NOTES.

The Resolution of n-*Heptan*-2-*ol.* *By* J. KENYON *and* A. M. WALCH.

BY application of the simplified procedure for the resolution of *n*-octan-2-ol (Kenyon, *J.*, 1922, **121**, 2540), the closely related *n*-heptan-2-ol has been readily resolved into its optically pure isomerides.

Experimental.—A commercial sample of *n*-heptan-2-ol distilled almost completely at 158°.

(±)-*Heptyl hydrogen phthalate.* A mixture of the alcohol (64 g.), phthalic anhydride (82 g.), and pyridine (100 g.) was heated on the steam-bath for 3 hours, and the resulting homogeneous liquid cooled and diluted with 3 volumes of acetone, and the whole made acid (Congo-red) by addition of hydrochloric acid (1 : 1).

After the addition of several litres of iced water the hydrogen phthalic ester separated as an oil which soon became crystalline. This was filtered off and washed with very dilute hydrochloric acid, to remove the last traces of pyridine, and then with water. After being dried the ester (132 g.) had m. p. 57·5—58°.

(+)-*Heptyl hydrogen phthalate.* Brucine, anhydrous (197 g.) or the tetrahydrate (233 g.), was dissolved in a hot solution of the (±)-ester (132 g.) in acetone (700 c.c.); the crystalline brucine salt began to separate almost immediately. After several hours this was filtered off, washed with acetone (300 c.c.), and heated on the steam-bath with acetone (2 l.). The resulting suspension was then cooled and filtered. This extraction was repeated twice more; the dried brucine salt (143 g.) had m. p. 137—138°. By evaporation of the acetone extraction liquors, a further crop (11 g.) of the brucine salt, m. p. 136—137°, was obtained.

The combined brucine salts (154 g.) were covered with acetone (300 c.c.) and decomposed by slightly more than the calculated amount of 6N-hydrochloric acid; addition of iced water (2 l.) precipitated an oil which rapidly set to a crystalline mass (55 g.). This, after 2 or 3 recrystallisations from acetic acid (about 90%), gave optically pure (+)-2-heptyl hydrogen phthalate (47 g.), m. p. 74·5—75°, $[\alpha]_{6438}$ + 38·7°, $[\alpha]_{5893}$ + 48·5°, $[\alpha]_{5461}$ + 58·7°, $[\alpha]_{5086}$ + 71·4°, $[\alpha]_{4358}$ + 108·5° (*c*, 4·995; *l*, 2; in absolute ethyl alcohol at 20°). The values of λ^2 plotted against $1/\alpha$ lie on a straight line.

(−)-*Heptyl hydrogen phthalate.* The various filtrates and wash-liquors from which the less soluble brucine salt had been removed were concentrated to about 300 c.c.; after several hours a small amount of the less soluble brucine salt which had separated was filtered off and kept for incorporation in a subsequent resolution. Decomposition of the final filtrate with hydrochloric acid yielded an acid phthalic ester (62 g.), from which by 3 or 4 recrystallisations from acetic acid (about 90%) there was obtained optically pure (−)-2-heptyl hydrogen phthalate (40 g.), m. p. 74·5—75°, $[\alpha]_{5893}^{19}$ −48·3° (*c*, 5·0280; *l*, 2; in absolute ethyl alcohol).

These rotatory powers agree closely with those of the two acid esters prepared by Pickard and Kenyon (*J.*, 1911, **99**, 63) which, by hydrolysis with aqueous sodium hydroxide, yielded the optically pure (+)- and (−)-heptan-2-ols in almost theoretical amounts.

The award of a grant from Imperial Chemical Industries Ltd, is gratefully acknowledged.—BATTERSEA POLYTECHNIC, LONDON, S.W.11. [*Received, May* 21*st*, 1949.]

The Preparation of Some Esters of 3 : 3-*Dimethylbutanol and* 3 : 3-*Dimethylpentanol.*

By ARTHUR J. BIRCH.

FOR an investigation of the specificities of the human-erythrocyte and the human-plasma cholinesterase (Adams and Whittaker, *Biochem. J.*, 1948, **43**, xiv; *Biochem. et Biophys. Acta*, 1949, **3**, 358; Adams, *ibid.*, 1949, **3**, 1) it was necessary to prepare some analogues of acylcholines having a carbon atom in place of the quaternary nitrogen. Although 3 : 3-dimethylbutanol has been prepared, the yields by most methods are bad (*e.g.*, Strating and Backer, *Rec. Trav. chim.*, 1936, **55**, 903; Huston and Agett, *J. Org. Chem.*, 1941, **6**, 123). The most satisfactory method appears to be the Bouveault–Blanc reduction of ethyl ββ-dimethylbutyrate (Sutter, *Helv. Chim. Acta*, 1938, **21**, 1266) which is fairly readily available from the oxidation of di*iso*butylene (Homeyer, Whitmore, and Wallingford, *J. Amer. Chem. Soc.*, 1933, **55**, 4209), or by the Willgerodt reaction on pinacone (Cavalieri, Pattison, and Carmack, *ibid.*, 1945, **67**, 1785).

