137. *Dihydroresorcinols. Part I. The Alkylation of Substituted Dihydroresorcinols.*

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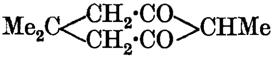
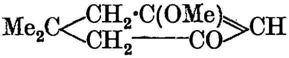
METHYLATION of 5 : 5-dimethyldihydroresorcinol in presence of sodium ethoxide gives mainly 1 : 1 : 4-*trimethyl*cyclo*hexane*-3 : 5-*dione* (I) together with the 1 : 1 : 4 : 4-*tetramethyl* compound and 5-methoxy-1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one (II), but ethylation produces the *O*-ether (type II) and a small amount of the *C*-ethyl derivative (type I).

(I.) 
$\mathrm{Me_2C}{<}\begin{matrix}\mathrm{CH_2{\cdot}CO}\\ \mathrm{CH_2{\cdot}CO}\end{matrix}{>}\mathrm{CHMe}$

 (II.)
$\mathrm{Me_2C}{<}\begin{matrix}\mathrm{CH_2{\cdot}C(OMe)}\\ \mathrm{CH_2}\text{——}\mathrm{CO}\end{matrix}{>}\mathrm{CH}$

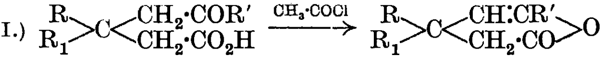
As dimethyldihydroresorcinol is known to react as either a diketone or a keto-enol (Crossley and Le Sueur, J., 1903, **83**, 110, etc.), the formation of compounds of types (I) and (II) can be readily understood, but the marked disparity between the behaviour of methyl and ethyl iodides seems inexplicable. A similar observation was made by Moore and Thorpe (J., 1908, **93**, 167), who found that α-cyano-β-hydrindone was methylated on the *C*-atom but ethylated on the *O*-atom, and explained the result by assuming "steric inhibition." A steric effect in dimethyldihydroresorcinol is possible only if this is a derivative of the boat-shaped strainless form of *cyclo*hexane, but the supposition seemed unwarrantable when it was found that certain groups, such as benzyl and allyl, were easily linked to the carbon atom and others (propyl, *iso*propyl, butyl) attached themselves to oxygen. The explanation was looked for in another direction, and though it was difficult to determine quantitatively the proportions of *C*-alkyl and *O*-alkyl derivatives, the qualitative data recorded below suggested that alkyl iodides possessing the greater degree of electrolytic dissociability facilitated the formation of *C*-alkyl derivatives, and vice versa. The following table shows the relation between the alkyl iodides and the nature of the products formed by their action on dimethyldihydroresorcinol and phenyldihydroresorcinol in presence of sodium ethoxide (compare Hecht, Conrad, and Brückner, *Z. physikal. Chem.*, 1889, **4**, 273; Menschutkin, *ibid.*, 1890, **5**, 589; Wislicenus, *Annalen*, 1882, **212**, 239; Preston and Jones, J., 1912, **101**, 1930; Segaller, J., 1913, **103**, 1154).

Alkyl iodide.		Nature of products.
Methyl	Mainly	*C*-methyl and *C*-dimethyl
Benzyl	,,	*C*-benzyl and *C*-dibenzyl
Allyl	,,	*C*-allyl and *C*-diallyl
Ethyl	,,	*O*-ethyl; *C*-ethyl in small amount
Propyl	,,	*O*-propyl; *C*-propyl in small amount
*iso*Propyl	,,	*O*-*iso*propyl; *C*-*iso*propyl in small amount
Butyl	,,	*O*-butyl; *C*-butyl in small amount

Moreover, the fact that benzyl and allyl iodides gave greater amounts of C-*dibenzyl* and C-*diallyl* derivatives than methyl iodide showed that the order of reactivity was benzyl>allyl>methyl>ethyl>propyl, etc. Thus it was the polar and not the steric factor that governed the course of alkylation.

With the view of determining whether the substituents in the dihydroresorcinol molecule had any effect on the amount of *C*-methyl derivatives formed, the methylation of methylethyldihydroresorcinol, *cyclo*pentane*spirocyclo*hexane-3 : 5-dione, and *cyclo*hexane*spirocyclo*hexane-3 : 5-dione was studied, but the results were identical with those of the dimethyl and phenyl series.

