydrate of* (I). The triketone hydrate (0·2 g.) in ethyl alcohol (90%; 150 c.c.) was refluxed for 3 hours, during which a stream of hydrogen sulphide was passed through the mixture; after some hours at room temperature the crystals were filtered off and recrystallised from 2-methylnaphthalene in dark violet crystals, m. p. 340° (*ca.* 50%), soluble in aqueous sodium hydroxide to a dark red solution (Found : C, 63·2; H, 2·5. Calc. for $C_{20}H_{10}O_8$: C, 63·4; H, 2·7%).

(b) *From the hydrindantin.* The procedure was as described under (a), the yield being *ca.* 70%.

The powdered substance reacted vigorously with ethereal diazomethane, dissolving in the cold after 24 hours; after evaporation, the residue of the dimethyl ether crystallised from methyl alcohol in orange crystals, m. p. 170° (decomp.), soluble in alcohol, difficulty soluble in ether, and insoluble in sodium hydroxide solution (Found : C, 64·8; H, 3·2. Calc. for $C_{22}H_{14}O_8$: C, 65·0; H, 3·4%).

The dimethyl ether was treated with cold sulphuric acid for 2 hours at 60°. The red-violet solution was poured into ice-cold water, giving a red-violet deposit of (III; R = H) which, dried and crystallised, had m. p. 340° undepressed by an authentic sample prepared as above.

Action of Oxygen on (III; R = H) *in Presence of Selenium.*—The substance (0·2 g.) was powdered with red selenium (2 g.) and heated at 320° in a current of air for 3 hours. A sublimate of colourless crystals, after recrystallisation from hot water, was identified as hydrastic acid.

Action of 5 : 6-*Methylenedioxyindane*-1 : 2 : 3-*trione Hydrate on* α-*Amino-acids.*—(*a*) A solution of 0·2 g. of alanine in 25 c.c. of water was added to a suspension of 0·3 g. of the hydrate in 100 c.c. of water in a Claisen flask fitted with an upright condenser, to which was attached a sloping condenser and a receiver, whilst a continuous current of carbon dioxide was passed through the whole. The receiver contained a solution of 2 : 4-dinitrophenylhydrazine hydrochloride. The mixture in the flask was distilled until its volume was reduced to about 25 c.c. The receiver was then left to cool, whereupon acetaldehyde 2 : 4-dinitrophenylhydrazone (*ca.* 30%) was obtained, having m. p. 166° (cf. Bryant, *J. Amer. Soc.*, 1932, **54**, 3760) alone or mixed with an authentic sample.

In the reaction vessel a dark red-violet substance separated, which was filtered off, dried, and recrystallised from 2-methylnaphthalene giving (III ; R = H) in needles (0·1 g.).

(*b*) Heating a mixture of alanine (0·2 g.) with the hydrate (0·3 g.) in 50 c.c. of water gave carbon dioxide and ammonia.

Action of Aqueous Ammonia on the Indanetrione Hydrate.—The hydrate (0·2 g.), dissolved in hot water (100 c.c.), was cooled and excess of aqueous ammonia was added, a violet solution being obtained. After ½ hour at room temperature this was filtered and acidified with concentrated hydrochloric acid. The resulting brownish-red gelatinous precipitate of 5 : 6-*methylenedioxy*-2′-(2-*carboxy*-4 : 5-*methylene*-

dioxybenzoyl)glyoxalino(4′ : 5′-2 : 3)*inden*-1-*one* (IV) was filtered off, washed with hot water, dried, and crystallised from dioxan–ethyl alcohol, forming scarlet prisms (0·1 g.), which changed at 350° to an intensely red solid and melted at 380° (decomp.) (varies with the rate of heating). The substance is soluble in aqueous ammonia and alkali and is reprecipitated by acids (Found : C, 58·6; H, 2·2; N, 6·6. $C_{20}H_{10}O_8N_2$ requires C, 59·1; H, 2·4; N, 6·8%).

The powdered product (0·1 g.) with an excess of ethereal diazomethane gave a *methyl* ester, red needles (from methyl alcohol) (0·09 g.), m. p. 320 (red melt), insoluble in aqueous alkali and alkali carbonate (Found : C, 60·4; H, 2·8; N, 6·8. $C_{21}H_{12}O_8N_2$ requires C, 60·0; H, 2·8; N, 6·6%).

When boiled in acetic anhydride (25 c.c.) or acetic acid (50 c.c.) for ½ hour and then cooled, (IV) gave the *anhydro*-compound (V or VI) as a crystalline red deposit, which was filtered off and recrystallised from glacial acetic acid in intensely red prisms (0·09 g.), m. p. 380°, insoluble in cold or hot ammonia solution (Found : C, 61·7; H, 1·8; N, 6·8. $C_{20}H_8O_7N_2$ requires C, 61·8; H, 2·0; N, 7·1%). The same substance was obtained when (IV) was heated in a vacuum at 360°/4 mm.—FOUAD I UNIVERSITY, FACULTY OF SCIENCE, CAIRO, EGYPT. [*Received, April 11th*, 1950.]

The Action of Ammonia on β-Benzoylacrylic Acid. By M. M. FRASER and R. A. RAPHAEL.

THE action of ammonia on β-benzoylacrylic acid has been studied by Bougault (Bougault, *Ann. Chim.*, 1908, **15**, 491; Bougault and Chabrier, *Compt. rend.*, 1948, **226**, 1378). At first the product was tentatively described as α-amino-β-benzoylpropionic acid but in the later communication this was altered to β-amino-β-benzoylpropionic acid; in neither case were the formulations accompanied by analyses or chemical evidence of structure. The mode of addition giving rise to the β-amino-acid would be surprising (cf. Jones, Shen, and Whiting, *J.*, 1950, 236) especially as an α-amino-ketone such as this would be expected to undergo ready self-condensation to a dihydropyrazine. Because of the potentialities of this approach to the synthesis of kynurenin (α-amino-β-2-aminobenzoylpropionic acid) an investigation of this reaction has been undertaken and chemical evidence has been adduced which shows the product to be the α-amino-acid.

In the ninhydrin reaction the product does not give results typical of an α-amino-acid; during prolonged boiling an orange coloration slowly develops, followed by the sudden formation of a white crystalline precipitate possessing properties identical with Ruhemann's hydrindantin (Ruhemann, *J.*, 1911, **99**, 792, 1306; cf. West and Rinehart, *J. Biol. Chem.*, 1942, **146**, 105). In any event this colour reaction would not serve as a discriminatory test between the two structures since α-amino-ketones also give colorations under such conditions (Cherbuliez and Herzenstein, *Helv. Chim. Acta*, 1934, **17**, 1440). Reduction of the keto-amino-acid with sodium amalgam furnished the corresponding hydroxy-amino-acid which gave an intense purple coloration on being gently warmed with aqueous ninhydrin solution. The original product is therefore correctly formulated as the α-amino-acid. This conclusion was confirmed by the nitrous acid deamination of the original product whereupon the well-characterised α-hydroxy-β-benzoylpropionic acid was obtained, the structure of which has been established by its preparation by the hydrolysis of chloral-acetophenone (Konigs, *Ber.*, 1882, **15**, 557).