A general method of preparing this acid and its homologues is that of Birch and Robinson (*J.*, 1942, 501; cf. Hook and Robinson, *J.*, 1944, 152; Wideqvist, *Arkiv Kemi., Min. Geol.*, 1946, *B*, **23**, no. 4) and 3 : 3-dimethylbutanol (R′ = R″ = R‴ = Me) and 3 : 3-dimethylpentanol (R′ = R″ = Me, R‴ = Et) have now been made by the following reactions :

$$\mathrm{CR'R''{:}C(CN){\cdot}CO_2Et + R'''MgX \longrightarrow CR'R''R'''{\cdot}CH(CN){\cdot}CO_2Et \longrightarrow CR'R''R'''{\cdot}CH_2{\cdot}CN \longrightarrow}$$
$$\mathrm{CR'R''R'''{\cdot}CH_2{\cdot}CO_2H \longrightarrow CR'R''R'''{\cdot}CH_2{\cdot}CO_2Et \longrightarrow CR'R''R'''{\cdot}CH_2{\cdot}CH_2{\cdot}OH.}$$

Moreover, by alkylating the intermediate cyanoacetic esters it should be possible to make the 2-alkyl derivatives.

3 : 3-*Dimethylbutanol.*—Ethyl α-cyano-β-methylcrotonate (prepared according to Cope, *J. Amer. Chem. Soc.*, 1937, **59**, 2327) (17 g.) was cooled in ice and the Grignard reagent, from methyl iodide (22 g.) and magnesium (3·5 g.) in ether (100 c.c.), was slowly added with stirring. After decomposition of the complex with ice and hydrochloric acid (5%) the ether layer was collected and distilled, giving a colourless oil with a sweet camphor-like odour (7 g.), b. p. 103—105°/14 mm. This was warmed with sodium hydroxide solution (50 c.c.; 10%) to 50° for 5 minutes with vigorous shaking, and dissolved to a yellow solution. Acidification of this solution gave an oil which rapidly solidified to prisms (5 g.), m. p. 100°. This solid was dried and distilled from an oil-bath at 200° in the presence of copper powder (0·2 g.), whereupon smooth decarboxylation took place, and ββ-dimethylbutyronitrile distilled as a colourless oil with a camphor-like odour (3·2 g.), b. p. 137°, m. p. 28—30° (Found : C, 74·2; H, 11·1; N, 13·9. Calc. for

$C_6H_{11}N$: C, 74·2; H, 11·3; N, 14·4%). Homeyer, Whitmore, and Wallingford (*loc. cit.*) give m. p. 32·5°.

The nitrile was hydrolysed by being heated under reflux with concentrated sulphuric acid (5 c.c.), acetic acid (5 c.c.), and water (5 c.c.) for 3 hours. The acid product was isolated by dilution with water (30 c.c.) and ether extraction, followed by extraction from the ether with potassium carbonate solution (10%) and re-acidification. It was dried and converted by the usual method into ethyl ββ-dimethylbutyrate (2·2 g.), b. p. 146—148° (Found : C, 66·5; H, 11·3. Calc. for $C_8H_{16}O_2$: C, 66·7; H, 11·1%). Reduction of this ester with sodium (4 g.) and calcium-dried ethanol (35 c.c.) gave 3 : 3-dimethylbutanol (1·4 g.), b. p. 143° (Found: C, 70·4; H, 13·5. Calc. for $C_6H_{14}O$: C, 70·6; H, 13·7%) [acetate, b. p. 154—155° (Found : C, 67·0; H, 11·0. Calc. for $C_8H_{16}O_2$: C, 66·7; H, 11·1%); *propionate*, b. p. 172° (Found : C, 68·3; H, 11·3. $C_9H_{18}O_2$ requires C, 68·3; H, 11·4%); *chloroacetate*, b. p. 201—203° (Found : C, 53·4; H, 8·5. $C_8H_{15}O_2Cl$ requires C, 53·2; H, 8·5%)].

3 : 3-*Dimethylpentanol*, b. p. 167° (Found : C, 72·4; H, 13·6. $C_7H_{16}O$ requires C, 72·4; H, 13·8%), was similarly prepared in somewhat better yield, and gave the *acetate*, b. p. 178° (Found : C, 68·6; H, 11·3. $C_9H_{18}O_2$ requires C, 68·3; H, 11·4%); *propionate*, b. p. 194° (Found : C, 69·5; H, 11·6. $C_{10}H_{20}O_2$ requires C, 69·8; H, 11·6%); and *chloroacetate*, b. p. 112—114°/18 mm. (Found : C, 55·5; H, 8·5. $C_9H_{17}O_2Cl$ requires C, 55·9; H, 8·8%).

The chloroacetates were made by heating the alcohols under reflux with a slight excess of chloroacetyl chloride in dry benzene.

This work was carried out during the tenure of an I.C.I. Research Fellowship.—THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, May 23rd*, 1949.]

New Toluene-p-*sulphonamides.*

By S. J. ANGYAL, (MISS) P. J. MORRIS, R. C. RASSACK, (MISS) J. A. WATERER, and J. G. WILSON.