The constitution of the *C*-methyl derivatives (I) was proved by their rational synthesis by ring closure of the *keto-esters* (III; R′ = Et), which were prepared by the action of ethylzinc iodide on the chlorides of the acid esters of the appropriate glutaric acid. The dihydroresorcinol ring of the *C*-dialkylated products was easily opened by dilute alkali with the formation of γ-iso*butyryl*-ββ-*dialkylbutyric acids* (III; R′ = Pr^{β}), which were identified by synthesis.

(III.)

$$\frac{R}{R_1}\!>\!C\!<\!\frac{CH_2\cdot COR'}{CH_2\cdot CO_2H} \xrightarrow{CH_3\cdot COCl} \frac{R}{R_1}\!>\!C\!<\!\frac{CH{:}CR'}{CH_2\cdot CO}\!>\!O$$
(IV.)

The keto-acids (type III) are stable substances which are changed into unsaturated *lactones* (IV) by the action of acetyl chloride (compare Bredt, *Annalen*, 1898, **299**, 179; Qudrat-i-Khuda, J., 1929, 201, 718, etc.), but the keto-acid (III; R′ = Et) of the *cyclo*hexane series gives a considerable amount of the unsaturated lactone on distillation. In fact, the lactone is the sole product if the operation is slowly carried out, showing that in this monobasic keto-acid the ethyl group is more effective than even *iso*propyl in promoting the keto-lactol change.

EXPERIMENTAL.

Dimethyldihydroresorcinol was prepared by the method of Vorländer (*Annalen*, 1897, **294**, 253) as modified by Norris and Thorpe (J., 1921, **119**, 1205).

Methylation.—Methyl iodide (15 c.c.) was slowly added to a cooled solution of dimethyldihydroresorcinol (28 g.) in alcoholic sodium ethoxide (4·6 g. of sodium in 60 c.c. of absolute alcohol), and the mixture warmed on the steam-bath for 3 hours. The alcohol was removed, the residue dissolved in ether, and the solution extracted with 10% aqueous sodium carbonate. The solid obtained from the alkaline extract by acidification crystallised from dilute alcohol in prismatic needles, m. p. 163°, of 1 : 1 : 4-*trimethyl*cyclo*hexane*-3 : 5-*dione* (I) (yield, 50%) (Found : C, 70·0; H, 9·2. $C_9H_{14}O_2$ requires C, 70·1; H, 9·1%), which gave a red colour with alcoholic ferric chloride, and gradually decomposed to a viscous liquid.

The ethereal solution on evaporation left a viscous liquid, much of which dissolved in petroleum (b. p. 60—80°). This solution on cooling gave 1 : 1 : 4 : 4-*tetramethyl*cyclo*hexane*-3 : 5-*dione* (25%) in flattened needles, m. p. 95° (Found : C, 71·2; H, 9·5. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·5%), stable in the air. The petroleum mother-liquor contained the *O*-methyl ether (II), b. p. 135°/17 mm. (Found : C, 69·9; H, 9·1. Calc. for $C_9H_{14}O_2$: C, 70·1; H, 9·1%) (compare Vorländer and Kohlmann, *Annalen*, 1902, **322**, 239).

Oxidation of the Dione (I).—A solution of the dione (2·5 g.) in 10% aqueous sodium hydroxide (15 c.c.) at 0° was treated with ice-cold sodium hypobromite (8 g. of bromine in 175 c.c. of 10% sodium hydroxide solution) in portions, and kept for 1 hour. From the acidified solution, ether extracted ββ-dimethylglutaric acid, m. p. 101°, identified by direct comparison.

Synthesis of γ-Propionyl-ββ-dimethylbutyric Acid (III; R′ = Et).—The acid chloride (b. p. 133°/35 mm.) of ethyl hydrogen ββ-dimethylglutarate (36 g.), diluted with an equal volume of benzene, was gradually added to an ice-cold solution of ethylzinc iodide (prepared by heating over-night a mixture of zinc–copper couple, 40 g., ethyl iodide, 30 c.c., ethyl acetate, 10 c.c., and toluene, 22 c.c.). The product was worked up after 2 hours and the crude keto-ester (32 g.), b. p. 123—125°/25 mm., was hydrolysed with 50% aqueous-alcoholic caustic potash. The *keto-acid* obtained was converted into the *semicarbazone*, which crystallised from dilute ethyl alcohol in clusters of needles, m. p. 138° (Found : C, 52·3; H, 8·2. $C_{10}H_{19}O_3N_3$ requires C, 52·4; H, 8·3%), and regenerated therefrom;

it then had b. p. 177°/35 mm., $d_4^{18°}$ 1·020, $n_D^{18°}$ 1·4492, whence $[R_L]_D$ 45·24 (calc., 45·31) (Found : C, 62·8; H, 9·5. $C_9H_{16}O_3$ requires C, 62·8; H, 9·3%).