The atypical ninhydrin reaction given by α-amino-β-benzoylpropionic acid is probably due to the immediate interaction of the two degradation products, ammonia and hydroxymethyleneacetophenone, to form the stable aminomethylene compound; the non-availability of the ammonia would preclude the formation of the characteristic deep-blue coloration.

Experimental.—β-Benzoylacrylic acid (5 g.) was dissolved in ammonia (30 c.c.; *d* 0·88). After 16 hours the liquid was concentrated *in vacuo* to about 5 c.c.; the precipitated white solid (4·1 g.) consisting of the keto-amino-acid was filtered off and washed with water. The crude product was dissolved in warm 6N-hydrochloric acid; on cooling the *hydrochloride* crystallised rapidly in plates, m. p. 202° (Found : C, 52·5; H, 5·5; N, 5·9. $C_{10}H_{11}O_3N$,HCl requires C, 52·4; H, 5·3; N, 6·1%). Treatment of an aqueous solution of the hydrochloride with the requisite quantity of dilute ammonia solution resulted in the crystallisation of the free *keto-amino-acid*, which crystallised from aqueous alcohol in plates, m. p. 197° (decomp.; rapid heating) (Found : C, 62·25; H, 5·75; N, 7·15. $C_{10}H_{11}O_3N$ requires C, 62·15; H, 5·75; N, 7·2%).

The presence of the carbonyl, amino-, and carboxyl groups was confirmed by preparation of the relevant derivatives : the *benzoyl* derivative, made by the usual Schotten–Baumann procedure, crystallised from alcohol in needles, m. p. 182° (Found : C, 68·8; H, 5·3; N, 4·9. $C_{17}H_{15}O_4N$ requires C, 68·65; H, 5·1; N, 4·7%); the action of diazomethane in acetone solution on this derivative furnished the corresponding *methyl* ester, m. p. 116°, crystallising from alcohol in needles (Found : C, 69·9; H, 5·5; N, 4·6. $C_{18}H_{17}O_4N$ requires C, 69·5; H, 5·5; N, 4·5%). The action of semicarbazide acetate on the benzoyl derivative yielded the corresponding *semicarbazone*, crystallising from alcohol in needles, m. p. 187° (Found : C, 61·3; H, 5·0; N, 15·6. $C_{18}H_{18}O_4N_4$ requires C, 61·0; H, 5·1; N, 15·8%). Treatment of the benzoyl derivative with ethanolic 2 : 4-dinitrophenylhydrazine sulphate furnished the corresponding 2 : 4-*dinitrophenylhydrazone ethyl* ester, m. p. 196°, crystallising from alcohol in orange rosettes (Found : C, 59·6; H, 4·7; N, 13·8. $C_{25}H_{23}O_7N_5$ requires C, 59·4; H, 4·6; N, 13·85%).

Reduction. The keto-amino-acid (3 g.) was dissolved in the minimum amount of warm aqueous acetic acid (*ca.* 30 c.c.; 20%) and alcohol (70 c.c.) added. Sodium amalgam (from 48 g. of mercury and 2·4 g. of sodium) was added slowly with stirring during two hours; after a further 30 minutes the solution was filtered to remove unchanged material (0·8 g.). The filtrate was concentrated *in vacuo* to 15 c.c.; on cooling the hydroxy-amino-acid (1·5 g.) crystallised. Crystallisation from water gave prisms, m. p. 219° (decomp.; rapid heating) (Bougault and Chabrier, *loc. cit.*, give m. p. 215°) (Found : C, 61·35; H, 6·25; N, 7·2. $C_{10}H_{13}O_3N$ requires C, 61·5; H, 6·7; N, 7·15%). This hydroxy-amino-

acid gave a strongly positive ninhydrin reaction. Although in theory the reduction should produce two racemates in practice only the one product was isolated.

An attempted reduction to α-amino-γ-phenylbutyric acid by a modified Kishner–Wolff procedure (Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487) resulted in the production of γ-phenylbutyric acid.

Deamination. The keto-amino-acid hydrochloride (2 g.) was dissolved in water (10 c.c.), and an aqueous solution of sodium nitrite (1 g.) added slowly in the cold. The solution was filtered from a small amount of gummy material, and the filtrate acidified with dilute sulphuric acid. The resulting turbid solution was kept at 0° for 16 hours. The solid thus formed was filtered off, dried, and crystallised from carbon tetrachloride, from which solvent it formed small prisms, m. p. 125—125·5° undepressed on admixture with an authentic specimen of α-hydroxy-β-benzoylpropionic acid (Rice, *J. Amer. Chem. Soc.*, 1923, **45**, 229, gives m. p. 126°).

If the deamination was carried out in hydrochloric acid solution the product was found to be α-chloro-β-benzoylpropionic acid, m. p. 113° (decomp.) undepressed on admixture with an authentic sample (Bougault, *loc. cit.*, gives m. p. 114°) (Found: C, 56·65; H, 4·35. Calc. for $C_{10}H_9O_3Cl$: C, 56·5; H, 4·25%). This radical interchange during such deamination reactions has been noted before (Jochem, *Z. physiol. Chem.*, 1900, **31**, 119).

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The Oxidation of Anthrone by Aromatic Nitro-compounds. By V. M. Ingram.

Attempts to prepare 10-*m*-nitrodiphenylmethyleneanthrone by the condensation of anthrone with dichloro-*m*-nitrodiphenylmethane in boiling xylene were unsuccessful (cf. Schönberg *et al.*, *J.*, 1946, 442); the nitro-compound acted as an oxidising agent converting the anthrone into dianthron-9-yl.* The same oxidising action was also shown by nitrobenzene, *m*-nitrobenzaldehyde, and *m*-nitrobenzophenone, and it would thus appear to be a general characteristic of aromatic nitro-compounds.

With nitrobenzene, which underwent reduction to aniline, it was found that the yield of dianthron-9-yl was greatly improved by carrying out the oxidation in the presence of hydrogen chloride, but was very seriously diminished when a little piperidine was added to the reaction mixture.

Experimental.—(M. p.s are uncorrected.) *Oxidation of anthrone.* (a) *By dichloro*-m-*nitrodiphenylmethane.* The keto-chloride was prepared by heating molecular proportions of *m*-nitrobenzophenone and phosphorus pentachloride on the water-bath for 8 hours. After being cooled, filtered from unchanged ketone, and freed from phosphorus oxychloride by distillation with petroleum (b. p. 100—120°) under diminished pressure, the crude keto-chloride solidified overnight and was used without further purification.

