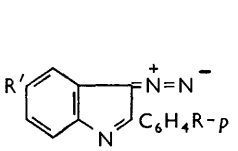
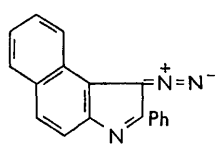
873. *Heterocyclic Diazo-compounds. Part IV.*[1] *3-Diazoindoles.*

By H. P. Patel and J. M. Tedder.

3-Diazo-2-phenylindole (I; R = R′ = H) was first prepared by Castellana and d'Angelo,[2] who diazotised the 3-amino-compound and treated the diazonium salt with alkali. We have been unable to extend our techniques for the direct introduction of the diazonium group to 2-substituted indoles. Nitrosation proceeds readily but the nitroso-compound exists almost entirely in the oxime form and there is no further reaction. To obtain 3-diazoindoles it has been necessary to have recourse to the conventional method (nitrosation ⟶ reduction ⟶ diazotisation); in this way 3-diazo-2-phenyl- (I; R = R′ = H), -2-*p*-methoxyphenyl- (I; R = OMe, R′ = H), and -5-methoxy-2-*p*-methoxy-



(I)



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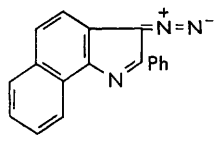

(III)

phenyl-indole (I; R = R′ = OMe), and 3-diazo-2-phenyl-4,5- (II) and -6,7-benzindole (III) have been synthesised. These proved to be stable crystalline compounds. Like diazopyrroles,[3] they couple with β-naphthol in an inert solvent although their rates of coupling vary considerably; 3-diazo-2-phenyl-4,5-benzindole did not couple with β-naphthol although it gave qualitative evidence of coupling with resorcinol.

Experimental.—3-Diazo-2-phenylindole was prepared from 3-amino-2-phenylindole[4] by treatment in acetic acid with aqueous sodium nitrite according to the method of Castellana and d'Angelo.[2] The crude diazo-compound, m. p. 107—108°, recrystallised from benzene as yellow plates, m. p. 107—108° (Castellana and d'Angelo report 115°; this is not the only discrepancy we encountered), $\nu_{max.}$ (KBr disc) 2120 cm.$^{-1}$ (diazo), $\lambda_{max.}$ (in 95% EtOH) 350 mμ (ε 11,600) (Found: C, 76·4; H, 4·3; N, 19·0. Calc. for $C_{14}H_9N_3$: C, 76·7; H, 4·1; N, 19·2%). A benzene solution (30 c.c.) of the diazo-compound (0·43 g.) and β-naphthol (0·43 g.) was refluxed for 3 hr., then the solvent was boiled off and the residue heated on a steam-bath for a further ½ hr. The residue was taken up in chloroform and washed with dilute sodium hydroxide solution and water. The solution was dried (Na_2SO_4) and evaporated, to leave a red residue (0·71 g.). The crude dye was purified by chromatography on activated alumina and then recrystallised from benzene–light petroleum (b. p. 60—80°). 1-(2-*Phenylindol*-3-*ylazo*)-2-*naphthol* had m. p. 191—192°, $\lambda_{max.}$ (in 95% EtOH) 483 mμ (ε 22,400) (Found: C, 79·7; H, 5·0; N, 11·4. $C_{24}H_{17}N_3O$ requires C, 79·3; H, 4·7; N, 11·6%) and gave an intense red-violet colour in concentrated sulphuric acid.

2-p-*Methoxyphenyl*-3-*nitrosoindole*. 2-*p*-Methoxyphenylindole[5] (7·8 g.) was suspended in glacial acetic acid (600 c.c.), and sodium nitrite (2·42 g.) was added. The solution was stirred for 2 hr., then diluted and poured into water (2·5 l.). The brown nitroso-compound was washed thoroughly with water and dried *in vacuo* over sodium hydroxide (yield, 7·85 g.; m. p. 230°). 2-p-*Methoxyphenyl*-3-*nitrosoindole* recrystallised from benzene as orange plates, m. p. 232° (Found: 71·6; H, 5·0; N, 11·4. $C_{15}H_{12}N_2O_2$ requires C, 71·4; H, 4·8; N, 11·1%).

3-*Amino*-2-p-*methoxyphenylindole*. The above nitroso-compound (7·0 g.) in 95% ethanol (200 c.c.) was treated with zinc dust (23·0 g.) on a steam-bath, and concentrated hydrochloric acid (25 c.c.) was added slowly. After ½ hour's stirring under reflux, the excess of zinc was removed, and the filtrate was cooled and made alkaline with dilute aqueous ammonia. The amine was filtered off, washed with water, and dried *in vacuo* over phosphorus pentoxide to give

[1] Part III, preceding paper.
[2] Castellana and d'Angelo, *Atti R. Accad. Lincei*, 1905 [5], **14**, II, 145, 167; *Gazzetta*, 1906, **36**, II, 56.
[3] Tedder and Webster, *J.*, 1960, 3270.
[4] Fischer and Schmidt, *Ber.*, 1888, **21**, 1073.
[5] Kaji and Nagashima, *J. Pharm. Soc. Japan*, 1952, **72**, 1589.

a grey amorphous product (6·3 g.), m. p. 145—146°. The *amine* was unstable in the air but a small portion was recrystallised from benzene as pink crystals, m. p. 150—151° (Found: C, 76·1; H, 6·4; N, 11·0. $C_{15}H_{14}N_2O$ requires C, 75·6; H, 5·9; N, 11·8%).

3-*Diazo*-2-p-*methoxyphenylindole*. The crude amino-compound (5·5 g.) was dissolved in acetic acid (90 c.c.), and sodium nitrite (1·6 g.) in water (16 c.c.) was added. The mixture was kept at 10° for ½ hr., then diluted with cold water (500 c.c.). A dark blue precipitate was removed and the diazo-compound precipitated by basification with sodium carbonate. The crude diazo-compound (3·4 g.; m. p. 114°) was filtered off, dried *in vacuo*, and recrystallised from ether to give yellow needles of the 3-*diazo-compound* (2·4 g.), m. p. 115—116°, $\nu_{max.}$ (KBr disc) 2085 cm.$^{-1}$ (diazo), $\lambda_{max.}$ (in 95% EtOH) 347 mμ (ε 9300) (Found: C, 72·3; H, 4·6; N, 16·8. $C_{15}H_{11}N_3O$ requires C, 72·3; H, 4·4; N, 16·9%). A solution of the diazo-compound (0·25 g.) and β-naphthol (0·22 g.) in benzene (50 c.c.) was refluxed for 6 hr. The red *dye* (0·38 g.), worked up and recrystallised as above, had m. p. 205—206°, $\lambda_{max.}$ (in 95% EtOH) 472 mμ (ε 35,300) (Found: C, 76·6; H, 5·0; N, 10·6. $C_{25}H_{19}N_3O_2$ requires C, 76·3; H, 4·8; N, 10·7%).