The *ethyl* ester, prepared with alcoholic hydrogen chloride, boiled at 135°/30 mm., had $d_4^{18°}$ 0·9519, $n_D^{18°}$ 1·4352, whence $[R_L]_D$ 54·80 (calc., 54·66) (Found : C, 65·8; H, 10·1. $C_{11}H_{20}O_3$ requires C, 66·0; H, 10·0%), and gave a *semicarbazone*, which crystallised from dilute alcohol in lustrous scales, m. p. 88° (Found : C, 55·8; H, 9·0. $C_{12}H_{23}O_3N_3$ requires C, 56·0; H, 8·9%).

The ester (4 g.), dissolved in a solution of sodium (0·5 g.) in absolute alcohol (10 c.c.), was heated on the steam-bath for 6 hours, the alcohol removed, and the aqueous solution acidified. The precipitate, crystallised from dilute alcohol, had m. p. 163° and was identical with the above trimethyl compound (I).

γ-iso*Butyryl*-ββ-*dimethylbutyric Acid* (III; R′ = Pr^{β}).—A solution of tetramethyldihydroresorcinol (5 g.) in 10% aqueous-alcoholic caustic soda was heated on the water-bath for 12 hours, the alcohol removed, and the diluted solution extracted with ether to remove neutral impurities. The *acid* precipitated on acidification with hydrochloric acid was extracted with ether, dried, and recovered; it boiled at 160°/15 mm. and had $d_4^{20°}$ 0·9995, $n_D^{20°}$ 1·44773, whence $[R_L]_D$ 49·83 (calc., 49·93) (Found : C, 64·3; H, 9·8. $C_{10}H_{18}O_3$ requires C, 64·5; H, 9·7%). The *semicarbazone* crystallised from alcohol in stout needles, m. p. 155° (decomp.) (Found : C, 54·0; H, 8·5. $C_{11}H_{21}O_3N_3$ requires C, 54·3; H, 8·6%). The *ethyl* ester, b. p. 124°/15 mm., $d_4^{21°}$ 0·9387, $n_D^{21°}$ 1·4327, whence $[R_L]_D$ 59·19 (calc., 59·28) (Found : C, 67·2; H, 10·5. $C_{12}H_{22}O_3$ requires C, 67·3; H, 10·3%), formed a *semicarbazone*, which crystallised in silky needles, m. p. 98° (Found : C, 57·5; H, 9·2. $C_{13}H_{25}O_3N_3$ requires C, 57·6; H, 9·2%).

The keto-acid (m. p. and mixed m. p. of the semicarbazone, 155°) was also prepared by the action of *iso*propylzinc iodide on the acid chloride of ethyl hydrogen ββ-dimethylglutarate.

*Action of Acetyl Chloride on γ-Propionyl- and γ-*iso*Butyryl-*ββ-*dimethylbutyric Acids.*—The acids (5 g.) were gently refluxed for 4 hours with acetyl chloride (15 c.c.), the excess of this removed, and the residue dissolved in ether, washed with a dilute solution of sodium carbonate, dried, and recovered.

δ-*Hydroxy*-ββ-*dimethyl*-Δ$^{\gamma}$-*heptenolactone* (IV; R′ = Et), b. p. 99°/20 mm., had a characteristic odour (Found : C, 70·0; H, 9·3. $C_9H_{14}O_2$ requires C, 70·1; H, 9·1%). δ-*Hydroxy*-ββ-*dimethyl*-Δ$^{\gamma}$-iso*octenolactone* boiled at 105°/20 mm. and had $d_4^{17°}$ 0·9912, $n_D^{19°}$ 1·45473, whence $[R_L]_D$ 47·70 (calc., 47·37) (Found : C, 71·4; H, 9·6. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·5%).

Ethylation of Dimethyldihydroresorcinol.—The details are exactly similar to those of methylation. The acid product (20%) was crystallised repeatedly from alcohol, and 1 : 1-*dimethyl*-4-*ethyl*cyclo*hexane*-3 : 5-*dione* obtained in long flattened needles, m. p. 153°, which decomposed in the air (Found : C, 71·2; H, 9·6. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·5%).

The *O*-ethyl ether crystallised from petroleum in plates, m. p. 60° (compare Crossley, J., 1899, **75**, 771) (Found: C, 71·3; H, 9·6. Calc. for $C_{10}H_{16}O_2$: C, 71·4; H, 9·5%).