IN connection with our work on the Sommelet reaction (this vol., pp. 2700, 2704) the following new p-*toluenesulphonamides* were prepared in the usual way from the corresponding amines :

Derivative of :	M. p.	Formula.	N, %, found.	N, %, reqd.
Dibenzylamine	78°	$C_{21}H_{21}O_2NS$	3·95	4·0
2 : 4 : 6-Trimethylbenzylamine	138	$C_{17}H_{21}O_2NS$	4·65	4·6
p-Bromobenzylamine	115·5—116	$C_{14}H_{14}O_2NSBr$	4·2	4·1
N-Methyl-*p*-bromobenzylamine	90—90·5	$C_{15}H_{16}O_2NSBr$	4·0	3·95
p-Nitrobenzylamine	120·5—121	$C_{14}H_{14}O_4N_2S$	9·2	9·1
N-Methyl-*p*-nitrobenzylamine	129·5	$C_{15}H_{16}O_4N_2S$	8·8	8·75
2 : 6-Dichlorobenzylamine	128	$C_{14}H_{13}O_2NSCl_2$	4·3	4·2
1-Aminomethylnaphthalene	153—154	$C_{18}H_{17}O_2NS$	4·5	4·5
1-Methylaminomethylnaphthalene	146	$C_{19}H_{19}O_2NS$	4·4	4·3
2-Methyl-1-aminomethylnaphthalene	196·5	$C_{19}H_{19}O_2NS$	4·4	4·3
(±)-3-Aminocamphor	139	$C_{17}H_{23}O_3NS$	4·4	4·4
(±)-3-Methylaminocamphor	77—77·5	$C_{18}H_{25}O_3NS$	4·2	4·2

All the compounds were crystallised from alcohol. The m. p.s are corrected. Microanalyses were done by Mrs. E. Smith and Miss J. Fildes.—UNIVERSITY OF SYDNEY. [*Received, May 23rd*, 1949.]

Some Mono- and Di-guanidine Compounds.

By JOHN MILLER.

CARTER *et al.* (*Science*, 1946, **103**, 53) have shown that streptomycin contains a 1 : 3-diguanidino-2 : 4 : 5 : 6-tetrahydroxy*cyclo*hexane moiety and therefore several new mono- and di-guanidino-compounds have been prepared for antibacterial test.

p-*Acetamidophenylguanidine Hydrochloride*.—*p*-Aminoacetanilide hydrochloride (m. p. 238°; 9·3 g.) and cyanamide (3·0 g.) were heated under reflux in absolute alcohol (30 c.c.) for 3 hours. The *product* separated on cooling and formed white crystals (4·3 g.), m. p. 269°, from water (Found : C, 47·5; H, 5·5; N, 24·7; Cl, 15·5. $C_9H_{13}ON_4Cl$ requires C, 47·2; H, 5·7; N, 24·5; Cl, 15·5%).

p-*Aminophenylguanidine Dihydrochloride*.—The foregoing salt (2·0 g.), heated under reflux with 50% hydrochloric acid (20 c.c.) for 5 hours, gave p-*aminophenylguanidine dihydrochloride* on evaporation. Boiled with absolute alcohol, it formed white crystals (1·9 g.), m. p. 303° (decomp.) (Found : N, 24·9; Cl, 31·6. $C_7H_{12}N_4Cl_2$ requires N, 25·1; Cl, 31·8%).

m-*Acetamidophenylguanidine Hydrochloride*.—Prepared from *m*-aminoacetanilide hydrochloride (9·3 g.) and cyanamide (3·0 g.), and crystallised from alcohol, the colourless *product* (5·0 g.) had m. p. 224—225° (Found : N, 24·2; Cl, 15·5. $C_9H_{13}ON_4Cl$ requires N, 24·5; Cl, 15·5%). It afforded m-*aminophenylguanidine dihydrochloride* (0·8 g. from 1 g.), m. p. 232° (decomp.) (from alcohol) (Found : N, 24·7; Cl, 31·9. $C_7H_{12}N_4Cl_2$ requires N, 25·1; Cl, 31·8%).

m-*Phenyleneguanidine Di*-p-*toluenesulphonate*. The dihydrochloride obtained by heating *m*-aminophenylguanidine dihydrochloride (5·6 g.) and cyanamide (2·5 g.) under reflux in absolute alcohol (50 c.c.) for 5 hours could not be crystallised. Toluene-*p*-sulphonic acid (9·2 g.) added to the boiling solution gave a buff-coloured *di*-p-*toluenesulphonate* (10·6 g.) on cooling. Recrystallised from water it formed colourless crystals, m. p. 251—252° (Found : N, 15·8. $C_{22}H_{28}O_6N_4S_2$ requires N, 15·7%). The *dipicrate* crystallised as small matted needles, m. p. 265° (decomp.), from 2-ethoxyethanol and water (Found : N, 26·2. $C_{20}H_{18}O_{14}N_{12}$ requires N, 25·8%).

p-*Acetamidomethylphenylguanidine Picrate*.—The hydrochloride formed when *N*-*p*-aminobenzylacetamide hydrochloride (4·0 g.) and cyanamide (1·0 g.) were heated under reflux in *n*-butyl alcohol (20 c.c.) for 5 hours could not be crystallised. The *picrate* obtained from an alcoholic solution of the tar left after removal of the butyl alcohol crystallised from alcohol as a yellow granular solid (4·6 g.), m. p. 205—207° (Found : N, 22·5. $C_{16}H_{17}O_8N_7$ requires N, 22·5%).

p-*Nitrobenzylguanidine Hydrochloride.*—*p*-Nitrobenzylamine hydrochloride (4·0 g.) and cyanamide (2·0 g.), heated under reflux for 5 hours in *n*-butyl alcohol (30 c.c.), gave, on cooling, the *product* (2·7 g.), which formed cream-coloured crystals, m. p. 210—211°, from absolute alcohol (Found : N, 24·4. $C_8H_{11}O_2N_4Cl$ requires N, 24·3%). The derived *picrate*, when boiled out with alcohol, had m. p. 193—194° (Found : N, 23·0. $C_{14}H_{13}O_9N_7$ requires N, 23·2%).