5-*Methoxy*-2-p-*methoxyphenyl*-3-*nitrosoindole*. 5-Methoxy-2-*p*-methoxyphenylindole [6] (3·0 g.) was dissolved in hot glacial acetic acid (300 c.c.). The solution was cooled to 25°, some of the indole crystallising. Sodium nitrite (1·05 g.) in water (5·0 c.c.) was added and the mixture was stirred for 3 hr. The *nitroso-compound* (2·9 g.; m. p. 244—245°) was isolated as before. A portion recrystallised twice from 95% ethanol, gave red crystals, m. p. 248° (Found: C, 67·8; H, 5·0; N, 10·3. $C_{16}H_{14}N_2O_3$ requires C, 68·1; H, 5·0; N, 9·9%).

3-*Diazo*-5-*methoxy*-2-p-*methoxyphenylindole*. The preceding crude nitroso-compound (2·5 g.) was heated in 95% ethanol (200 c.c.) with zinc dust (8·5 g.), and concentrated hydrochloric acid (9·0 c.c.) was added slowly. The amine was worked up as before except that no attempt was made to purify a portion. The crude amine was treated in acetic acid (70 c.c.) with sodium nitrite (0·65 g.) in water (2 c.c.). After ½ hr. water (300 c.c.) was added and then sulphamic acid. The mixture was treated with charcoal, filtered, and neutralised with sodium carbonate. The crude *diazo-compound* (1·5 g.), m. p. 131—132°, isolated by filtration, was recrystallised twice from ether to give golden-yellow crystals, m. p. 136—138°, $\nu_{max.}$ (KBr disc) 2100 cm.$^{-1}$ (diazo), $\lambda_{max.}$ (in 95% EtOH) 346 mμ (ε 4000) (Found: C, 68·8; H, 4·7; N, 15·0. $C_{16}H_{13}N_3O_2$ requires C, 68·8; H, 4·7; N, 15·1%). A solution of the diazo-compound (0·28 g.) and β-naphthol (0·22 g.) in benzene (60 c.c.) was refluxed for 4 hr. The dye was isolated as before, chromatographed on activated alumina, and recrystallised from benzene. 1-(5-*Methoxy*-2-p-*methoxyphenylindol*-3-*ylazo*)-β-*naphthol* had m. p. 188—189°, $\lambda_{max.}$ (in 95% EtOH) 476 mμ (ε 18,600) (Found: C, 73·8; H, 4·8; N, 10·0. $C_{26}H_{21}N_3O_3$ requires C, 73·8; H, 5·0; N, 9·9%) and gave a grey colour in concentrated sulphuric acid which became intense red on dilution.

2-*Phenyl*-6,7-*benzindole*. 1-Naphthylhydrazine [7] (90 g.) was treated with acetophenone (66 c.c.) in acetic acid solution. The purified *hydrazone*, m. p. 101—102° (Found: C, 82·6; H, 6·3. $C_{18}H_{16}N_2$ requires C, 83·1; H, 6·2%) (47·0 g.), was heated at 170° for 10 min. with anhydrous zinc chloride (260 g.) to give a viscous residue which was treated with boiling water (500 c.c.) and then acidified with concentrated hydrochloric acid (25 c.c.). The product (46·0 g.) was extracted with benzene, and the extract refluxed with charcoal. The mixture was filtered and light petroleum (b. p. 60—80°) was added. An oil separated and the remaining solution was decanted and on evaporation gave a pale yellow solid (2·9 g.), m. p. 154°. Recrystallisation from benzene–light petroleum gave 2-*phenyl*-6,7-*benzindole*, m. p. 166—167° (Found: C, 88·4; H, 5·4; N, 5·9. $C_{18}H_{13}N$ requires C, 88·9; H, 5·3; N, 5·8%).

2-*Nitroso*-2-*phenyl*-6,7-*benzindole*. 2-Phenyl-6,7-benzindole (1·8 g.) was treated in acetic acid (100 c.c.) with sodium nitrite (0·51 g.) in water (1·0 c.c.). The *nitroso-compound* was isolated as before. Recrystallised from acetone, it had m. p. 260—261° (Found: C, 79·0; H, 4·5; N, 10·5. $C_{18}H_{12}N_2O$ requires C, 79·4; H, 4·4; N, 10·3%).

3-*Diazo*-2-*phenyl*-6,7-*benzindole*. The last-mentioned nitroso-compound (1·89 g.) was treated in ethanol (100 c.c.) with zinc dust. Concentrated hydrochloric acid (10 c.c.) was added to the refluxing mixture which was heated for a further ½ hr. The amine was isolated as before and was diazotised directly in conditions similar to those used for 3-diazo-5-methoxy-2-*p*-methoxyphenylindole. The *diazo-compound* (1·0 g.) was recrystallised from ether as orange plates (0·6 g.), m. p. 166—167°, $\nu_{max.}$ (KBr disc) 2100 cm.$^{-1}$ (diazo), $\lambda_{max.}$ (in 95% EtOH) 368 mμ

[6] Korczyński and Kierzek, *Roczniki Chem.*, 1925, **5**, 23 (*J.*, 1925, **128**, 973).
[7] Fischer, *Annalen*, 1885, **232**, 237.

(ε 7700) (Found: C, 80·2; H, 4·3; N, 15·3. $C_{18}H_{11}N_3$ requires C, 80·3; H, 4·1; N, 15·6%). Crude diazo-compound from the mother-liquor (0·13 g.) was refluxed with β-naphthol (0·08 g.) in chloroform for an hour. The solvent was boiled off and the residue heated on a steam-bath for ½ hr. The dye was purified as before and after chromatography on alumina it was recrystallised twice from methanol to give 1-(2-*phenyl*-6,7-*benzindol*-3-*ylazo*)-2-*naphthol*, m. p. 253—254°, $\lambda_{max.}$ (in 95% EtOH) 476 mμ (ε 20,600) (Found: C, 80·2; H, 4·7; N, 10·5. $C_{28}H_{19}N_3O,\frac{1}{2}H_2O$ requires C, 79·6; H, 4.7; N, 10·0%), that gave a red-violet colour with concentrated sulphuric acid.

2-*Phenyl*-4,5-*benzindole*. Acetophenone 2-naphthylhydrazone [7] was treated with zinc chloride, and 2-phenyl-4,5-benzindole,[8] m. p. 133—134°, was isolated as above (Found: C, 88·7; H, 5·6; N, 5·7%).

3-*Nitroso*-2-*phenyl*-4,5-*benzindole*. 2-Phenyl-4,5-benzindole (7·2 g.) treated in acetic acid (250 c.c.) with sodium nitrite (2·05 g.) in water (5 c.c.). The *nitroso-compound* (7·5 g.; m. p. 242°) was isolated as before. Recrystallised from acetone, it formed a red powder, m. p. 248—249° (Found: C, 79·0; H, 4·7; N, 9·9. $C_{18}H_{12}N_2O$ requires C, 79·4; H, 4·4; N, 10·3%).

3-*Diazo*-2-*phenyl*-4,5-*benzindole*. The preceding nitroso-compound (4·2 g.) was treated with zinc dust (10 g.) in ethanol (150 c.c.). The amine was isolated and diazotised directly in conditions similar to those described for 3-diazo-5-methoxy-2-*p*-methoxyphenylindole. The brown *diazo-compound* (2·4 g.), recrystallised from ether, had m. p. 142—143°, $\nu_{max.}$ (KBr disc) 2085 cm.$^{-1}$ (diazo), $\lambda_{max.}$ (in 95% EtOH) 359 mμ (ε 6000) (Found: C, 80·6; H, 4·3; N, 15·3%).