γ-n-*Butyryl*-ββ-*dimethylbutyric Acid* (III; R′ = Pr^{α}).—The ethyl ester prepared by the action of butylzinc iodide on the chloride of ethyl hydrogen ββ-dimethylbutyrate was hydrolysed with 50% alcoholic caustic potash, and the crude acid was purified through the *semicarbazone*, which crystallised from ethyl alcohol in stout needles, m. p. 137° (Found : C, 54·2; H, 8·6. $C_{11}H_{21}O_3N_3$ requires C, 54·3; H, 8·6%). The *acid* regenerated from the semicarbazone boiled at 176°/23 mm. and had $d_{4^\circ}^{22^\circ}$ 0·9951, $n_{\mathrm{D}}^{22^\circ}$ 1·4491, whence $[R_L]_{\mathrm{D}}$ 50·14 (calc., 50·05) (Found : C, 64·6; H, 9·9. $C_{10}H_{18}O_3$ requires C, 64·5; H, 9·7%). The *ethyl* ester boiled at 139°/22 mm. and had $d_{4^\circ}^{21^\circ}$ 0·9445, $n_{\mathrm{D}}^{21^\circ}$ 1·43297, whence $[R_L]_{\mathrm{D}}$ 58·9 (calc., 59·3) (Found: C, 67·2; H, 10·4. $C_{12}H_{22}O_3$ requires C, 67·3; H, 10·3%); the *semicarbazone* crystallised from alcohol in laminæ, m. p. 68° (Found : C, 57·7; H, 9·4. $C_{13}H_{25}O_3N_3$ requires C, 57·6; H, 9·2%). When the ethyl ester was heated with alcoholic sodium ethoxide, 1 : 1-dimethyl-4-ethyl*cyclo*hexane-3 : 5-dione, m. p. 153°, was obtained.

Action of Benzyl Iodide on Dimethyldihydroresorcinol.—The acid product (36%) was crystallised from dilute alcohol, and 4-*benzyl*-1 : 1-*dimethyl*cyclo*hexane*-3 : 5-*dione* obtained in needles, m. p. 154—155° (Found: C, 78·3; H, 8·0. $C_{15}H_{18}O_2$ requires C, 78·3; H, 7·8%). The neutral product (60%), crystallised from light petroleum (b. p. 40—60°), gave 4 : 4-*dibenzyl*-1 : 1-*dimethyl*cyclo*hexane*-3 : 5-*dione* in cubes, m. p. 135° (Found : C, 82·3; H, 7·6. $C_{22}H_{24}O_2$ requires C, 82·5; H, 7·5%). When this was hydrolysed with aqueous-alcoholic caustic potash, an acid was obtained which, crystallised from petroleum (b. p. 40—60°), gave *γ-dibenzylacetyl*-ββ-*dimethylbutyric acid* [III; R′ = $CH(CH_2Ph)_2$] in prismatic rods, m. p. 61° (Found : C, 78·0; H, 7·8; equiv., 337. $C_{22}H_{26}O_3$ requires C, 78·1; H, 7·7%; equiv., 338).

1 : 1-*Dimethyl*-4-*propyl*cyclo*hexane*-3 : 5-*dione* (15—20% yield) crystallised from dilute alcohol in flattened needles, m. p. 162° (Found: C, 72·3; H, 9·8. $C_{11}H_{18}O_2$ requires C, 72·5; H, 9·9%), 5-*propoxy*-1 : 1-*dimethyl*-Δ^4-cyclo*hexen*-3-*one* from light petroleum in plates, m. p. 65°, b. p. 150°/18 mm. (Found : C, 72·4; H, 9·9. $C_{11}H_{18}O_2$ requires C, 72·5; H, 9·9%). 1 : 1-*Dimethyl*-4-iso*propyl*cyclo*hexane*-3 : 5-*dione* (10—15% yield) crystallised from dilute

alcohol in needles, m. p. 156° (Found : C, 72·4; H, 9·9%), and 5-iso*propoxy*-1 : 1-*dimethyl*-Δ^4-cyclo*hexen*-3-*one* from petroleum (b. p. 40—60°); m. p. 55°, b. p. 139°/17 mm. (Found : C, 72·3; H, 10%).

1 : 1-*Dimethyl*-4-*butyl*cyclo*hexane*-3 : 5-*dione* (20% yield) crystallised from dilute alcohol in needles, m. p. 155° (Found : C, 73·2; H, 10·3. $C_{12}H_{20}O_2$ requires C, 73·5; H, 10·2%). The isomeric O-*ether*, b. p. 163°/17 mm., crystallised from petroleum (b. p. 40—60°) in cubes, m. p. 69—70° (Found : C, 73·4; H, 10·1%).