A solution of anthrone (20 g.) and this chloride (35 g.) in xylene (100 c.c.) was boiled for 2 hours. When cooled the solution deposited dianthron-9-yl (12·5 g., 63%) which, after crystallisation from acetic acid–methyl salicylate (2 : 1), had m. p. 266—267° (decomp.) not depressed by admixture with an authentic specimen prepared according to Barnett (*J.*, 1923, 387).

(b) *By nitrobenzene.* A solution of anthrone (5·0 g.) and nitrobenzene (3·0 c.c.) in dry xylene (30 c.c.), containing a little hydrogen chloride, was boiled under reflux for 5 hours. Leaflets of aniline hydrochloride and drops of water appeared in the condenser, and, when cooled, the liquid, which had become dark orange, furnished dianthron-9-yl (4·2 g., 86%) in an almost pure condition.

The xylene mother-liquor was extracted several times with small portions of dilute hydrochloric acid. On the addition of bromine (in acetic acid) to the acid extract *s*-tribromoaniline was precipitated and corresponded in amount (0·9 g.) to 82% of that required for the formation of the dianthronyl.

In a further experiment in which the same amounts of nitrobenzene and anthrone were employed, but in which the hydrogen chloride was omitted, the yield of dianthron-9-yl fell to 40%, and when the hydrogen chloride was replaced by piperidine (3 drops) the yield was only 6%.

(c) *By* m-*nitrobenzophenone.* After being boiled for 5 hours, a solution of anthrone (2·5 g.) and *m*-nitrobenzophenone (3·0 g.) in dry xylene (15 c.c.) deposited unchanged anthrone. Hydrogen chloride was then passed into the liquid and heating continued for a further 2 hours. Extraction of the resulting crystals with a little boiling acetone followed by crystallisation from glacial acetic acid–methyl salicylate (1 : 1) furnished a small amount (0·25 g., 10%) of dianthron-9-yl.

(d) *By* m-*nitrobenzaldehyde.* A solution of *m*-nitrobenzaldehyde (2·0 g.) and anthrone (2·5 g.) in dry xylene (15 c.c.), after 5 hours' refluxing yielded dianthron-9-yl (0·9 g., 36%).

The oxidation of anthrone to dianthron-9-yl by aromatic nitro-compounds apparently depends on the preliminary treatment of the xylene. In the experiments described above the xylene had been purified by prolonged storage over sodium at ordinary temperature, but other samples which had been more rapidly purified by boiling over sodium, sometimes after previous refluxing with anhydrous aluminium chloride, yielded tarry products from which little or no dianthron-9-yl could be isolated. —Birkbeck College, London, E.C.4. [*Received, April 11th*, 1950.]

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* See footnote, p. 2211.

Preparation of m-*Dimethylaminobenzaldehyde.* By V. M. INGRAM.

m-DIMETHYLAMINOBENZALDEHYDE, which has been previously prepared by Cocker *et al.* (*J.*, 1938, 751) from *m*-nitrobenzaldehyde by a laborious method involving successive conversion into the acetal, reduction, and hydrolysis, followed by the methylation of the resulting *m*-aminobenzaldehyde, can be readily obtained in one operation by the catalytic reduction of *m*-nitrobenzaldehyde in the presence of formaldehyde in alcoholic solution.

Experimental.—(M. p.s and b. p.s are uncorrected.) The catalyst was prepared by stirring a suspension of charcoal (5·0 g.) in an aqueous solution (100 c.c.), containing palladous chloride (1·0 g. dissolved in 1 c.c. of 10N-hydrochloric acid) and hydrated sodium acetate (5·0 g.), in an atmosphere of hydrogen at room temperature and pressure until the absorption of hydrogen ceased. After being filtered off and washed with water, the catalyst was added to a solution of *m*-nitrobenzaldehyde (10·0 g., 0·1 mol.) in alcohol (400 c.c.) containing aqueous formaldehyde (60 c.c.; 40%), and the mixture stirred vigorously in hydrogen at ordinary temperature and pressure. The reduction proceeded rapidly at first, but the rate of absorption slowly decreased until after 5 hours it had fallen to zero; the total volume of hydrogen absorbed amounted to 11 l. (theory, 11·2 l. at N.T.P.).

The solution was filtered from the catalyst and acidified with dilute hydrochloric acid, and most of the alcohol was then removed by distillation. After extraction with ether to remove unchanged nitro-compound, the almost black solution was made alkaline with sodium hydroxide, and the amino-aldehyde collected in benzene. On fractionation of the product under reduced pressure *m*-dimethylaminobenz-aldehyde was obtained as a pale oil (4·0 g., 27%), b. p. 112—114°/3 mm., and was identified by conversion into *ω*-*m*-dimethylaminobenzylideneacetophenone, which had m. p. 105—106°, identical with the value given by Cocker *et al.* (*loc. cit.*).—BIRKBECK COLLEGE, LONDON, E.C.4. [*Received, April* 11*th*, 1950.]

The Reaction of Diacetyl with Ethyl Orthoformate. By D. A. HARRIS.

PARFENT'EV and MIRZAEV (*J. Gen. Chem. Russia*, 1941, **11**, 707) reported that diacetyl reacted with two molecular equivalents of ethyl orthoformate in the presence of a trace of sulphuric acid to give 2 : 2 : 3 : 3-tetraethoxybutane in 69% yield. This reaction has been repeated but the tetraethoxybutane was not obtained. The product, after careful fractionation, showed an absorption band in the ultra-violet ($\varepsilon_{max.}$ 33·8 at $\lambda_{max.}$ 294 mμ.) characteristic in position and intensity for a ketone; and its molecular weight corresponded to that required for 3 : 3-diethoxybutan-2-one. This conclusion was confirmed by a comparison of the physical constants with those reported by Calder and Fleer (U.S.P. 2,401,336; *Chem. Abs.*, 1946, **40**, 5070).

This butanone was prepared more conveniently by reaction of equimolecular proportions of diacetyl and ethyl orthoformate, since the use of two molecular equivalents of the latter gave a product from which the excess of ethyl orthoformate was difficult to fractionate. Another compound with a boiling point between that of ethyl orthoformate and the ketone was formed in a small amount; its presence was detected from its absorption in the ultra-violet at 250 mμ., but it was not identified.

3 : 3-Diethoxybutan-2-one gave the dioxime and disemicarbazone of diacetyl when it reacted with hydroxylamine and semicarbazide, respectively.