The authors thank Messrs. Whiffen and Sons Ltd. for financial support.

THE UNIVERSITY, SHEFFIELD, 10. [*Received, March 11th*, 1963.]

[8] Ince, *Annalen*, 1890, **253**, 42—44.

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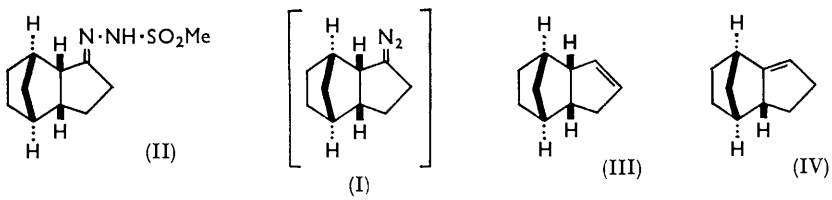
874. *The Thermolysis of* endo,endo-3-*Diazotricyclo*[5,2,1,0^{2,6}]-*decane*.

By R. W. ALDER and M. C. WHITING.

ALKALINE decomposition of methane- or -toluene-*p*-sulphonylhydrazones gives aliphatic diazo-compounds; [1] these undergo thermolysis at the high temperatures of their formation, provided that intrinsically acidic solvents capable of converting them into diazonium ions are avoided.[1,2] The intermediates formed may be less reactive than carbenes obtained photochemically, and when simple and secondary these intermediates react mainly by hydrogen migration. In carbonium-ion chemistry skeletal rearrangements are most readily observed in compact polycyclic systems, and we have therefore examined the " carbenoid " decomposition of a diazo-compound (I) to see if rearrangement of the skeleton



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

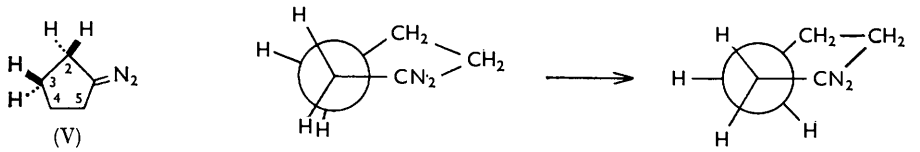
would occur. The required ketone is known, the sulphonylhydrazone (II) was prepared without difficulty and reacted in the normal way, and the product was identical with the

[1] (*a*) Powell and Whiting, *Tetrahedron*, 1959, **7**, 305; (*b*) Friedman and Shechter, *J. Amer. Chem. Soc.*, 1959, **81**, 5512; (*c*) De Puy and Froemsdorf, *ibid.*, 1960, **82**, 634; (*d*) Powell and Whiting, *Tetrahedron*, 1961, **12**, 168.

[2] Clarke, Whiting, Papenmeier, and Reusch, *J. Org. Chem.*, 1962, **27**, 3356.

known [3] and unrearranged olefin (III). It was formed in good yield and was gas-chromatographically homogeneous; its structure was confirmed by permanganate oxidation to an acid, $C_{10}H_{14}O_4$. Partly because of the chaotic situation caused by the very variable melting points of these compounds and the known [4] and potential rearrangements, especially to *exo*-isomers, a number of standard transformations were carried out, but all the evidence obtained suggests that no rearrangements in fact occurred; gas-chromatographic methods provide the best means of assuring purity in this field.

Mechanistically this result is mainly of negative significance, reinforcing earlier [1] conclusions and those of Swithenbank and Whiting [5] on the related compound *exo,exo*-3-diazotricyclo[6,2,1,$0^{2,7}$]undecane as to the strong preference shown by secondary carbenes for moving hydrogen, rather than carbon, from neighbouring atoms. Powell and Whiting's suggestion [1d] that the decomposition of diazo-compounds may be concerted would fit the



complete specificity of this reaction. Thus, in diazocyclopentane (V), distortion of a molecular model to bring one of the β-hydrogen atoms, say, that on C-2, toward a position antiparallel to the C=N bond increases the dihedral angle between the other β-hydrogen and the *cis*-hydrogen atom on C-3. Replacement of these two hydrogen atoms by a bicyclo-[2,2,1]heptane residue would mean that this process increased the existing Baeyer strain; if the bicycloheptane residue were fused at positions 4,5, a smaller increase in strain would result. Thus Powell and Whiting's suggestion [1d] rationalises the result, that olefin (III), not (IV), is formed from (I); admittedly it is conceivable that this occurs for thermodynamic reasons.

Attempts were made to obtain tricycle[6,2,2,$0^{2,7}$]dodecan-3-one for a similar experiment, but cyclohexa-1,3-diene could not be induced to add to cyclohexenone, while removal of one keto-group from the hydrogenated benzoquinone adduct by the method used by Swithenbank and Whiting [5] for the lower homologue encountered the complications discussed in the accompanying Note.

Experimental.—Compounds in this series are extraordinarily volatile, and, though they form waxy crystals with ease, they show exceptionally large freezing-point depression constants and usually melt over a considerable range. M. p.s depend on the technique used and are a poor guide to purity; we used sealed capilliary tubes. Solvents were removed through a fractionating column, and final purification was by vacuum-sublimation.

endo,endo-*Tricyclo*[5,2,1,$0^{2,6}$]*deca*-4,8-*dien*-3-*ol*. This was prepared by the method of Woodward and Katz,[4] in 35% yield, with b. p. 67—68°/3 mm., m. p. 28—34° (Woodward and Katz [4] give b. p. 67°/0·1 mm., m. p. 36·6—37·4°; Alder and Flock [6] give m. p. 40—50°). Although the skeleton is known to be *endo,endo* in configuration, this alcohol, as obtained, may well be a mixture of epimers at the CH·OH group. Oxidation, again by the method of Woodward and Katz, gave the corresponding ketone (53%), m. p. 58—59° (Woodward and Katz [4] record m. p. 65·3—65·6°; Rosenblum,[7] 59·0—59·5°; Alder and Flock,[6] 80°). The 2,4-dinitrophenylhydrazone had m. p. 190—192° (Woodward and Katz [4] give m. p. 199·2—199·5°, Rosenblum [7] 203·5—204°). Hydrogenation of the ketone (uptake 1·94 mol.) in ethanol at atmospheric

[3] Staudinger and Rheiner, *Helv. Chim. Acta*, 1924, **7**, 23; Wieland and Bergel, *Annalen*, 1926, **446**, 13; Staudinger and Bruson, *ibid.*, 1926, **447**, 97; Bergel and Widmann, *ibid.*, 1928, **467**, 76; K. Alder and Stein, *ibid.*, 1931, **485**, 223; Pirsch, *Ber.*, 1934, **67**, 101; Kohlrausch and Seka, *Ber.*, 1936, **69**, 729.
[4] Woodward and Katz, *Tetrahedron*, 1959, **5**, 70.
[5] Swithenbank and Whiting, *J.*, 1963, 4573.
[6] K. Alder and Flock, *Chem. Ber.*, 1954, **87**, 1916.
[7] Rosenblum, *J. Amer. Chem. Soc.*, 1957, **79**, 3179.