1 : 1-*Dimethyl*-4-*allyl*cyclo*hexane*-3 : 5-*dione* (35%) crystallised from alcohol in needles, m. p. 143° (Found : C, 73·1; H, 9·0. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·9%), and 1 : 1-*dimethyl*-4 : 4-*diallyl*-cyclo*hexane*-3 : 5-*dione* (35% yield) in needles, m. p. 75° (Found : C, 76·1; H, 9·2. $C_{14}H_{20}O_2$ requires C, 76·4; H, 9·1%). The isomeric O-*allyl* ether boiled at 155°/20 mm. (Found : C, 73·2; H, 8·9%).

Phenyldihydroresorcinol Series.—1-Phenyl-4-methyl*cyclo*hexane-3 : 5-dione (50%) crystallised from dilute alcohol in scales, m. p. 214° (compare Mattar, Hastings, and Walker, J., 1930, 2456) (Found : C, 77·0; H, 6·9. Calc. for $C_{13}H_{14}O_2$: C, 77·2; H, 6·9%). When hydrolysed with 50% barium hydroxide solution, it gave γ-propionyl-β-phenylbutyric acid, which was identified by synthesis.

Synthesis of γ-Propionyl-β-phenylbutyric Acid.—β-Phenylglutaric acid was prepared by condensing ethyl cinnamate and ethyl sodiocyanoacetate (compare Thorpe and Udall, J., 1899, **75**, 905), and hydrolysing the ethyl α-cyano-β-phenylglutarate, which was formed in good yield, with 50% sulphuric acid. A considerable amount of the acid ester was also formed, but as this gave the required acid, the yield of β-phenylglutaric acid was excellent.

Ethyl α-cyano-β-phenylglutarate is a viscous, pale yellow liquid, b. p. 208—210°/18 mm. (Found : C, 66·4; H, 6·7. $C_{16}H_{19}O_4N$ requires C, 66·4; H, 6·6%).

Ethyl hydrogen β-phenylglutarate was prepared by decomposing the crystallised anhydride (40 g.) with a solution of 4·6 g. of sodium in 100 c.c. of absolute alcohol, removing the alcohol, and acidifying the aqueous solution. The viscous oil, isolated by means of ether, was warmed with an excess of thionyl chloride, and the crude acid chloride, diluted with an equal volume of benzene, was added to cooled ethylzinc iodide ($\frac{1}{4}$ mol.) in toluene solution. The crude ester, b. p. 192°/17 mm., was hydrolysed with 50% aqueous-alcoholic potash, and the keto-acid was separated from β-phenylglutaric acid by extraction with petroleum (b. p. 60—80°), which did not dissolve the latter. After two crystallisations from the same solvent, *γ-propionyl-β-phenylglutaric acid* was obtained in needles, m. p.

87—88° (Found: C, 70·7; H, 7·5. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%). The *semicarbazone* crystallised from alcohol in needles, m. p. 185° (decomp.) (Found: C, 60·4; H, 7·1. $C_{14}H_{19}O_3N_3$ requires C, 60·6; H, 6·9%). The keto-acid (and its semicarbazone) did not depress the m. p. of the keto-acid (and the semicarbazone) obtained from the hydrolysis of the methylation product. The *ethyl* ester, b. p. 197°/23 mm., had $d_{4^\circ}^{21^\circ}$ 1·049 and $n_{D}^{21^\circ}$ 1·4966, whence $[R_L]_D$ 69·3 (calc., 69·5) (Found: C, 72·4; H, 8·2. $C_{15}H_{20}O_3$ requires C, 72·6; H, 8·1%).

1-Phenyl-4 : 4-dimethyl*cyclo*hexane-3 : 5-dione (25%), isolated from the neutral product of methylation, crystallised from petroleum in long needles, m. p. 86° (Found: C, 77·7; H, 7·5. Calc. for $C_{14}H_{16}O_2$: C, 77·8; H, 7·4%) (compare Dieckmann and Kron, *Ber.*, 1908, **41**, 1260). On hydrolysis with dilute caustic soda solution, it yielded γ-*iso*butyryl-β-phenylbutyric acid, which crystallised from petroleum in needles, m. p. 106—107° (Found: C, 71·8; H, 7·7. Calc. for $C_{14}H_{18}O_3$: C, 72·0; H, 7·6%).