p-*Aminobenzylguanidine Dihydrochloride.*—The foregoing hydrochloride (1·0 g.) in 90% alcohol and water (100 c.c.) was hydrogenated in the presence of Raney nickel catalyst at 50 lb. per sq. in., to give a brown monohydrochloride, isolated after removal of the solvent from the filtered reaction solution. This salt gave the colourless *dihydrochloride* (0·9 g.), m. p. 260—265° (decomp.), on treatment with concentrated hydrochloric acid (Found : N, 23·3; Cl, 29·6. $C_8H_{14}N_4Cl_2$ requires N, 23·6; Cl, 29·9%).

N^1-D-*Glucosyldiguanide Picrate.*—D-Glucosamine hydrochloride (2·3 g.) and cyanamide (1·0 g.) were heated under reflux in 60% aqueous ethyl alcohol (25 c.c.) for 5 hours. Addition of picric acid (3·0 g.), dissolved in hot alcohol (20 c.c.), gave, on cooling, the *picrate* which formed long bright-yellow needles (2·0 g.), m. p. 189—190°, from water (Found : C, 34·4; H, 3·9; N, 22·4. $C_{14}H_{20}O_{12}N_8$ requires C, 34·2; H, 4·1; N, 22·8%). D-Glucosamine hydrochloride was recovered when isolation of the product was attempted by evaporation or by precipitation with acetone.

N^1-D-*Glucosyldiguanide Oxime Picrate.*—D-Glucosamine oxime hydrochloride (3·5 g.) and cyanamide (1·8 g.) were heated under reflux in 90% alcohol (40 c.c.) for 4 hours. Addition of picric acid (4·8 g.) dissolved in hot water (60 c.c.) gave the *picrate* as small yellow needles (1·3 g.), m. p. 180—185° (Found : C, 33·2; H, 3·9; N, 24·8. $C_{14}H_{21}O_{12}N_9$ requires C, 33·1; H, 4·2; N, 24·8%).

The author thanks Dr. G. M. Dyson for his interest in this work, the Board of Directors of British Chemicals and Biologicals Limited for permission to publish the paper, and Miss P. A. Page and Mr. J. V. Smart for the analyses.—CENTRAL RESEARCH ORGANISATION, BRITISH CHEMICALS AND BIOLOGICALS LTD., LOUGHBOROUGH, LEICESTERSHIRE. [*Received, May* 26*th*, 1949.]

Reactions of Crotonaldehyde with Ethanethiol. By R. H. Hall and B. K. Howe.

THE reactions between crotonaldehyde and ethanethiol under both basic and acidic conditions have recently been studied in connection with another investigation and have resulted in the synthesis of 3-*ethylthiobutanal* and 1 : 1-*diethylthiobut*-2-*ene*, respectively.

3-Ethylthiobutanal had previously been described by Szabo and Stiller (*J. Amer. Chem. Soc.*, 1948, **70**, 3667) as being obtained in 30% yield from crotonaldehyde and ethanethiol in benzene solution with " Triton B " as catalyst. The physical constants (b. p. 160—180°/2 mm., n_D^{27} 1·5291) recorded for the compound by these authors, however, appear to be in error (by comparison with those recorded in the literature for closely related compounds, *e.g.*, 3-ethylthiopropanal) or, more probably, the product isolated was really a polymer of the desired aldehyde.

3-Ethylthiobutanal has now been prepared from crotonaldehyde and ethanethiol in 60% yield, triethylamine being employed as catalyst according to the method used by Catch, Cook, Graham, and Heilbron (*J.*, 1947, 1609) for 3-ethylthiopropanal. The 3-ethylthiobutanal had b. p. 92—93°/24 mm., n_D^{20} 1·4720, and was characterised as its *semicarbazone*. The ethylthio-group was assumed to be in the 3-position by analogy with the findings of Catch *et al.* (*loc. cit.*).

When crotonaldehyde was treated with excess of ethanethiol in carbon tetrachloride under acid conditions (0·02 mol. of anhydrous hydrogen chloride per mol. of crotonaldehyde), the expected, but hitherto unknown, 1 : 1-diethylthiobut-2-ene (crotonaldehyde diethyl mercaptal) was obtained in 68% yield. When less hydrogen chloride (0·0036 mol. per mol.) was used the " uncatalysed " addition of thiol to the double bond also occurred (cf. E.I. du Pont de Nemours & Co., U.S.P. 2,461,013), and a mixture of 3-ethylthiobutanal and 1 : 1-diethylthiobut-2-ene was obtained in low yield. The latter compound gave no aldehyde reactions but on decomposition with aqueous mercuric chloride solution regenerated crotonaldehyde. The mercaptal was further characterised by oxidation with hydrogen peroxide in glacial acetic acid solution to the crystalline disulphone, 1 : 1-*diethylsulphonylbut*-2-*ene*.