pressure over platinum gave *endo,endo*-tricyclo[5,2,1,$0^{2,6}$]decan-3-one (60%), m. p. 96—100° (Pirsch [8] gives m. p. 101°) (Found: C, 79·75, 79·35; H, 9·5, 8·85%. Calc. for $C_{10}H_{14}O$: C, 80·0; H, 9·35%). Its *methanesulphonylhydrazone* (7·13 g., 84%) was obtained by heating the ketone (5·23 g.), methanesulphonylhydrazide [1a] (3·51 g.), and ethanol (19 c.c.) under reflux for 30 min. and keeping the mixture at 5° for 3 days. After crystallisation from ethanol it had m. p. 98—101° (Found: C, 54·5; H, 7·55; $C_{11}H_{18}N_2O_2S$ requires C, 54·55; H, 7·45%).

endo,endo-*Tricyclo*[5,2,1,$0^{2,6}$]*dec*-3-*ene*. (*a*) Sodium (850 mg.) was dissolved in molten acetamide (23 g.) *in vacuo*, and the above methanesulphonylhydrazone (2·6 g.) and porous pot were added. The mixture was heated at 150° until evolution of nitrogen ceased (40 min.). Water (150 c.c.) was added after cooling, and the mixture was extracted with light petroleum (b. p. 40—60°), which was washed, dried, and evaporated. Sublimation at 40°/10 mm. gave the hydrocarbon (700 mg., 49%), m. p. 45—48° (Found: C, 89·4; H, 10·5. Calc. for $C_{10}H_{14}$: C, 89·55; H, 10·45%), $\nu_{max.}$ (in CS_2) 733 cm.$^{-1}$ (*cis*-CH=CH). A mixture with that from (*d*) below had m. p. 45—48°.

(*b*) A similar reaction on a smaller scale gave an extract which when chromatographed on benzyldiphenyl (5%) on Embacel (2·5 m.) at 90° and on Apiezon L (20%) on firebrick at 150° gave, in each case, a single symmetrical peak, augmented by addition of the product from method (*c*).

(*c*) *endo,endo*-Tricyclo[5,2,1,$0^{2,6}$]decan-3-ol was prepared (56%) by hydrogenation of the dienol, m. p. 28—34°, and had m. p. 75—80° (Pirsch [8] gives m. p. 85°). It was treated with methyl chloroformate [9] and pyridine in excess for 24 hr. at 20°; isolation of the product and infrared examination showed that acylation was complete. The ester was dissolved in light petroleum and passed at 0·5 c.c./min. through a tube packed with glass wool and heated to 400° in nitrogen. The pyrolysate was used directly in gas-chromatographic experiments, and showed one additional, much smaller, peak of lower retention time on Apiezon L.

(*d*) " Dicyclopentadiene " (2·28 g.) in ethanol (30 c.c.) and palladium–barium carbonate (1 g.) were shaken in hydrogen at atmospheric pressure until the absorption of 1 mol. was complete (6 min.). Filtration, extraction with light petroleum, and evaporation left a residue which was distilled at 50° (bath-temp.)/16 mm., m. p. 44—48° (1·18 g., 52%). Recorded m. p.s [3] are in the range 48—57°. A few drops of the light petroleum extract showed a single peak when chromatographed on Apiezon L as above, coincident with those obtained by methods (*a*)—(*c*).

endo,endo-*Tricyclo*[5,2,1,$0^{2,6}$]*decane* was prepared (i) by total hydrogenation of " dicyclopentadiene " (53%; m. p. 77—78°), and (ii) by hydrogenation of the olefin from the sulphonylhydrazone decomposition (m. p. 77—78°).

(iii) *endo,endo*-Tricyclo[5,2,1,$0^{2,6}$]decan-3-one (1 g.), hydrazine hydrate (6 c.c.), diethylene glycol (50 c.c.), and potassium hydoxide (5 g.) were heated under reflux for 3 hr. in nitrogen. Water (30 c.c.) was added and the mixture was distilled until the internal temperature reached 220°. The distillate was extracted with ether, and the extract washed with 2N-hydrochloric acid and saturated brine. After drying and evaporating, sublimation at 30°/10 mm. gave the hydrocarbon (450 mg., 50%), m. p. 77—79°.

The three specimens behaved similarly during gas chromatography, had similar spectra, and did not depress each others' m. p.s; Pirsch [8] gives m. p. 77°.

2-*Hydroxycarbonylbicyclo*[2,2,1]*heptan*-3-*ylacetic acid*. Tricyclo[5,2,1,$0^{2,6}$]dec-3-ene [510 mg.; prepared by method (*a*)] and acetone (25 c.c.; redistilled from potassium permanganate) were heated under reflux for 1 hr. while potassium permanganate (1·62 g.) was added in small portions. Half the acetone was evaporated and water (200 c.c.) was added, sulphur dioxide was passed in until a homogeneous solution was obtained, and the excess was removed by agitation under reduced pressure. The solution was extracted with ether (6 × 15 c.c.), and the extract was dried and evaporated. The residue was dissolved in benzene, and light petroleum was added; during 7 days crystals (*ca.* 50 mg.) separated. Recrystallisation from benzene–light petroleum gave the *acid*, m. p. 97—98·5° (Found: C, 60·05; H, 6·85. $C_{10}H_{14}O_4$ requires C, 60·7; H, 7·1%.) The acids, m. p. 134° and 137° previously reported [1b,c] are probably another stereoisomer.

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[8] Pirsch, *Ber.*, 1934, **67**, 1115.
[9] Fieser, Herz, Klohs, Romero, and Utre, *J. Amer. Chem. Soc.*, 1952, **74**, 3309.

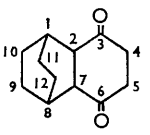
875. *Generalisation of Robins–Walker Aromatisation.*

By R. W. Alder and M. C. Whiting.

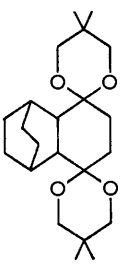
Robins and Walker described [1] a reaction in which a cyclohexa-1,4-dione, methanol, and an acidic catalyst interact to give an aromatic methyl ether. Most of their examples were complex, the simplest, which proceeded in low yield, being (I) ⟶ (II). Methanol was unique as the alcoholic component, and a necessary role was allotted to the ethylenic linkage, which indeed often migrated during the reaction.