1-Phenyl-4-ethyl*cyclo*hexane-3 : 5-dione (20%) crystallised from alcohol in small plates, m. p. 198° (Found: C, 77·6; H, 7·6. Calc. for $C_{14}H_{16}O_2$: C, 77·8; H, 7·4%). 5-Ethoxy-1-phenyl-Δ^4-*cyclo*hexene-3-one was the sole neutral product of ethylation and boiled at 220°/16 mm. (Found: C, 77·7; H, 7·5. Calc. for $C_{14}H_{16}O_2$: C, 77·8; H, 7·4%).

Benzylation gave 1-phenyl-4-benzyl*cyclo*hexane-3 : 5-dione (45%), which crystallised from alcohol in prisms, m. p. 170° (Found: C, 81·7; H, 6·7. Calc. for $C_{19}H_{18}O_2$: C, 82·0; H, 6·5%). The neutral product, which has been described as the *O*-benzyl ether (Vorländer, *Annalen*, 1897, **294**, 304), is now found to be 1-*phenyl*-4 : 4-*dibenzyl*-cyclo*hexane*-3 : 5-*dione* (yield, 55%). It crystallised from petroleum (b. p. 40—60°) in cubes, m. p. 128—129° (Found: C, 84·5; H, 6·7. $C_{26}H_{24}O_2$ requires C, 84·7; H, 6·5%), and on hydrolysis with dilute caustic soda solution gave γ-*dibenzylacetyl*-β-*phenylbutyric acid*, which crystallised from alcohol in needles, m. p. 145° (Found: C, 80·5; H, 6·9; equiv., 386. $C_{26}H_{26}O_3$ requires C, 80·8; H, 6·7%; equiv., 386).

1-Phenyl-4-propyl*cyclo*hexane-3 : 5-dione crystallised from dilute alcohol in needles, m. p. 184° (Found: C, 77·9; H, 8·0. Calc. for $C_{15}H_{18}O_2$: C, 78·2; H, 7·8%). The isomeric *O*-ether boiled at 230°/16 mm. (Found: C, 78·1; H, 7·9%).

1-*Phenyl*-4-iso*propyl*cyclo*hexane*-3 : 5-*dione* crystallised from alcohol in plates, m. p. 190° (Found: C, 78·0; H, 7·8. $C_{15}H_{18}O_2$ requires C, 78·2; H, 7·8%). The isomeric O-*ether* boiled at 222°/20 mm. (Found: C, 78·3; H, 8·0%).

1-*Phenyl*-4-*butyl*cyclo*hexane*-3 : 5-*dione* crystallised from alcohol in needles, m. p. 188° (Found : C, 78·5 ; H, 8·1. $C_{16}H_{20}O_2$ requires C, 78·7 ; H, 8·2%). The O-*ether* boiled at 245°/20 mm. (Found : C, 78·6 ; H, 8·3%).

Methylethyldihydroresorcinol Series.—Methylethyldihydroresorcinol was prepared by Qudrat-i-Khuda's method (J., 1929, 1917). The *methylene* derivative crystallised from alcohol in plates, m. p. 89° (Found : C, 71·0 ; H, 8·6. $C_{19}H_{28}O_4$ requires C, 71·3 ; H, 8·8%).

1 : 4-Dimethyl-1-ethyl*cyclo*hexane-3 : 5-dione (45%) crystallised from alcohol in needles, m. p. 114° (Found : C, 71·2 ; H, 9·6. Calc. for $C_{10}H_{16}O_2$: C, 71·4 ; H, 9·5%) (compare Becker and Thorpe, J., 1922, **121**, 1303). 5-*Methoxy*-1-*methyl*-1-*ethyl*-Δ^4-cyclo*hexen*-3-*one* was a liquid, b. p. 147°/25 mm. (Found : C, 71·1 ; H, 9·6. $C_{10}H_{16}O_2$ requires C, 71·4 ; H, 9·5%).

1 : 4 : 4-*Trimethyl*-1-*ethyl*cyclo*hexane*-3 : 5-*dione*, formed by methylating the monomethylated dione, crystallised from petroleum (b. p. 60—80°) in needles, m. p. 68° (Found : C, 72·3 ; H, 10·0. $C_{11}H_{18}O_2$ requires C, 72·5 ; H, 9·9%). When hydrolysed with dilute alcoholic potash it gave γ-iso*butyryl*-β-*methyl*-β-*ethylbutyric acid*, b. p. 170°/15 mm. (Found : C, 65·7 ; H, 10·2. $C_{11}H_{20}O_3$ requires C, 66·0 ; H, 10·0%). The *semicarbazone* melted at 157° (decomp.) (Found : C, 55·8 ; H, 9·0. $C_{12}H_{23}O_3N_3$ requires C, 56·0 ; H, 8·9%).