Experimental.—3-*Ethylthiobutanal.* Ice-cold ethanethiol (18·6 g.) was added slowly to an ice-cold mixture of redistilled crotonaldehyde (17·5 g.) and triethylamine (about 0·4 c.c.). Heat was evolved and the mixture was cooled. The crude product was fractionated *in vacuo* at once and, after a small fore-run, 3-*ethylthiobutanal* was collected as a colourless, evil-smelling liquid (20 g.), b. p. 92—93°/24 mm., n_D^{20} 1·4720 (Found : C, 54·4, 54·5; H, 9·25, 9·0; S, 24·2. $C_6H_{12}OS$ requires C, 54·5; H, 9·15; S, 24·25%). The *semicarbazone* separated from methanol as tiny white needles, m. p. 137·5° (Found : C, 44·9; H, 7·85; N, 21·7. $C_7H_{15}ON_3S$ requires C, 44·4; H, 8·0; N, 22·2%).

1 : 1-*Diethylthiobut*-2-*ene*. Crotonaldehyde (52·5 g.), ethanethiol (151·1 g.), and dry carbon tetrachloride (300 c.c.) containing anhydrous hydrogen chloride (0·6 g.) were cooled separately to 0° and then mixed. The mixture became cloudy and heat was evolved, necessitating cooling in ice-water. After 3 days at room temperature the mixture was shaken with solid anhydrous sodium carbonate, washed twice with 20% aqueous sodium carbonate and twice with water, and dried (K_2CO_3). The resulting crude product was distilled at atmospheric pressure to remove excess of ethanethiol and the carbon tetrachloride, and the residual liquid was fractionated *in vacuo*. After a fore-run (15 g.) boiling below 128°/24 mm., pure 1 : 1-*diethylthiobut*-2-*ene* was collected as a colourless, unpleasant-smelling liquid (90 g.), b. p. 128°/24 mm., 116°/10 mm., n_D^{20} 1·5250 (Found : C, 54·85, 54·4; H, 8·75, 9·65; S, 36·8. $C_8H_{16}S_2$ requires C, 54·5; H, 9·15; S, 36·4%), a small residue (5 g.) remaining in the distilling-flask. The mercaptal did not react with cold aqueous-alcoholic semicarbazide acetate or 2 : 4-dinitrophenylhydrazine sulphate solution.

When crotonaldehyde (17·5 g.), ethanethiol (50·4 g.), and dry carbon tetrachloride (160 c.c.) containing anhydrous hydrogen chloride (0·033 g.) were mixed at 0° and set aside at room temperature for 3 days, the mixture, worked-up as described above, yielded 7·25 g. of slightly impure 3-ethylthiobutanal, b. p. 100—111°/35 mm., and 1 : 1-diethylthiobut-2-ene (13 g.), b. p. 130—140°/35 mm. (mainly 139°/35 mm.), n_D^{20} 1·5249.

Hydrolysis of 1 : 1-*diethylthiobut*-2-*ene*. A mixture of 1 : 1-diethylthiobut-2-ene (about 0·8 g.), mercuric chloride (15 g.), calcium carbonate (1 g.), and water (10 c.c.) was heated under gentle reflux for 30 minutes. Filtration of the product, steam-distillation of the filtrate, and treatment of the distillate with aqueous 2 : 4-dinitrophenylhydrazine hydrochloride solution gave a solid which on recrystallisation from ethyl acetate formed small red crystals, m. p. 187—188°, undepressed on admixture with an authentic specimen of crotonaldehyde 2 : 4-dinitrophenylhydrazone.

Oxidation of 1 : 1-*diethylthiobut*-2-*ene*. Hydrogen peroxide (40 c.c.; 30% w/w) was added cautiously to a solution of 1 : 1-diethylthiobut-2-ene (5 g.) in glacial acetic acid (80 c.c.) and, when the initial vigorous reaction had subsided, the mixture was heated on the steam-bath for 30 minutes. The cooled mixture was evaporated to a small bulk *in vacuo*, diluted with ethyl acetate, and washed with aqueous sodium carbonate to remove acetic acid. The ethyl acetate layer was washed with water, dried (Na_2SO_4), and evaporated *in vacuo*. A highly viscous liquid (3 g.) was obtained which crystallised slowly, and the solid on recrystallisation from ethanol yielded white crystals, m. p. 79°, of 1 : 1-*diethylsulphonylbut*-2-*ene* (Found : C, 40·05; H, 6·85; S, 26·85. $C_8H_{16}O_4S_2$ requires C, 40·0; H, 6·7; S, 26·7%).

Microanalyses are by Drs. Weiler and Strauss of Oxford. M. p.s are uncorrected.

The authors thank Dr. H. M. Stanley for his interest in this work and The Directors of the Distillers Co., Ltd., for permission to publish this note.—THE DISTILLERS CO. LTD., RESEARCH AND DEVELOPMENT DEPT., GREAT BURGH, EPSOM, SURREY. [*Received, July 7th*, 1949.]

Preparation of Digeranyl Ether [*Di*-(3 : 7-*dimethylocta*-2 : 6-*dienyl*) *Ether*].—By RALPH F. NAYLOR.

AN attempt to convert geraniol into its ether by distillation with toluene-*p*-sulphonic acid led only to the formation of geraniene, charring, and polymerisation. The alternative method of treating geranyl chloride with sodium or potassium geranoxide was therefore adopted.