(I) (II)

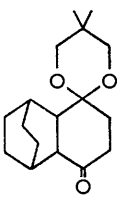
During an attempted synthesis [2] of tricyclo[6,2,2,$0^{2,7}$]dodecan-3-one, the readily available [3] tricyclo[6,2,2,$0^{2,7}$]dodecane-3,6-dione (III) was heated with 2,2-dimethylpropane-1,3-diol and toluene-*p*-sulphonic acid in benzene. The expected ketals (IV) and (V) were obtained (in low yield; stereochemistry [2] unknown) but the major products



(III)

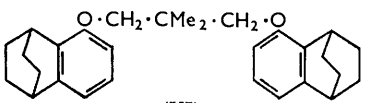


(IV)

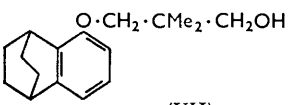


(V)

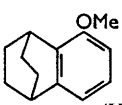
were compounds $C_{29}H_{36}O_2$ (VI) and $C_{17}H_{24}O_2$ (VII), the four being separable chromatographically. (The ill-defined mixture obtained along with a bisketal when ethylene glycol was used instead of the dimethylpropanediol may well have contained analogous but less readily separable compounds.) The major products were the aromatic ethers; a similar compound, $C_{13}H_{16}O$ (VIII), was obtained when methanol was substituted for the diol. The C_{29} ether (VI) resulted when the hydroxy-ether (VII) was subjected to the same conditions along with the tricyclododecanedione (III). The structures (VI—VIII) follow from spectra and from the inertness of products (VI) and (VII) to hydrogenation and



(VI)



(VII)



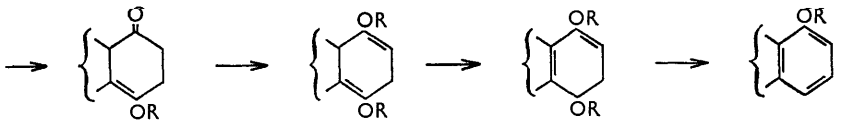
(VIII)

hydrolysis. An infrared band of exceptional sharpness at 1336 ± 1 cm.$^{-1}$ in the spectra of compounds (VI—VIII) is unusual, but reminiscent of one at 1350 cm.$^{-1}$ reported [4] for

[1] Robins and Walker, *J.*, 1956, 3260; 1957, 177; 1958, 409.
[2] Swithenbank and Whiting, *J.*, 1963, **4573**.
[3] Alder and Stein, *Annalen*, 1933, **501**, 247.
[4] Hine, Brown, Zalkow, Gardner, and Hine, *J. Amer. Chem. Soc.*, 1955, **77**, 594.

bicyclo[2,2,2]oct-2-ene; it is presumably correlated with the presence of pairs of methylene groups in these compounds which are constrained into a nearly eclipsed conformation. No other proof of the continued presence of the bicyclo[2,2,2]octane grouping in the new ethers was sought, as no means of rationalising a rearrangement [5] was found, consistent with the presence of three adjacent aromatic hydrogen atoms (infrared).

It is clear that the structural requirements for the Robins–Walker reaction can now be relaxed. The alcohol need probably be merely one which does not readily yield a carbonium ion by loss of a protonated hydroxyl group. The cyclohexanedione component evidently does not need to contain an additional double bond; however, the evidence that this aids the reaction remains. The reaction probably involves intermediates such as:



the formation of the allylic, rather than the vinylic, ether being a necessary preliminary to aromatisation. The penultimate stage is clearly disadvantageous electronically, and some conformational driving force may be necessary and available from either the ethylenic linkage or the ethylene bridge.

Experimental.—Tricyclo[6,2,2,$0^{2,7}$]dodecane-3,6-dione (III) was prepared by hydrogenation of the *p*-benzoquinone–cyclohexa-1,3-diene adduct over platinic oxide; it had m. p. 63—65° (Alder and Stein [3] give m. p. 65°). 2,2-Dimethylpropane-1,3-diol was recrystallised three times from benzene.

Reaction of the diketone (III) *with* 2,2-*dimethylpropane*-1,3-*diol.* The diketone (5·09 g.), the diol (2·76 g., 1 mol.), toluene-*p*-sulphonic acid (200 mg.), and benzene (150 c.c.) were heated under reflux for 6 hr., the water formed being collected in a Dean and Stark apparatus. Potassium carbonate (150 mg.) was added and heating was continued for a further 15 min.; the cooled solution was washed with potassium carbonate solution, dried ($MgSO_4$), and evaporated. The residue (5·88 g.) was dissolved in light petroleum (100 c.c.; b. p. 60—80°) and chromatographed on alumina (Peter Spence, grade H, 750 g.). Four colourless solids were successively eluted: with 2% benzene in light petroleum, 2′,2′-*dimethyl*-3,3′-*trimethylenedioxybistricyclo*-[6,2,2,$0^{2,7}$]*dodeca*-2,4,6-*triene* (VI) (2·28 g.), m. p. 142—144°, raised on recrystallisation from light petroleum to 144—145°; with benzene–light petroleum (1 : 1), the *bis*-(2,2-*dimethyltrimethylene*) *ketal* (IV) (0·88 g.), m. p. 186—188°, raised on recrystallisation to 198·5—199·5°; with 5% ether in benzene, the *mono*-(2,2-*dimethyltrimethylene*)*ketal* (V) (0·41 g.), m. p. 113—116°, raised to 117—119°; and with ether, 2,2-*dimethyl*-3-{*tricyclo*[6,2,2,$0^{2,7}$]*dodeca*-2(7),3,5-*trien*-3-*yloxy*}*propan*-1-*ol* (VII) (1·89 g.), m. p. 80—83°, raised to 84—84·5°. Analytical data were as follows: Found, for (VI): C, 83·25, 83·7, 82·9; H, 8·55, 9·0, 8·7; *M* (Rast), 438. $C_{29}H_{36}O_2$ requires C, 83·6; H, 8·7; *M*, 416. Found, for (IV): C, 71·95; H, 9·85. $C_{22}H_{36}O_4$ requires C, 72·5; H, 9·9%. Found, for (V): C, 73·4; H, 9·25. $C_{17}H_{26}O_3$ requires C, 73·4; H, 9·3%. Found, for (VII): C, 77·9, 78·35, 78·85; H, 9·05, 9·4, 9·25%. $C_{17}H_{24}O_2$ requires C, 78·4, H, 9·3%. Spectrographic results agreed with the structures postulated; thus compound (IV) was transparent above 2200 Å, (V) showed a maximum at 2850 Å (ε 23) in ethanol, and (VI) and (VII) showed bands at 2760, 2680, and 2170 (ε 2700, 2500, and 20,000) and at 2760, 2680, and 2180 Å (ε 1400, 1300, and 10,500, respectively). In the infrared region (CS_2), (IV) and (V) showed strong ketal bands at 1100 and 1125 $cm.^{-1}$ and (V) additionally had a carbonyl band (1710 $cm.^{-1}$); the aromatic ethers (VI) and (VII) had bands at 1337, 1260, 1103, 1072, 1059, 797, and 744 and 1335, 1258, 1102, 1072, 1057, 796, and 746 $cm.^{-1}$, respectively; the latter also absorbed at 3620 and 3566 $cm.^{-1}$.

Reaction of diketone (III) *with methanol.* The diketone (599 mg.), methanol (4 c.c.), toluene-*p*-sulphonic acid (93 mg.), and benzene (120 c.c.) were heated under a Soxhlet extractor filled

[5] Bickel, Knotnerus, Kooyman, and Vegter, *Tetrahedron*, 1960, **9**, 230.

with anhydrous magnesium sulphate, and the product was isolated as described above. Elution with benzene in light petroleum (5%) gave an oil (364 mg.) which crystallised; recrystallisation gave 3-*methoxytricyclo*[6,2,2,$0^{2,7}$]*dodeca*-2,4,6-*triene* (245 mg.) as hexagonal plates, m. p. 56—57° (Found: C, 83·05; H, 8·6. $C_{13}H_{16}O$ requires C, 82·95; H, 8·55%), $\lambda_{max.}$ (in EtOH) 2750, 2680, and 2170 Å (ε 1350, 1250, and 8000, respectively), $\nu_{max.}$ (in CS_2) 1335, 1256, 1106, 1070, 1058, 797, and 745 cm.$^{-1}$.