Experimental.—Reaction of diacetyl with two molecular equivalents of ethyl orthoformate. Following the directions of Parfent'ev and Mirzaev (*loc. cit.*) diacetyl (14·4 g., 0·167 mol.) was added dropwise to ethyl orthoformate (50·0 g., 0·34 mol.) and sulphuric acid (4 drops). Stirring was continued for four hours at a temperature of 40—50°; the mixture was then taken up in ether, shaken with 10% sodium carbonate solution, washed with water, and dried (K_2CO_3). The ether was removed by distillation and the residue fractionally distilled giving a main fraction (36·8.), b. p. 55—65°/20 mm. Re-fractionation yielded 3 : 3-diethoxybutan-2-one (9·5 g., 36%), b. p. 64—65·5°/19 mm [Found : C, 59·8; H, 10·1%; *M* (cryoscopic in benzene), 167. Calc. for $C_8H_{16}O_3$: C, 60·0; H, 10·0%; *M*, 160].

Reaction of diacetyl with one molecular equivalent of ethyl orthoformate. Equimolecular amounts of diacetyl and ethyl orthoformate reacted exactly as above to give, after fractionation, 3 : 3-diethoxy-butan-2-one (yield, 47·5%), b. p. 66·5—67·5°/20 mm. {Found : C, 59·4; H, 9·9%; *M* (cryoscopic in benzene), 166; n_D^{25} 1·4033; d_4^{25} 0·9217; $[R_L]_D$ 42·39. Calc. for $C_8H_{16}O_3$: C, 60·0; H, 10·0%; *M*, 160; $[R_L]_D$ 42·44}.

By refractionation of the lower-boiling component, fractions were obtained which gave absorption bands at 250 mμ., the fraction in which this band was most pronounced having $E_{1\,cm.}^{1\%}$ 10·1 at $\lambda_{max.}$ 250 mμ.

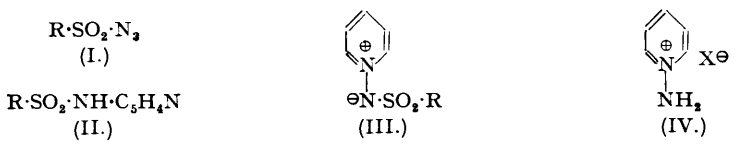
Reaction of 3 : 3-*diethoxybutan-2-one with hydroxylamine and semicarbazide.* The ketone was added to an aqueous solution of hydroxylamine hydrochloride containing sodium acetate and heated. The oxime separated out as colourless crystals, m. p. 233° (after recrystallisation from dilute alcohol) not depressed in admixture with dimethylglyoxime, m. p. 235°.

Reaction with semicarbazide hydrochloride and sodium acetate gave colourless crystals, m. p. 276° (after recrystallisation from glacial acetic acid) not depressed in admixture with diacetyl disemicarbazone, m. p. 279°.

Thanks are due to Mr. F. W. G. Schöning for carrying out the microanalyses and to the South African Council for Scientific and Industrial Research for permission to publish this note.—NATIONAL CHEMICAL RESEARCH LABORATORY, PRETORIA, SOUTH AFRICA. [*Received, April* 25*th*, 1950.]

The Reaction of Some Sulphonazides with Pyridine. By G. L. BUCHANAN and R. M. LEVINE.

THE reaction of sulphonazides (I) with pyridine was first studied by Curtius (*J. pr. Chem.*, 1930, **125**, 303) who formulated the products as sulphonamides of type (II). In no case did he prove the structure, although he demonstrated that on hydrolysis they yielded the corresponding sulphonic acid and a basic material which had the composition of an aminopyridine. In one such case (R = β-naphthyl)



the base gave a picrate and a platinichloride closely resembling those of 2-aminopyridine, but the identity was not tested.

More recently, Ashley, Buchanan, and Easson (*J.*, 1947, 60) and Datta (*J. Indian Chem. Soc.*, 1947, **24**, 109) have proved that *p*-acetamidobenzene- (I; R = *p*-NHAc·C_6H_4·) and toluene-*p*-sulphonazide (I; R = *p*-C_6H_4Me·) give condensation products of type (III) which are hydrolysed to salts (IV) of the unstable free base.

These results suggest that the reaction does not always follow the same course. We have confirmed the results reported by Curtius for two azides (I; R = Ph and *p*-C_6H_4Cl) but not for (I; R = β-$C_{10}H_7$). The products are insoluble in alkali and yield, on hydrolysis, the appropriate sulphonic acid and 1-aminopyridinium salts (IV). We have also confirmed that no rearrangement has occurred during the hydrolysis of the β-naphthyl compound by re-synthesising 1-(naphthalene-β-sulphonimido)pyridine (III; R = β-$C_{10}H_7$) from the hydrochloride (IV; R = Cl) and naphthalene-β-sulphonyl chloride.

These results establish the point of attachment to the pyridine nucleus. Hence the condensation product are of type (III).

Experimental.—Pyridine was previously redistilled and dried over potassium hydroxide pellets, although we have no reason to believe this to have been necessary. The azides were prepared in 83—89% yield from the corresponding sulphonyl chlorides and sodium azide, by the aqueous acetone method described by Ashley *et al.* (*loc. cit.*). Condensations were effected as described by Curtius except where otherwise stated. Hydrolysis products or their salts were identified by mixed m. p. determinations.

1-Benzenesulphonimidopyridine (III; R = Ph), prepared from the azide (90 g.) and pyridine (1·5 l.) and recrystallised from methanol, had m. p. 152° (36 g.) and gave a hydrochloride, m. p. 198—200°. Although isolation (cf. Curtius) involves dissolving the tarry crude product in alkali and reprecipitating it with acid, the pure product is not soluble in alkali, but dissolves in acids. The anomalous properties of the tar must be due to acidic by-products (see Ashley *et al.*, *loc. cit.*) and the solvent action of residual pyridine.

1-(*p*-Chlorobenzenesulphonimido)pyridine (III; R = *p*-C_6H_4Cl·) was prepared by boiling the azide (85 g.) and pyridine (1·5 l.) for 48 hours. The excess of pyridine was distilled off under reduced pressure, and the dark residual tar treated with methanol. Next morning, the product which had crystallised was recrystallised from alcohol, forming colourless prisms, m. p. 182° (40 g.) (Found: C, 48·9; H, 3·4; N, 10·4. $C_{11}H_9O_2N_2SCl$ requires C, 49·2; H, 3·35; N, 10·4%), insoluble in alkali, but soluble in acid, and yielding a picrate m. p. 192°.

1-(Naphthalene-β-sulphonimido)pyridine (III; R = β-$C_{10}H_7$), prepared from the azide (90 g.) and pyridine (1·5 l.) at the b. p. (72 hours), was isolated as described above for the *p*-chloro-compound. Recrystallisation from water yielded colourless crystals, m. p. 197—198° (23 g.), soluble in acids but insoluble in alkali and yielding a picrate, m. p. 199—200° (Curtius gives 192°).

Hydrolysis of 1-*benzenesulphonimidopyridine.* The conditions successfully employed by Ashley *et al.* (*loc. cit.*), namely boiling for a few hours with *ca.* 6N-hydrochloric acid, were ineffective.