Geraniol (22·3 g.) in dry ether (250 ml.) was heated under reflux with sodium (3·4 g.) for 18 hours. Undissolved sodium (*ca.* 2 g.) was removed, geranyl chloride (10·5 g.) (Forster and Cardwell, *J.*, 1913, **103**, 1341) added, and refluxing continued for a further 18 hours. After filtration and two distillations, *digeranyl ether* (3 g.) was obtained as a colourless liquid, b. p. 132°/0·1 mm., n_D^{20} 1·4846 (Found : C, 82·7; H, 12·0. $C_{20}H_{34}O$ requires C, 82·7; H, 11·8%). Use of potassium gave better yields in a shorter time. Thus, potassium (25·3 g.) was dissolved in geraniol (100 g. in 500 ml. of ether) during 6 hours and after being heated under reflux with geranyl chloride (112 g.) for 12 hours yielded digeranyl ether (50 g.).

The infra-red absorption spectrum of this ether [described by Barnard, Bateman, Harding, Koch, Sheppard, and Sutherland (in the press)] is compatible with the primary ether structure of di-(3 : 7-dimethylocta-2: 6-dienyl) ether. In particular the spectrum shows absence of terminal *iso*propenyl or of vinyl groups which would be expected if allylic rearrangement had taken place during the reaction.—BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION, 48, TEWIN ROAD, WELWYN GARDEN CITY, HERTS. [*Received, July 8th*, 1949.]

Isomeric Methoxystilbenes. By GEORGE A. R. KON and R. G. W. SPICKETT.

2-, 3-, and 4-METHOXYSTILBENES were required in connection with some spectrographic studies on compounds of the stilbene series. The 2-methoxy-compound had previously been prepared by Funk and Kostanecki (*Ber.*, 1905, **38**, 939) by decarboxylation of the corresponding phenylcinnamic acid (m. p. 70°) or from salicylaldehyde (Kaufmann, *Annalen*, 1923, **433**, 237, who gives m. p. 68°). When prepared by the method generally used in these laboratories, by dehydrating the carbinol obtained from benzylmagnesium chloride and *o*-methoxybenzaldehyde, the product, presumably the pure *trans*-form, had m. p. 59°. Kaufmann's synthesis was repeated, but the product again had m. p. 59° in spite of careful purification; we can only assume that the higher m. p. given in the literature is incorrect. The *cis*-form of the compound has now been prepared by the pyrolysis of 2-methoxy-α-phenylcinnamic acid and is a liquid.

Both the 3-methoxystilbenes are new and have been obtained by methods similar to those described above.

cis- and *trans*-4-Methoxystilbene have been prepared by Stoermer and Prigge (*Annalen*, 1915, **409**, 33), the *cis*-form as an oil obtained by the irradiation of the *trans*-form, m. p. 136°. It has now been prepared by pyrolysis of 4-methoxy-α-phenylcinnamic acid; measurements of the ultra-violet absorption suggest that Stoermer and Prigge's liquid irradiation product is an equilibrium mixture of the two forms.

Experimental.—2-*Phenyl*-1-o-*methoxyphenylethanol*. *o*-Methoxybenzaldehyde (13·6 g.) in ether (50 c.c.) was slowly dropped into a stirred, cold solution of Grignard reagent prepared from benzyl chloride (11·5 c.c.) and magnesium (2·4 g.) in ether (100 c.c.). The mixture was warmed for an hour and then decomposed with ice and dilute sulphuric acid. The product (12 g.) obtained after evaporation of the dried ethereal solution distilled at 205—215°/15 mm. It solidified and, crystallised from light petroleum, had m. p. 67—68° (Found : C, 78·8; H, 7·1. $C_{15}H_{16}O_2$ requires C, 78·9; H, 7·0%).

trans-2-*Methoxystilbene*. The carbinol (1 g.) in 15 c.c. of benzene–light petroleum (1 : 1) was boiled under reflux for 15 minutes with 1 g. of phosphoric oxide. The fluorescent solution was decanted, the phosphoric oxide washed with more light petroleum, and the combined solutions were passed through a column of alumina, which was eluted with light petroleum. From the percolate 0·5 g. of solid stilbene was recovered, m. p. 59° after repeated crystallisation from petroleum (b. p. 40—60°) and finally methyl alcohol (Found : C, 85·7; H, 6·8. Calc. for $C_{15}H_{14}O$: C, 85·7; H, 6·7%). A specimen prepared as described by Kaufmann (*loc. cit.*) and purified as above had the same properties.

cis-2-*Methoxystilbene.* 2-Methoxy-α-phenylcinnamic acid (Funk and Kostanecki, *loc. cit.*) (12 g.) was boiled for an hour with 10 c.c. of quinoline and 1 g. of copper chromite. The cooled mixture was poured into dilute hydrochloride acid, the solution thoroughly extracted with ether, the extract washed with more acid and then with alkali, dried, and evaporated. The residue was distilled, giving 6 g. of colourless oil, b. p. 167—169°/10 mm. (Found : C, 85·2; H, 6·8. Calc. : C, 85·7; H, 6·7%).