Conversion of compound (VII) *into compound* (VI). When compound (VII) (66 mg.) and the diketone (III) (52 mg.) were treated as in the first experiment, chromatography gave product (VI) (82 mg.) along with about 25 mg. of a mixture of the starting materials. A similar experiment with compound (VI) and 2,2-dimethylpropane-1,3-diol resulted simply in the recovery of the starting material (VI) in 73% yield.

Reaction of diketone (III) *with ethylene glycol.* The diketone (1·0 g.), ethylene glycol (0·78 g., 2·5 mol.), benzene (30 c.c.), and toluene-*p*-sulphonic acid (20 mg.) were heated under reflux in a Dean and Stark apparatus for 6 hr., a little potassium carbonate being added 15 min. before the end of the period. After washing (K_2CO_3) and evaporation, the residue solidified; recrystallisation from light petroleum (b. p. 60—80°) gave the *bis*(*ethylene ketal*) (640 mg., 51%), m. p. 186—187·5° (in a sealed tube), of tricyclo[6,2,2,$0^{2,7}$]dodecane-3,6-dione (Found, after sublimation: C, 68·15; H, 8·6. $C_{16}H_{24}O_4$ requires C, 68·5; H, 8·6%). It showed no infrared bands suggesting carbonyl or aromatic groups.

When the molar ratio of diketone to alcohol was reduced to 1 : 1, the yields of recovered diketone and bisketal were 29% and 20%, respectively, and a small inseparable intermediate fraction was obtained.

This work was supported by a Maintenance Grant awarded to R. W. A. by the Department of Scientific and Industrial Research.

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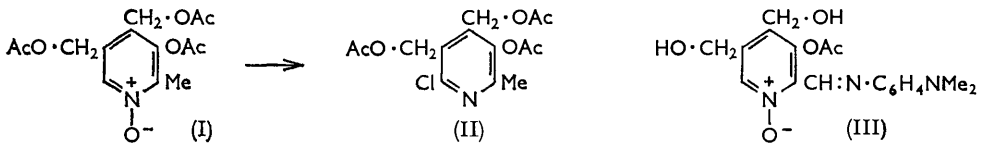
876. N-*Oxides and Related Compounds. Part XXIII.*[1] *Some Pyridoxine Analogues.*

By G. R. BEDFORD, A. R. KATRITZKY, and H. M. WUEST.

IN view of recent interest in pyridoxine analogues, we investigated modification of the 2-methyl group. Pyridoxine triacetate *N*-oxide (I), prepared by perbenzoic acid oxidation,[2] on reaction with phosphorus oxychloride formed the 6-chloro-derivative (II). The



nuclear magnetic resonance (n.m.r.) spectrum, particularly the absence of an aromatic proton (Table) excluded any other position for the chlorine atom.

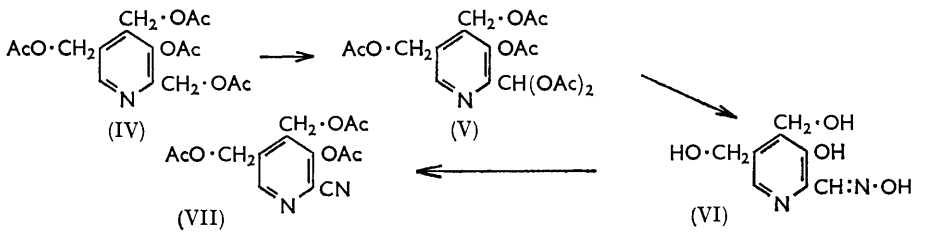
2-Picoline *N*-oxide and phosphorus oxychloride give similarly 4-chloro-2-picoline.[3] With *NN*-dimethyl-*p*-nitrosoaniline in ethanol,[4] the *N*-oxide (I) yielded the phenylimino-derivative (III). Treatment of the *N*-oxide (I) with acetic anhydride formed the tetra-acetate (IV), the orientation of the extra acetate group being shown by n.m.r. spectroscopy

[1] Part XXII, Boulton and Katritzky, *Rev. Chim.* (*Rumania*), in the press.
[2] Meisenheimer, *Ber.*, 1926, **59**, 1848.
[3] Ochiai, Fujimoto, and Ichimiera, *Pharm. Bull.* (*Japan*), 1957, **2**, 137; *Chem. Abs.*, 1956, **50**, 991.
[4] Kaufmann and Vallette, *Ber.*, 1912, **45**, 1739.

Proton resonance spectra.

Cpd.	2-Subst.	τ	3-Subst.	τ	4-Subst.	τ	5-Subst.	τ	6-Subst.	τ
II	Me	7·60	Ac	8·00	Me	7·95	Me	7·62	Cl	—
					CH_2	4·83	CH_2	4·61		
III	CH=N	1·59	Ac	7·90	CH_2·OH	4·68	CH_2·OH	4·60	H	1·05
IV	Me	7·93	Ac	7·99	Me	7·93	Me	7·64	H	1·42
	CH_2	4·84			CH_2	4·84	CH_2	4·70		
VII	C≡N	—	Ac	7·96	Me	7·88	Me	7·53	H	1·27
					CH_2	4·76	CH_2	4·58		

(see Table). Conversion of the tetra-acetate into an *N*-oxide and further vigorous treatment with acetic anhydride yielded the penta-acetate (V). Hydrolysis in the presence of hydroxylamine hydrochloride now yielded a 2-formyl derivative which was obtained



as the oxime (VI); this with acetic anhydride afforded the cyano-acetate (VII), whose n.m.r. spectrum is included in the Table.

Experimental.—3-*Acetoxy*-4,5-*di*(*acetoxymethyl*)-2-*methylpyridine* 1-*oxide*. 3-Acetoxy-4,5-di(acetoxymethyl)-2-methylpyridine [5] (760 mg.) in chloroform (7 ml.) was treated with perbenzoic acid (1 g., 3 equiv.) in chloroform at 20° for 3 days. The mixture was shaken with saturated aqueous sodium hydrogen carbonate (3 × 5 ml.), dried ($MgSO_4$), and evaporated. The residual *oxide* crystallised from benzene as needles (454 mg., 60%), m. p. 114—115° (Found: C, 54·5; H, 5·5; N, 4·6. $C_{14}H_{17}NO_7$ requires C, 54·0; H, 5·5; N, 4·5%).