The *lactone* of δ-*hydroxy*-β-*methyl*-β-*ethyl*-Δ^{γ}-iso*octenoic acid*, which was readily formed by the action of acetyl chloride on the above acid, boiled at 110°/18 mm. and had $d_{4^\circ}^{19^\circ}$ 0·9920 and $n_{D}^{19^\circ}$ 1·4605, whence $[R_L]_D$ 51·92 (calc., 51·99) (Found : C, 72·6 ; H, 9·8. $C_{11}H_{18}O_2$ requires C, 72·5 ; H, 9·9%).

cyclo*Pentane*spirocyclo*hexane*-3 : 5-*dione Series*.—The acid product of monomethylation, m. p. 175° after one crystallisation (Found : C, 73·0 ; H, 9·0. Calc. for $C_{11}H_{16}O_2$: C, 73·3 ; H, 8·9%), was identified as *cyclo*pentane*spiro*-4-methyl*cyclo*hexane-3 : 5-dione by synthesis (compare Dickins, Hugh, and Kon, J., 1929, 576). The neutral product consisted mainly of cyclo*pentane*spiro-4 : 4-*dimethyl*cyclo*hexane*-3 : 5-*dione*, which crystallised from dilute alcohol in plates, m. p. 78° (Found : C, 74·0 ; H, 9·5. $C_{12}H_{18}O_2$ requires C, 74·2 ; H, 9·3%).

Synthesis of 1-*Propionylmethyl*cyclo*pentane*-1-*acetic Acid*.—The crude ethyl ester prepared by the action of ethylzinc iodide on the chloride of ethyl hydrogen *cyclo*pentane-1 : 1-diacetate was hydrolysed by 50% aqueous-alcoholic potash. The keto-acid obtained was freed from diacetic acid by solution in petroleum (b. p. 60—80°), recovered, and converted into its *semicarbazone*, which crystallised from alcohol in needles, m. p. 157° (decomp.) (Found : C, 56·1 ; H, 8·1. $C_{12}H_{21}O_3N_3$ requires C, 56·4 ; H, 8·2%). The *acid* regenerated from the semicarbazone boiled at 215°/50 mm. and had $d_{4^\circ}^{18^\circ}$ 1·063 and $n_{\mathrm{D}}^{18^\circ}$ 1·4770, whence $[R_L]_{\mathrm{D}}$ 52·65 (calc., 52·46) (Found : C, 66·3; H, 9·3. $C_{11}H_{18}O_3$ requires C, 66·6; H, 9·1%).

The *ethyl* ester, b. p. 165°/30 mm., $d_{4^\circ}^{20^\circ}$ 0·9974, $n_{\mathrm{D}}^{20^\circ}$ 1·4582, whence $[R_L]_{\mathrm{D}}$ 61·83 (calc., 61·70) (Found : C, 68·7; H, 9·9. $C_{13}H_{22}O_3$ requires C, 69·0; H, 9·7%), formed a *semicarbazone,* which crystallised from dilute alcohol in needles, m. p. 89° (Found : C, 59·1; H, 9·0. $C_{14}H_{25}O_3N_3$ requires C, 59·4; H, 8·8%). When the ethyl ester was heated with the calculated amount of alcoholic sodium ethoxide, *cyclo*pentane*spiro*-4-methyl*cyclo*hexane-3 : 5-dione, m. p. 175°, was obtained in quantitative yield.

1-iso*Butyrylmethyl*cyclo*pentane*-1-*acetic acid,* which was readily obtained by hydrolysing *cyclo*pentane*spiro*-4 : 4-dimethyl*cyclo*hexane-3 : 5-dione with dilute alcoholic potash, boiled at 194—195°/20 mm. and had $d_{4^\circ}^{22^\circ}$ 1·040 and $n_{\mathrm{D}}^{22^\circ}$ 1·4713, whence $[R_L]_{\mathrm{D}}$ 56·99 (calc., 56·96) (Found : C, 67·8; H, 9·6. $C_{12}H_{20}O_3$ requires C, 67·9; H, 9·4%). The *semicarbazone,* crystallised from alcohol, had m. p. 195° (decomp.) (Found : C, 57·9; H, 8·7. $C_{13}H_{23}O_3N_3$ requires C, 58·0; H, 8·6%). The *ethyl* ester boiled at 153°/15 mm. and had $d_{4^\circ}^{21^\circ}$ 0·9849 and $n_{\mathrm{D}}^{21^\circ}$ 1·4557, whence $[R_L]_{\mathrm{D}}$ 66·24 (calc., 66·32) (Found : C, 69·8; H, 10·3. $C_{14}H_{24}O_3$ requires C, 70·0; H, 10·0%).