The substance (1 g.) in concentrated hydrochloric acid (15 c.c.) was heated at 150° for 2½ hours. Evaporation on the steam-bath then yielded a hygroscopic product, m. p. 110°, probably the crude benzenesulphonate described by Curtius as having m. p. 115°, but an attempt to free the base with alkali led to darkening and liberation of pyridine. This would be difficult to explain if the base were 2-, 3-, or 4-aminopyridine, but agrees with the properties of 1-aminopyridinium salts, as described by Ashley *et al.* (*loc. cit.*). The hygroscopic sulphonate yielded 1-aminopyridinium picrate [IV; X = O·$C_6H_2(NO_2)_3$], m. p. 152°, and *S*-benzylthiuronium benzenesulphonate, m. p. 146°.

Hydrolysis of 1-(p-*chlorobenzenesulphonimido*)*pyridine.* The conditions described above were necessary and the base could not be isolated by treatment with alkali. It was identified as 1-aminopyridinium picrate, m. p. 152°. The *p*-chlorobenzenesulphonic acid was identified as its *S*-benzylthiuronium salt, m. p. 173—174°.

Hydrolysis of 1-(*naphthalene-β-sulphonimido*)*pyridine.* In order to confirm that no rearrangement occurs under the conditions of hydrolysis, this was carried out in three ways. The second and third correspond to those employed by Curtius (*loc. cit.*).

(*a*) The compound (5 g.) in hydrochloric acid (45 c.c.; *ca.* 8N.) was refluxed for 4½ hours. On cooling, naphthalene-β-sulphonic acid separated and was identified as its *S*-benzylthiuronium salt, m. p. 188—189°. The filtrate was concentrated on the steam-bath, to a syrup, and treated with aqueous picric

acid, yielding 1-(naphthalene-β-sulphonimido)pyridine picrate, m. p. 199—200°, and the mother-liquors therefrom gave 1-aminopyridinium picrate, m. p. 152°.

(*b*) The compound (5 g.) in concentrated hydrochloric acid (40 c.c.) was boiled for 12 hours. Naphthalene-β-sulphonic acid crystallised out and was identified as above. A portion of the filtrate was concentrated to a syrup and triturated with alcohol. The resulting 1-aminopyridinium chloride, recrystallised from alcohol, had m. p. 158—160°. The remainder of the filtrate was treated with aqueous picric acid; in spite of Curtius's claim to have isolated a picrate of m. p. 216—217°, we isolated only 1-aminopyridinium picrate, m. p. 152°.

(*c*) The compound (5 g.) in concentrated hydrochloric acid (20 c.c.) was heated at 125° for 7 hours. Naphthalene was isolated in almost quantitative yield. The filtrate, concentrated to a syrup and treated with aqueous picric acid, gave only 1-aminopyridinium picrate, m. p. 152°.

Re-synthesis of 1-*(naphthalene-β-sulphonimido)pyridine.* To naphthalene-β-sulphonyl chloride (1·7 g.) in acetone (5 c.c.) there were added 1-aminopyridinium chloride (1 g.) in water (2 c.c.), and then solid potassium carbonate till the solution was alkaline, and further amounts of carbonate, water, and acetone till a homogeneous solution was obtained. This was shaken for some time and left overnight. The acetone was removed. The solid product which separated was recrystallised from alcohol and then had m. p. 198° (1·5 g.), alone or when mixed with the reaction product described above. The picrates, m. p. 199—200°, were similarly shown to be identical, and the synthetic material gave a nitrate of m. p. 156—157°, which agreed with that quoted by Curtius (*loc. cit.*).

The micro-analysis was carried out by Miss R. H. Kennaway.—UNIVERSITY OF GLASGOW. [*Received, May 4th,* 1950.]

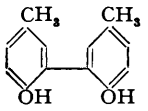
Reactions of Ferric Chloride with o- *and* p-*Cresol.* By K. BOWDEN and C. H. REECE.

WITH ferric chloride α- and β-naphthol have long been known to give dinaphthols (Dianin, *J. Russ. Phys. Chem. Soc.*, 1874, **6**, 183). The action of the same reagent on simple phenols not containing a bicyclic system but having a methyl group in the *ortho*- or the *para*-position has now been examined.

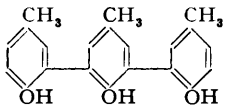
Anhydrous ferric chloride, or ferric chloride hexahydrate, with *p*-cresol under mild conditions gives the diphenyl derivative (I) and the terphenyl derivative (II). In a dilute aqueous solution the compound (I) is formed, together with a neutral compound to which Pummerer *et al.* (*Ber.*, 1925, **58**, 1808) assigned the structure (III) (cf. Westerfield and Lowe, *J. Biol. Chem.*, 1942, **145**, 463). There was no reaction between ferric chloride and *p*-cresol in 10% hydrochloric acid.

o-Cresol with ferric chloride hexahydrate or an ethereal solution of anhydrous ferric chloride gave a polyphenol of unknown constitution.

Experimental.—Reaction of anhydrous ferric chloride with p-*cresol.* *p*-Cresol (21 g.) and anhydrous ferric chloride (35 g.) were stirred together at 30° for 12 hours, hydrogen chloride being evolved. The product was extracted with benzene (100 c.c.), and the extract washed with dilute hydrochloric acid,



(I.)



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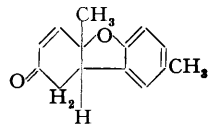

(III.)

dried (Na_2SO_4), and distilled under reduced pressure to give unchanged *p*-cresol (13·1 g.), 2 : 2′-dihydroxy-5 : 5′-dimethyldiphenyl (I) (2·2 g.), m. p. 154°, b. p. 160—175° (air-bath temp.)/10^{-4} mm., and 2 : 2′ : 2″-trihydroxy-5 : 5′ : 5″-trimethyl-*m*-terphenyl (II) (1·2 g.), m. p. 197°, b. p. 200—220° (air-bath temp.)/2×10^{-4} mm.

Reaction of ferric chloride hexahydrate with p-*cresol.* Ferric chloride hexahydrate (50 g.) and *p*-cresol (21 g.) were stirred together at 35—40° for 12 hours, giving the diphenyl (I) (2·4 g.) and the terphenyl derivative (II) (1·9 g.).

Reaction of ferric chloride with p-*cresol in dilute aqueous solution.* *p*-Cresol (21 g.) and ferric chloride hexahydrate (65 g.) in water (3 l.) were stirred together for 4 hours at 20°, the solution changing from orange to green. A white precipitate which formed was filtered off and dissolved in ether, and the ethereal solution extracted with 8% sodium hydroxide solution (100 c.c.). After being dried (Na_2SO_4), the ethereal solution was evaporated, to give a solid (III) which crystallised from alcohol as colourless plates, m. p. 128° (0·3 g.) (Found: C, 78·7; H, 6·4. Calc. for $C_{14}H_{14}O_2$: C, 78·5; H, 6·5%). The compound gave an oxime, m. p. 195° (cf. Pummerer *et al.*, *Ber.*, 1922, **55**, 3116). On acidification of the alkaline extract the diphenyl derivative (I) was obtained which, crystallised from *cyclo*hexane, had m. p. 154° (1·1 g.).—THE UNIVERSITY, LEEDS, 2. [*Received, May 5th,* 1950.]