3-*Acetoxy*-4,5-*di*(*acetoxymethyl*)-6-*chloro*-2-*methylpyridine*. A slurry of 3-acetoxy-4,5-di(acetoxymethyl)-2-methylpyridine 1-oxide (1 g.) and phosphorus oxychloride (4 ml.) was heated at 100° for 30 min., at 120° for 30 min., and finally under reflux for 30 min. The resulting dark red solution was cooled and added to ice–water (15 ml.), neutralised with potassium carbonate, and extracted with ether. Evaporation of the dried extracts yielded the 6-*chloro-derivative* (0·39 g., 36%) which recrystallised from light petroleum (b. p. 40—60°) as needles, m. p. 71—72° (Found: C, 51·4; H, 4·7; N, 4·6. $C_{14}H_{16}ClNO_6$ requires C, 51·0; H, 4·7; N, 4·3%).

3-*Acetoxy*-2-(p-*dimethylaminophenyliminomethyl*)-4,5-*di*(*hydroxymethyl*)*pyridine* 1-*oxide*. 3-Acetoxy-4,5-di(acetoxymethyl)-2-methylpyridine 1-oxide (0·62 g.) and *NN*-dimethyl-*p*-nitrosoaniline (0·3 g.) were heated under reflux in ethanol (25 ml.) and piperidine (2 drops) for 3 hr. Concentration and recrystallisation from ethanol gave the *oxide* as red needles, m. p. 191—193° (Found: N, 11·4. $C_{18}H_{21}N_3O_5$ requires N, 11·7%).

3-*Hydroxy*-2,4,5-*tri*(*hydroxymethyl*)*pyridine hydrochloride*. 3-Acetoxy-4,5-di(acetoxymethyl)-2-methylpyridine 1-oxide (355 mg.) in acetic anhydride (4·5 ml.) was heated at 100° for 1·5 hr. and the anhydride evaporated off at 15 mm. Distillation of the residue gave a yellow viscous oil (360 mg.), b. p. 170—180°/0·3 mm. This oil (220 mg.) was heated at 100° for 1·5 hr. with 2N-hydrochloric acid (5 ml.). Evaporation to dryness and recrystallisation of the residue from ethanol–ethyl acetate gave the *hydrochloride* (95 mg., 50%) as white needles m. p. 172—173° (decomp.) (Found: C, 43·8; H, 5·1; N, 6·3. $C_8H_{12}ClNO_4$ requires C, 43·8; H, 5·4; N, 6·3%).

3-*Acetoxy*-2,4,5-*tri*(*acetoxymethyl*)*pyridine* 1-*oxide*. The yellow viscous oil (120 mg.) obtained

[5] Marcus and Fitzpatrick, *J. Org. Chem.*, 1959, **24**, 1030.

in the preceding experiment was treated with perbenzoic acid [as described for the preparation of 3-acetoxy-4,5-di(acetoxymethyl)-2-methylpyridine 1-oxide] to form the *tri(acetoxymethyl) oxide* (85 mg., 74%) which recrystallised from benzene–light petroleum (b. p. 60—80°) as white needles, m. p. 126—127° (Found: C, 52·1; H, 4·9; N, 3·5. $C_{16}H_{19}NO_9$ requires C, 52·0; H, 5·2; N, 3·8%).

3-*Acetoxy*-4,5-*di*(*acetoxymethyl*)-2-*diacetoxymethylpyridine*. 3-Acetoxy-2,4,5-tri(acetoxymethyl)pyridine 1-oxide (440 mg.) and acetic anhydride (15 ml.) were heated at 110—120° for 6 hr. After evaporation at 100°/15 mm., the residue was treated with ether to precipitate starting material (134 mg.). The ethereal solution was evaporated and the residue distilled, to give the *penta-acetate* (320 mg., 93% conversion) as a pale yellow oil, b. p. 175—180°/0·01 mm. (Found: C, 53·0; H, 5·3; N, 3·8. $C_{18}H_{21}NO_{10}$ requires C, 52·6; H, 5·2; N, 3·4%).

3-*Hydroxy*-4,5-*di*(*hydroxymethyl*)*pyridine*-2-*aldoxime hydrochloride*. 3-Acetoxy-4,5-di-(acetoxymethyl)-2-diacetoxymethylpyridine (700 mg.) and hydroxylamine hydrochloride (150 mg.) were heated at 100° in ethanol (15 ml.) for 3 hr. The ethanol was evaporated and the dark brown residue was recrystallised from ethanol with charcoal and then from ethanol–ethyl acetate, to yield the *oxime hydrochloride* (230 mg., 59%) as light fawn needles, m. p. 184—185° (decomp.) (Found: C, 41·1; H, 4·8; N, 11·4. $C_8H_{11}ClN_2O_4$ requires C, 40·9; H, 4·7; N, 11·9%).

3-*Acetoxy*-4,5-*di*(*acetoxymethyl*)-2-*cyanopyridine*. 3-Hydroxy-4,5-di(hydroxymethyl)-pyridine-2-aldoxime (0·8 g.), obtained from the hydrochloride, was heated with acetic anhydride (15 ml.) under reflux for 3 hr. while the acetic acid formed distilled out through a Vigreux column. The anhydride was then distilled off at 15 mm. Distillation of a sample of the residual black oil caused considerable decomposition and gave a small amount of a pale yellow oil, b. p. 135—140/2 × 10^{-2} mm. The black oil was therefore chromatographed on activated charcoal in ethyl acetate, to yield a pale yellow oil (630 mg.). Treatment with ether at −15° gave white needles of the *nitrile*, m. p. 56—58° (from ether at −15°) (Found: C, 55·2; H, 4·7; N, 9·1. $C_{14}H_{14}N_2O_6$ requires C, 54·9; H, 4·6; N, 9·2%).

Nuclear magnetic resonance spectra were obtained in chloroform solution (*ca.* 10% w/w) on a Perkin-Elmer (40 megacycles) spectrometer. Tetramethylsilane was used as internal standard.

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[*Received, February 6th,* 1963.]

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877. *Triphenylsilanol and Hexaphenylcyclotrisiloxane.*

By A. J. NEALE and B. B. MILLWARD.

TREATMENT of chlorosilanes with tertiary alcohols has been shown [1] to give, not the corresponding alkoxysilanes, but siloxanes, tertiary alkyl chloride, and water. It has now been found that reaction between chlorotriphenylsilane and t-butyl alcohol yields triphenylsilanol rather than hexaphenyldisiloxane,[2] while dichlorodiphenylsilane gives mainly hexaphenylcyclotrisiloxane.

Experimental.—Triphenylsilanol. After 2 days at 20°, a solution of chlorotriphenylsilane (30 g., 0·1 mole) in t-butyl alcohol (80 c.c.) had deposited triphenylsilanol, m. p. 150—155° (19·2 g., 70%). Recrystallisation from benzene–light petroleum gave prisms, m. p. 153—155° (lit.,[3] 155°). The infrared spectrum was in agreement with that reported.[4]

[1] Ridge and Todd, *J.*, 1949, 2637; Britton and Berhenke, U.S.P. 2,521,673/1950; Boye and Post, *J. Org. Chem.*, 1951, **16**, 391; Gerrard and Kilburn, *J.*, 1956, 1536.
[2] Gilman and Smart, *J. Org. Chem.*, 1954, **19**, 441, mention this reaction without naming the products.
[3] Dilthey and Eduardoff, *Ber.*, 1904, **37**, 1139.
[4] Richards and Thompson, *J.*, 1949, 124.