The acid reacted with acetyl chloride, giving a solid which crystallised from petroleum (b. p. 40—60°) in prismatic rods or from dilute alcohol in slender needles, m. p. 90° (Found : C, 70·9; H, 9·3. $C_{12}H_{18}O_2,\frac{1}{2}H_2O$ requires C, 70·9; H, 9·4%).

cyclo*Hexane*spirocyclo*hexane*-3 : 5-*dione Series.*—The acid product of monomethylation crystallised from alcohol in needles, m. p. 179°, and was identified as *cyclo*hexane*spiro*-4-methyl*cyclo*hexane-3 : 5-dione by comparison with a synthetic specimen (compare Dickins, Hugh, and Kon, J., 1928, 1636) (Found : C, 73·9; H, 9·5. Calc. for $C_{12}H_{18}O_2$: C, 74·2; H, 9·3%).

Synthesis of 1-*Propionylmethyl*cyclo*hexane*-1-*acetic Acid.*—This was done with ethylzinc iodide and the crude chloride of ethyl hydrogen *cyclo*hexane-1 : 1-diacetate as in the preceding case. The acid obtained gave a *semicarbazone,* which crystallised from alcohol in prismatic needles, m. p. 167° (decomp.) (Found : C, 57·6; H, 8·7. $C_{13}H_{23}O_3N_3$ requires C, 58·0; H, 8·5%). The regenerated *acid* boiled at 190°/20 mm. with considerable lactonisation (Found for a sample dried in a vacuum : C, 67·6; H, 9·2. $C_{12}H_{20}O_3$ requires C, 67·9; H, 9·4%).

The *ethyl* ester, b. p. 157°/12 mm., $d_{4^\circ}^{19^\circ}$ 1·007, $n_{\mathrm{D}}^{19^\circ}$ 1·4662, whence $[R_L]_{\mathrm{D}}$ 66·03 (calc., 66·3) (Found : C, 69·9; H, 9·8. $C_{14}H_{24}O_3$ requires C, 70·0; H, 10·0%), formed a *semicarbazone,* which crystallised from alcohol in needles, m. p. 79° (Found : C, 60·8; H, 9·2.

$C_{15}H_{27}O_3N_3$ requires C, 60·6; H, 9·1%), and regenerated the methylated dione, m. p. 179°, quantitatively when heated with alcoholic sodium ethoxide.

The unsaturated *lactone* produced by heating the acid alone for 2 hours, and extracting the acid product with sodium carbonate from an ethereal solution, boiled at 153°/15 mm. and had $d_{4^\circ}^{20^\circ}$ 1·035 and $n_{\mathrm{D}}^{20^\circ}$ 1·4930, whence $[R_L]_{\mathrm{D}}$ 54·48 (calc., 54·41) (Found: C, 74·1; H, 9·5. $C_{12}H_{18}O_2$ requires C, 74·2; H, 9·3%).

cyclo*Hexane*spiro-4 : 4-*dimethyl*cyclo*hexane*-3 : 5-*dione* was one of the neutral products of methylation; it crystallised from petroleum (b. p. 40—60°) in prismatic needles, m. p. 95° (Found: C, 74·9; H, 9·4. $C_{13}H_{20}O_2$ requires C, 75·0; H, 9·4%). When hydrolysed with dilute alcoholic potash, it gave 1-iso*butyrylmethyl*cyclo*hexane*-1-*acetic acid*, b. p. 191°/18 mm. (Found: C, 68·7; H, 9·8. $C_{13}H_{22}O_3$ requires C, 69·0; H, 9·7%), the *semicarbazone* of which, crystallised from alcohol, had m. p. 186° (decomp.) (Found: C, 59·1; H, 8·7. $C_{14}H_{25}O_3N_3$ requires C, 59·4; H, 8·8%). The unsaturated *lactone* produced by heating the acid with acetyl chloride boiled at 163°/20 mm. and had $d_{4^\circ}^{19^\circ}$ 1·012 and $n_{\mathrm{D}}^{19^\circ}$ 1·4882, whence $[R_L]_{\mathrm{D}}$ 59·15 (calc., 59·02) (Found: C, 75·2; H, 9·7. $C_{13}H_{20}O_2$ requires C, 75·0; H, 9·6%).

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