Isomerisation of cis-2-*methoxystilbene.* 500 Mg. of the liquid stilbene were boiled for 15 minutes with 5 c.c. of nitrobenzene and a crystal of iodine. The solvent was distilled off under reduced pressure, and the residue dissolved in light petroleum (b. p. 40—60°) and percolated through activated alumina. On evaporation the percolate gave the solid *trans*-2-methoxystilbene in colourless plates, m. p. 57° not depressed by admixture of a genuine specimen.

trans-3-*Methoxystilbene.* *m*-Methoxybenzaldehyde (7·3 g.) was treated with benzylmagnesium chloride (from 6·2 c.c. of benzyl chloride), and the product worked up exactly as described above, but the crude carbinol was used for the dehydration with phosphoric oxide. The *stilbene* was recovered as a colourless oil (2 g.), b. p. 173—174°/4 mm., which gradually solidified and then had m. p. 21—24° (Found : C, 85·9; H, 6·7%).

3-*Methoxy-α-phenylcinnamic acid.* *m*-Methoxybenzaldehyde (7·3 g.) and sodium phenylacetate (11·9 g.) were condensed as described by Funk and Kostanecki for the 2-methoxy-isomer. The *acid* (9·8 g.) had m. p. 188—190° after crystallisation from alcohol (Found : C, 75·6; H, 5·5. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%).

cis-3-*Methoxystilbene.* Decarboxylation of 5 g. of the foregoing acid as described above gave 2·5 g. of cis-*stilbene*, b. p. 122—123°/0·8 mm. (Found : C, 85·6; H, 6·8%). The *cis*-compound could be quantitatively isomerised by boiling it with nitrobenzene and a trace of iodine, to give the *trans*-isomeride, m. p. 21—24°.

cis-4-*Methoxystilbene.* 4-Methoxy-α-phenylcinnamic acid (13 g.) was decarboxylated as described above, to yield 6 g. of the cis-*stilbene*, b. p. 141—143°/3 mm. (Found : C, 85·9; H, 6·9%). The residue left in the flask after the distillation of the *cis*-compound gradually solidified and proved to be the *trans*-form, m. p. and mixed m. p. 136°. The *cis*-compound was readily isomerised to the *trans*-compound on boiling it with nitrobenzene and a trace of iodine.

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Isomeric Propenylnaphthalenes. By George A. R. Kon and R. G. W. Spickett.

1- and 2-Propenylnaphthalene were required as reference substances for the comparison of their absorption spectra with those of certain metabolites obtained from anthracene and phenanthrene. The 1-compound, usually obtained by the isomerisation of 1-allylnaphthalene, has been synthesised by Zalkind and Zonis (*J. Gen. Chem. Russia*, 1936, **6**, 988) by the dehydration of 1-1′-naphthylpropan-1-ol, obtained from 1-naphthylmagnesium bromide and propaldehyde; we have prepared the carbinol from ethylmagnesium bromide and 1-naphthaldehyde. In the same way 1-2′-*naphthylpropan*-1-*ol* was prepared and dehydrated to the solid 2-*propenylnaphthalene*, which was oxidised by permanganate to 2-naphthoic acid to establish the position of the double bond. The absorption spectra of the propenylnaphthalenes will be described elsewhere.

1-*Propenylnaphthalene.*—1-Naphthaldehyde (Badger, *J.*, 1941, 535) (15 g.) in 75 c.c. of ether was gradually added to a stirred ice-cold solution of ethylmagnesium bromide (from 15 c.c. of ethyl bromide) in 50 c.c. of ether. The mixture was heated under reflux for 2 hours, kept overnight, and decomposed with ice and dilute sulphuric acid. The dried ethereal layer gave on distillation 12 g. of carbinol as a pale yellow oil, b. p. 130°/1·5 mm. The carbinol in 200 c.c. of light petroleum–benzene (4 : 1) was boiled for 10 minutes with 15 g. of phosphoric oxide, and the supernatant liquid cooled and percolated through a column of alumina, which was further eluted with light petroleum (b. p. 60—80°). The oil recovered by evaporation of the solvent was converted into the picrate, m. p. 109—111° (4 g.), from which the pure hydrocarbon could be regenerated by chromatography. It was isolated by evaporation and dried *in vacuo*, but not distilled (to avoid polymerisation).

2-*Propenylnaphthalene.*—1-2′-*Naphthylpropan*-1-*ol* (12 g.), obtained from 2-naphthaldehyde (11 g.) as described above, distilled at 138—140°/1·5 mm. as an almost colourless oil (Found : C, 83·5; H, 7·6. $C_{13}H_{14}O$ requires C, 83·9; H, 7·6%). Dehydration with phosphoric oxide, followed by repeated chromatography, gave 2-*propenylnaphthalene* as an oil which solidified; it had m. p. 28° (Found : C, 92·5; H, 7·6. $C_{13}H_{12}$ requires C, 92·8; H, 7·2%). It did not form a picrate, but a *trinitrobenzene* complex, yellow needles (from light petroleum–benzene), m. p. 108°, was obtained (Found : N, 10·9. $C_{13}H_{12},C_6H_3O_6N_3$ requires N, 11·1%).

The hydrocarbon (100 mg.) in 10 c.c. of pure acetone was shaken overnight with 140 mg. of finely powdered potassium permanganate. The manganese dioxide sludge was washed with acetone, suspended in water, and brought into solution with sulphur dioxide, whereupon a colourless precipitate was obtained. This was twice crystallised from light petroleum (b. p. 80—100°) and identified as 2-naphthoic acid, m. p. and mixed m. p. 185°.

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1 : 5-*Dimethoxyanthracene*. By J. W. Cook and P. L. Pauson.