The Conversion of Aromatic Aldehydes into Primary Amines by a Simple Adaptation of the Leuckart Reaction. By K. G. LEWIS.

THE Leuckart reaction was first discovered in the reaction of benzaldehyde with formamide or ammoniun formate and yielded mainly tribenzylamine with a trace of benzylamine. In its subsequent application the reaction has found its principal use in the formation of primary amines from ketones of various types. During application of the reaction to various simple alicyclic ketones conditions were found

that markedly improved the yields of primary amine; *e.g.*, *cyclo*hexylamine was obtained from *cyclo*hexanone in 75% yield.

In view of recent statements (Moore, " The Leuckart Reaction " in " Organic Reactions," Vol. V, Wiley and Sons, New York, 1949, and Angyal and Rassack, *Nature*, 1948, **161**, 723) in regard to the non-formation of primary amines from aromatic aldehydes by this reaction, it was considered of interest to apply to these substances the conditions so successful with *cyclo*hexanone.

The modified Leuckart reaction, applied to various available aromatic aldehydes and to furfuraldehyde, gave the corresponding primary amines of the benzylamine type in yields ranging from 62 to 15%. In agreement with the work of Crossley and Moore (*J. Org. Chem.*, 1944, **9**, 529) it was found that hydrolysis of the whole reaction mixture, and not only of the extracted crude formyl derivative, led to improved yields: *e.g.*, benzylamine, 60% compared with 43%; *cyclo*hexylamine, 75% compared with 40%.

Experimental.—The general procedure used was as follows: The aldehyde (0·1 mol.) was added drop-wise with shaking to 50 g. (0·8 mol.) of ammonium formate (or the corresponding amount of ammonium formate–formamide reagent prepared according to Ingersoll, *J. Amer. Chem. Soc.*, 1936, **58**, 1808) at 165°. The reaction was carried out in a three-necked flask to which was attached a short column connected for distillation. The reaction temperature was raised as soon as possible to 185—190° and maintained in this range while the remainder of the aldehyde was added. Initially some of the aldehyde distilled, but as the reaction proceeded it largely reacted without loss. The aldehyde that distilled was recovered and returned to the reaction mixture. The addition required 30—40 minutes in most cases and the reaction was substantially complete in about 3 hours at 185—190° (including the time of addition). The reaction mixture was cooled, concentrated hydrochloric acid (100 ml.) added, the mixture refluxed for 2 hours, then made strongly alkaline, and the amine steam-distilled into hydrochloric acid. This solution was evaporated, the residue was made alkaline and the amine recovered by extraction and distillation.

The amines which were prepared and the yields obtained are set out in the Table. The derivatives were prepared by standard procedures and the m. p.s agreed with those recorded in the literature.

Amine.	Yield, %.	B. p./680 mm.	Derivatives (m. p.s, uncorr.; d. = decomp.).
Benzylamine	60	180—182°	Picrate, 197—198°; *N*-benzoyl, 105°.
p-Methylbenzylamine	62	198—200	Picrate, 205° d.; *N*-benzoyl, 137—138°.
o-Methoxybenzylamine ...	30	218—220	Hydrochloride, 150°; *N*-acetyl, 96—97°.
p-Methoxybenzylamine ...	23	232—234	Picrate, 188°; *N*-acetyl, 96°.
m-Nitrobenzylamine [1]	41	—	Hydrochloride, 224°; nitrate, 182—183°.
Furfurylamine [2]	15	140—142	Picrate, 183—184° d.; oxalate, 145—147°.

[1] *m*-Nitrobenzaldehyde was added to the reaction mixture dissolved in nitrobenzene; the amine was isolated as the hydrochloride. [2] In this case the crude formyl derivative was isolated and hydrolysed with 30% sodium hydroxide.

Acknowledgment is made to the Commonwealth Science Research Fund for financial assistance.—
NEW ENGLAND UNIVERSITY COLLEGE, ARMIDALE, N.S.W., AUSTRALIA. [*Received, May 22nd,* 1950.]

A Note on the Isomeric Benzoate–Toluene-p-sulphonates of Propylene Glycol. By G. A. HAGGIS and L. N. OWEN.

THE opening of the epoxide ring in propylene oxide under various conditions has been studied by many investigators (*inter al.*, Petrov, *J. Gen. Chem. Russia*, 1944, **14**, 1038; Chitwood and Freure, *J. Amer. Chem. Soc.*, 1946, **68**, 680; Swern, Billen, and Knight, *ibid.*, 1949, **71**, 1152; Reeve and Sadle, *ibid.*, 1950, **72**, 1251), and it has generally been found that under acid conditions ring-opening occurs in both of the possible directions to give a mixture of the primary and secondary products:

$$CH_3\cdot\overset{\diagup O \diagdown}{CH}\cdot CH_2 + HX \longrightarrow CH_3\cdot CH(OH)\cdot CH_2X + CH_3\cdot CHX\cdot CH_2\cdot OH$$

Chapman and Owen (*J.*, 1950, 579) found that by treatment of propylene oxide with toluene-*p*-sulphonic acid in dry ether, followed by benzoylation of the product, a mixture of the two isomeric benzoate–toluene-*p*-sulphonates of the diol was obtained, from which, by fractional crystallisation, 2-toluene-*p*-sulphonyloxypropyl benzoate, m. p. 104°, was isolated. The residual material, m. p. 79°, was shown to be a mixture of this compound with 1-toluene-*p*-sulphonyloxyprop-2-yl benzoate, but fractional crystallisation failed to effect any further separation. In a renewed investigation of this mixture, we have now found that by slow crystallisation from light petroleum two distinct types of crystals are formed, and pure 1-toluene-*p*-sulphonyloxyprop-2-yl benzoate, m. p. 93°, has thereby been obtained. Both compounds have also been prepared by selective esterification of propylene glycol.

It has already been shown (Chapman and Owen, *loc. cit.*) that the two isomers differ in their rates of reaction with potassium thiolacetate; this has now been found to be the case also with sodium iodide. Furthermore, the product thus formed from the compound of m. p. 104° is 2-iodopropyl benzoate, since on hydrogenation it furnishes *n*-propyl benzoate; this provides rigid proof of the structures.

Reaction of propylene oxide in aqueous solution with benzoic acid and potassium benzoate gave mainly (but not exclusively) the primary benzoate of propylene glycol, since the product, on toluene-*p*-sulphonation, consisted largely of the benzoate–toluene-*p*-sulphonate m. p. 104°. According to Fraenkel-Conrat and Olcott (*J. Amer. Chem. Soc.*, 1944, **66**, 1420), carboxylic acids react with propylene

oxide under these conditions to give only the primary esters, but their evidence is open to criticism. It is stated, for instance, that the compound obtained when the reaction is carried out with butyric acid is the pure 1-butyrate because it is identical (in refractive index) with that prepared by the reaction of sodium butyrate with 1-chloropropan-2-ol; since, however, a rearranged product (derived *via* a cyclic intermediate) may well be formed in the latter reaction, deduction of structure by such means is clearly unwarranted (compare Ross, *J.*, in the press).

Toluene-p-*sulphonyloxypropyl Benzoates.*—Propylene oxide was treated with toluene-*p*-sulphonic acid in dry ether, and the product was benzoylated, according to the procedure of Chapman and Owen (*loc. cit.*). Fractional crystallisation of the crude material from benzene–light petroleum (b. p. 60—80°) gave, as before, 2-toluene-*p*-sulphonyloxypropyl benzoate, m. p. 104°, and the mixture of isomers, m. p. *ca.* 79°. Slow crystallisation of this mixture from a dilute solution in light petroleum (b. p. 60—80°) gave a mixture of plates and needles. By careful warming and stirring, the needles were found to redissolve in the supernatant liquid more readily than the plates; the latter were then collected and were substantially pure 2-toluene-*p*-sulphonyloxypropyl benzoate, m. p. 101—103°, raised to 103—104° after one recrystallisation. Concentration of the mother-liquors, and repetition of the process several times, eventually resulted in the deposition of needles only; recrystallisation of this material from methanol then gave needles of 1-*toluene*-p-*sulphonyloxyprop*-2-*yl benzoate*, m. p. 93° (Found: C, 61·0; H, 5·45; S, 9·25. $C_{17}H_{18}O_5S$ requires C, 61·05; H, 5·4; S, 9·6%). Mixed m. p. determinations with various proportions of the isomers gave the following results:

Secondary benzoate, %	0	10	20	29	43
M. p.	104°	90—100°	80—95°	77—85°	76—80°
Secondary benzoate, %	50	57	75	90	100
M. p.	76—78°	76—78°	76—79°	80—86°	93°

Monoesterification of Propylene Glycol.—(i) Propylene glycol (5 g.) was dissolved in pyridine (100 c.c.) and the solution was cooled to 0°. A solution of toluene-*p*-sulphonyl chloride (12·5 g., 1·05 mols.) in pyridine (50 c.c.) was added in portions of 0·5 c.c. during 4 days. After removal of most of the pyridine under reduced pressure, the residue was taken up in chloroform and washed with dilute sulphuric acid, sodium hydrogen carbonate solution, and finally with water. After being dried (Na_2SO_4), the solvent was removed to give a brown viscous oil (5·9 g.) n_D^{20} 1·5135, which was dissolved in pyridine (30 c.c.), cooled to 0°, and treated with benzoyl chloride (7 g.). After 2 hours the solution was poured into water and worked up as above to give a dark oil which partly crystallised on addition of light petroleum. The crude solid was collected and recrystallised from methanol to give 1-toluene-*p*-sulphonyloxyprop-2-yl benzoate (1·9 g.), m. p. 92—93°, identical with that obtained previously.

(ii) Propylene glycol (5 g.) was dissolved in pyridine (50 c.c.) and cooled to 0°. A solution of benzoyl chloride (8·25 g.; 1·04 mols.) in pyridine (100 c.c.) was added in 0·5-c.c. portions during 4 days. Working up as above gave an oil, which on distillation gave propylene glycol monobenzoate (1·8 g.), b. p. 93—97°/2 mm., n_D^{20} 1·5229. Reaction of this oil with toluene-*p*-sulphonyl chloride (2·1 g.) in pyridine (15 c.c.) gave a product which on crystallisation from benzene–light petroleum (b. p. 60—80°) gave a main crop (1·2 g.) of 2-toluene-*p*-sulphonyloxypropyl benzoate, m. p. 104°.

Reactivity towards Sodium Iodide.—Each of the isomeric compounds (0·1 g.) was separately treated under identical conditions with a boiling solution of sodium iodide (0·15 g.) in acetone (6 c.c.) for 2½ hours under reflux. The solutions were cooled and filtered, and the precipitated sodium toluene-*p*-sulphonate was washed with cold acetone (5 c.c.) and dried. The yields (uncorrected for slight solubility in acetone) were: from the primary toluene-*p*-sulphonate, 0·028 g. (48%); from the secondary, 0·005 g. (9%).

2-*Iodopropyl Benzoate.*—2-Toluene-*p*-sulphonyloxypropyl benzoate (20 g.) in acetone (240 c.c.) containing sodium iodide (20 g.) was heated under reflux for 20 hours; precipitation of sodium toluene-*p*-sulphonate began after 30 minutes. The solid was filtered off, washed with acetone, and dried (Yield, 10·7 g.; calc., 10·8 g.). Acetone was removed from the filtrate by distillation, and water was added to the residue. The oil was extracted into light petroleum (b. p. 40—60°) and washed with aqueous sodium thiosulphate and with water. After drying (Na_2SO_4) and removal of solvent, distillation gave 2-*iodopropyl benzoate* as a pale yellow oil (13·2 g.), b. p. 96—98°/0·3 mm., n_D^{19} 1·5668 (Found: C, 40·9; H, 3·7; I, 45·8. $C_{10}H_{11}O_2I$ requires C, 41·4; H, 3·82; I, 43·75%). The slight discrepancy in analysis may be due to the formation of a trace of propylene di-iodide by replacement of the benzoate group.

Hydrogenation of 2-*Iodopropyl Benzoate.*—The ester (12·6 g.) was dissolved in methanol (160 c.c.) containing potassium acetate (5 g.) and hydrogenated at atmospheric pressure over Adams's platinum catalyst (0·4 g.). When uptake was complete the catalyst was filtered off, the solvent removed by distillation, and water added to the residue. The ester was extracted with light petroleum (b. p. 40—60°) and dried (Na_2SO_4). After removal of solvent, distillation gave *n*-propyl benzoate, b. p. 105—110°/13 mm., n_D^{19} 1·4994 (lit., n_D^{20} 1·5000). This was hydrolysed with aqueous 10% potassium hydroxide, and the resulting alcohol was characterised (*a*) as *n*-propyl 3 : 5-dinitrobenzoate, m. p. and mixed m. p. 72°, and (*b*) by oxidation with chromic acid and formation of propaldehyde 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 152°.

Reaction of Propylene Oxide and Benzoic Acid. (With J. H. Chapman.)—Propylene oxide (40 g.) was dissolved in water (400 c.c.) containing potassium hydroxide (1·0 g.). Benzoic acid (20 g.) was added, followed by sufficient acetone (*ca.* 150 c.c.) to give a homogeneous solution; after 5 days, a further 40 g. of propylene oxide were added. At the end of a further 5 days the solution was still acidic. Acetone was removed under reduced pressure and the aqueous solution was neutralised with sodium hydrogen carbonate and extracted with ether. The extract was dried (Na_2SO_4), concentrated, and distilled to give the benzoate as a colourless oil, b. p. 105—111°/0·4 mm., n_D^{19} 1·5170—1·5213 (9·8 g.).