The ready conversion of 1-chloroanthraquinones into the corresponding methoxy-compounds has been reported by Fischer and Sapper (*J. pr. Chem.*, 1911, **83**, 206) and by Decker and Laube (*Ber.*, 1906, **39**, 112), and we have found that 1 : 5-dimethoxyanthraquinone is conveniently prepared in excellent yield by the action of sodium methoxide on 1 : 5-dichloroanthraquinone. Like Hall and Hey (*J.*, 1948, 736) we had found the preparation from 1 : 5-dinitroanthraquinone unsatisfactory, as to both yield and purity, and the disulphonic acid was not available. By hydrogenation over copper chromite 1 : 5-dimethoxyanthraquinone yielded 1 : 5-*dimethoxy*-9 : 10-*dihydroanthracene*, which was smoothly dehydrogenated to 1 : 5-dimethoxyanthracene.

Other methods of reduction led to no useful result. Attree and Perkin (*J.*, 1931, 165) reduced the dimethoxy-quinone with stannous chloride in hydrochloric and acetic acids to 1 : 5-dimethoxyanthrone, brown-red leaflets, m. p. 181—182°. Under the reported conditions we obtained a product of higher m. p., with properties and analysis figures in agreement with those of the quinhydrone, although the anthraquinol is not excluded. With the same reducing agent under more vigorous conditions Attree and Perkin obtained 1-hydroxy-5-methoxyanthrone, m. p. 131—133° (they gave analysis figures only for the diacetate). The product which we obtained under the same conditions had m. p. 167—168°; its analysis agreed with 1-*hydroxy*-5-*methoxyanthrone*. Other methods of chemical reduction of 1 : 5-dimethoxyanthraquinone [zinc and ammonia; sodium hydrosulphite (dithionite); amalgamated zinc and hydrochloric acid] failed to give the desired result (cf. Zahn and Ochwat, *Annalen*, 1928, **462**, 72; Zahn, *Ber.*, 1934, **67**, 2063).

1 : 5-*Dimethoxyanthraquinone*.—Sodium wire (19 g.) under toluene (500 c.c.) was allowed to react with anhydrous methanol (300 c.c.); 1 : 5-dichloroanthraquinone (76 g.) was then added and the mixture boiled under reflux (oil-bath) for 10 hours. For hydrogenation, the product was recrystallised from glacial acetic acid or dioxan. It formed long yellow needles, m. p. 238—240° (yield, 85—90%).

1 : 5-*Dimethoxy*-9 : 10-*dihydroanthracene*.—A solution of the quinone (25 g.) in ethanol (200 c.c.) was hydrogenated over copper chromite (5 g.; *Org. Synth.*, 1939, **19**, 31) at 120—150°/150—160 atms. Hydrogen uptake ceased after 2—3 hours, but hydrogenation was incomplete and the product was a mixture of 1 : 5-dimethoxy-9 : 10-dihydroanthracene and unchanged quinone. This result could be explained by inactivation of the catalyst by hydrochloric acid formed from dichloroanthraquinone as a contaminant. However, hydrogenation was still incomplete when carried out with a specimen of dimethoxyanthraquinone which had been recrystallised 10 times. Complete reduction was readily achieved when the hydrogenated solution was filtered hot from catalyst and re-hydrogenated (5 hours) after addition of fresh copper chromite. 1 : 5-*Dimethoxy*-9 : 10-*dihydroanthracene* formed colourless needles (from ethanol), m. p. 147—147·5° (Found : C, 79·7; H, 6·4. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%). When this dihydro-compound was heated with palladium-black at 180° in a stream of carbon dioxide it gave 1 : 5-dimethoxyanthracene, m. p. 232—232·5° (lit., 224°), as pale yellow leaflets (from methanol or benzene) (Found : C, 80·6; H, 6·1. Calc. for $C_{16}H_{14}O_2$: C, 80·7; H, 5·9%). The colour could not be removed by vacuum-sublimation or chromatography on alumina.

Reduction of 1 : 5-*Dimethoxyanthraquinone with Stannous Chloride*.—(*a*) A solution of the quinone (1 g.) in acetic acid (30 c.c.) was treated at 100° with a solution of stannous chloride (5 g.) in concentrated hydrochloric acid (25 c.c.). After 10 minutes the green mass was filtered off and the solid rapidly recrystallised from acetic acid. The brownish-red crystals were twice recrystallised from acetic acid, in which they gave a yellow solution. The m. p. was indefinite (226—234°) (Found : C, 71·6; H, 4·9%). The mother-liquors from the crystallisation of this material slowly deposited the quinone.

(*b*) Solutions of the quinone (1 g.) in acetic acid (20 c.c.) and of stannous chloride (5 g.) in concentrated hydrochloric acid (25 c.c.) were mixed and boiled for an hour. After dilution of the mixture with hot hydrochloric acid the precipitate was collected. The resulting 1-*hydroxy*-5-*methoxyanthrone* crystallised from acetic acid or ethanol in yellow needles, m. p. 167—168° (Found : C, 74·8; H, 5·2; OMe, 12·8. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0; OMe, 12·9%). The colour of its solution in concentrated sulphuric acid slowly changed from pale yellow to green. The compound readily dissolved in hot 2N-sodium hydroxide, and the unstable solution soon deposited an amorphous red solid. Attempts to methylate it with methyl sulphate or to reduce it with zinc dust led to no crystalline product.—Universities of Glasgow and Sheffield. [*Received*, *July* 13*th*, 1949.]