This was treated in pyridine (50 c.c.) with toluene-*p*-sulphonyl chloride (11·7 g.), and gave a solid (14 g.), m. p. 75—95°, which by two recrystallisations from methanol gave 2-toluene-*p*-sulphonyloxypropyl benzoate (8 g.), m. p. and mixed m. p. 104°.—IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, SOUTH KENSINGTON, LONDON, S.W.7. [*Received, May 25th,* 1950.]

The Addition of Osmium Tetroxide to Dinaphthylethylenes. By C. A. COULSON.

IN a recent letter to *Nature* having the same heading as this note, Badger (*Nature*, 1950, **165**, 647) has shown experimentally that osmium tetroxide adds to the three *cis*- and *trans*-dinaphthylethylenes at a rate $\beta\beta > \alpha\beta > \alpha\alpha$. It has generally been presumed that, other things being equal, the rate of addition depended on the double-bond character of the bond to which the addition occurs—here the central ethylene link. This presumption would receive further support if it could be shown that the bond orders were also in the sequence $\beta\beta > \alpha\beta > \alpha\alpha$. Badger gives reasons why this is likely to be so. The argument depends on the known greater conjugating power (Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1948, *A*, **195**, 188) of naphthalene at the α- than at the β-position; but no absolute calculations of the bond order have hitherto been made. For that reason the three bond orders have now been calculated, and are shown below. Standard molecular-orbital technique was used, with numerical integration as in some earlier work (Coulson and Jacobs, *J.*, 1949, 2805). The values are: $\beta\beta$ 1·814, $\alpha\beta$ 1·803, $\alpha\alpha$ 1·792. The sequence is precisely what was expected, the differences between the three values being of the same order of magnitude as those commonly found (Berthier, Coulson, Greenwood, and Pullman, *Compt. rend.*, 1948, **226**, 1906) in polynuclear hydrocarbons, the addition of osmium tetroxide to which has been studied fairly fully (cf. Badger, *J.*, 1949, 456). To this extent, then, the present calculations provide further support for the general interpretation of this addition reaction.

It may be worth comparing the values for the ethylenic bond orders in the dinaphthylethylenes with the value in stilbene (1·820). Thus the replacement of two phenyl by two naphthyl groups increases the conjugation over the whole molecule and therefore weakens the central bond. A similar situation was fully discussed in a variety of other systems by Coulson and Jacobs (*loc. cit.*).—WHEATSTONE PHYSICS LABORATORY, KING'S COLLEGE, LONDON. [*Received, May 23rd,* 1950.]

6-*Ethyl*-1 : 3-*dimethylnaphthalene and* 1-*Ethyl*-1 : 2 : 3 : 4-*tetrahydro*-5-*hydroxy*-7 : 8-*dimethylnaphthalene.* By WESLEY COCKER and BRIAN E. CROSS.

6-ETHYL-1 : 3-DIMETHYLNAPHTHALENE has been prepared from 7-ethyl-1 : 2 : 3 : 4-tetrahydro-1-keto-2 : 4-dimethylnaphthalene (Cocker *et al.*, *J.*, 1950, in the press) by Clemmensen reduction to the tetralin, followed by dehydrogenation with palladised charcoal. The naphthalene was characterised as its picrate and its trinitrobenzene and trinitrotoluene adducts.

Catalytic hydrogenation of 1-ethyl-3 : 4-dihydro-5-methoxy-7 : 8-dimethylnaphthalene (Cocker, *et al.*, *loc. cit.*) followed by demethylation yielded 1-ethyl-1 : 2 : 3 : 4-tetrahydro-5-hydroxy-7 : 8-dimethylnaphthalene.

Experimental.—6-*Ethyl*-1 : 3-*dimethylnaphthalene.* 6-*Ethyl*-1 : 2 : 3 : 4-*tetrahydro*-1 : 3-*dimethylnaphthalene* (Found: C, 89·05; H, 10·35. $C_{14}H_{20}$ requires C, 89·4; H, 10·6%) was obtained as a colourless liquid (1·4 g.), b. p. 128—129°/10 mm., when 7-ethyl-1 : 2 : 3 : 4-tetrahydro-1-keto-2 : 4-dimethylnaphthalene (Cocker *et al.*, *loc. cit.*) (2·3 g.) was refluxed for 40 hours with amalgamated zinc (70 g.), concentrated hydrochloric acid (90 c.c.), and water (50 c.c.).

The tetralin (1·0 g.) was heated with palladised charcoal (0·9 g.) at 250—270° for 5 hours. The product was extracted with ether and distilled over sodium, yielding the *naphthalene* (0·84 g.), b. p. 148—150°/10 mm. (Found: C, 91·1; H, 9·1. $C_{14}H_{16}$ requires C, 91·3; H, 8·7%). Its *picrate* crystallised from methanol as rosettes of orange needles, m. p. 70° (Found: C, 58·1; H, 5·0. $C_{20}H_{19}O_7N_3$ requires C, 58·1; H, 4·6%). Its *trinitrobenzene* derivative crystallised from methanol as lemon-yellow needles, m. p. 97° (Found: C, 60·8; H, 4·8. $C_{20}H_{19}O_6N_3$ requires C, 60·45; H, 4·8%). Its *trinitrotoluene* adduct crystallised from methanol as lemon-yellow needles, m. p. 43·5° (Found: C, 61·2; H, 5·15. $C_{21}H_{21}O_6N_3$ requires C, 61·3; H, 5·1%).

1-*Ethyl*-1 : 2 : 3 : 4-*tetrahydro*-5-*hydroxy*-7 : 8-*dimethylnaphthalene.* 1-Ethyl-3 : 4-dihydro-5-methoxy-7 : 8-dimethylnaphthalene (Cocker *et al.*, *loc. cit.*) (3·33 g.) and palladised charcoal (2·0 g.) in ethyl acetate (50 c.c.) were shaken in hydrogen, giving the methoxy-tetralin (3·08 g.), b. p. 147—150°/6 mm. The methoxy-compound was refluxed for 2 hours with redistilled hydriodic acid (12 c.c.) and glacial acetic acid (15 c.c.). The *hydroxy*-compound, b. p. 146—152°/6 mm., crystallised from light petroleum (b. p. 40—60°); m. p. 59—60° (Found: C, 82·05; H, 9·55. $C_{14}H_{20}O$ requires C, 82·35; H, 9·8%).—CHEMICAL LABORATORY, TRINITY COLLEGE, DUBLIN. [*Received, June 6th,* 1950.]