Hexaphenylcyclotrisiloxane. After 20 days at 21°, a solution of dichlorodiphenylsilane (10 c.c., 0·048 mole) in t-butyl alcohol (50 c.c.) had deposited hexaphenylcyclotrisiloxane, m. p. 192—192·5° (lit.,[5] 190°) (4·8 g., 51%). The infrared spectrum was in agreement with that reported.[4] Distillation of the mother-liquor gave a fraction (16·7 g.), b. p. 47—51° (lit.,[6] 51—52° for Bu^{t}Cl) from which water separated; after drying, this fraction had a similar infrared spectrum to that of t-butyl chloride.

We are grateful to Mr. D. G. Lloyd for the infrared spectra and to Miss J. Pate for experimental assistance.

MONSANTO CHEMICALS LIMITED, RUABON, DENBIGHSHIRE. [*Received, February 26th,* 1963.]

[5] Burkhard, *J. Amer. Chem. Soc.*, 1945, **67**, 2173.
[6] Perkin, *J.*, 1884, **45**, 451.

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878. *Synthesis of 5,5′-Dihydroxy-2,2′-dimethylbibenzyl, and Some Observations on its Oxidation.*

By M. S. GIBSON and J. M. WALTHEW.

SINCE the correction of the formula of " Pummerer's ketone " and the related synthesis of usnic acid,[1] a variety of natural products have been synthesised by the oxidative coupling of phenolic precursors,[2] though the yields have been low in many cases. The present work was suggested by the consideration that intramolecular oxidative coupling of 5,5′-dihydroxy-2,2′-dimethylbibenzyl might yield 3a,8,9,9b-tetrahydro-7,9b-dimethylphenanthro-[4,5-*bcd*]furan-2(3*H*)-one (by *ortho–para* coupling) and (±)-2,4a,4b,7,9,10-hexahydro-4a,4b-dimethyl-2,7-dioxophenanthrene (by *para–para* coupling) as non-phenolic products. The former compound is of interest because of its structural relation to morphine, whilst the latter is a potential intermediate for the synthesis of pentacyclic triterpenes.

For the synthesis, 5-methoxy-2-methylbenzoic acid [3] was required in quantity. After preliminary experiments with *o*-toluic acid, dipotassium 2-naphthol-6,8-disulphonate was converted into 5-hydroxy-2-methylbenzoic acid by alkal-fusion, the process [4] being considerably improved. The methylation of the phenolic acid with dimethyl sulphate and alkali has been reported (75% yield) without details.[5] In our hands, the yield was normally 54—62%, and the isolation of the product was complicated by co-precipitation of the starting material. However, a reasonable method has been developed for separating the two acids, and, by re-cycling starting material, an overall methylation yield of 83% attained.

Reduction of the methoxy-acid with lithium aluminium hydride gave 5-methoxy-2-methylbenzyl alcohol (85%); the intermediate esterification step used previously [6] can thus be omitted. The alcohol was converted into the chloride by treatment with dry hydrogen chloride in ether–light petroleum; water separated as the reaction proceeded, the equilibrium shifting in the desired direction.[7] This process is preferable to the thionyl chloride method. Grignard formation from the chloride was sluggish under

[1] Barton, Deflorin, and Edwards, *J.*, 1956, 530.
[2] *E.g.*, Day, Nabney, and Scott, *J.*, 1961, 4067; Davidson and Scott, *J.*, 1961, 4075; Barton and Kirby, *J.*, 1962, 806.
[3] Jacobsen, *Ber.*, 1883, **16**, 1962; cf. Baudisch and Perkin, *J.*, 1909, **95**, 1883.
[4] Baudisch, Hibbert, and Perkin, *J.*, 1909, **95**, 1870.
[5] Charlesworth, Rennie, Sinder, and Yan, *Canad. J. Res.*, 1945, **22**,*B*, 17.
[6] Stork, Wagle, and Mukharji, *J. Amer. Chem. Soc.*, 1953, **75**, 3197.
[7] Cf. Reichstein, Cohen, Ruth, and Meldahl, *Helv. Chim. Acta*, 1936, **19**, 412.

normal conditions, but satisfactory when freshly etched magnesium was used; anhydrous ferric chloride was an effective catalyst for the coupling.[8] Demethylation then gave 5,5′-dihydroxy-2,2′-dimethylbibenzyl, which was characterised as the tetrabromo-derivative.

The oxidation of 5,5′-dihydroxy-2,2′-dimethylbibenzyl with aqueous potassium ferricyanide at high dilution gave polymeric material; the tetrabromo-diol behaved similarly, though some starting material was recovered. On oxidation of the diol with manganese dioxide, *ca.* 4% of a monomeric, non-phenolic material was isolated. Though impure, this almost certainly contains the bis-dienone arising from *para–para* coupling, as it shows $\lambda_{max.}$ 247 mμ (log ε 4·08) (cf. cholesta-1,4-dien-3-one; $\lambda_{max.}$ 242 mμ, log ε 4·18);[9] the alternative product, from *ortho–para* coupling, would show $\lambda_{max.}$ 228—230 mμ (log ε 4·3) (cf. Pummerer's ketone). (A small quantity of a substance showing this absorption was obtained when the oxidation product was sublimed, the bulk of the material charring.) The tetrabromo-diol, with manganese dioxide, similarly gave *ca.* 4% of a product showing $\lambda_{max.}$ 260 mμ (log ε 4·1), again suggestive of a *para–para*-coupled product. However, it has not proved possible to obtain either product pure.

Experimental. Microanalyses were by Mr. V. Manohin. Light petroleum refers to the fraction of b. p. 60—80°, freed from unsaturated compounds by repeated washing with concentrated sulphuric acid, then washed with sodium hydrogen carbonate solution and water, dried, distilled, and stored over sodium.

5-Hydroxy-2-methylbenzoic acid. A mixture of dipotassium 2-naphthol-6,8-disulphonate (165 g.), sodium hydroxide (300 g.), and water (100 ml.) was placed in an autoclave (1 l.), and the temperature of the mixture raised to 275° and maintained there for 20 hr.; the pressure rose rapidly to 34 atm., and then fell to *ca.* 4 atm. When the autoclave had cooled to 80°, the brown viscous contents were poured into water (300 ml., including washings). The hot solution was acidified with concentrated hydrochloric acid; sulphur dioxide was copiously evolved and 5-hydroxy-2-methylbenzoic acid began to separate. When cold, the precipitate was collected and washed; a further quantity of the acid was recovered from the filtrate by extraction with ether (4 × 50 ml.). The crude acid was dissolved in hot sodium carbonate solution, and the filtered solution cooled and acidified with hydrochloric acid. Crystallisation from water gave needles (45 g., 68%), m. p. 184° (lit.,[4] 183°).

5-Methoxy-2-methylbenzoic acid. Dimethyl sulphate (100·8 g.) was added during 30 min. to a stirred solution of 5-hydroxy-2-methylbenzoic acid (60·8 g.) and sodium hydroxide (96 g.) in water (864 ml.) at 65°. After 30 min. at 60—70°, sodium hydroxide (96 g.) was added, followed by more dimethyl sulphate (100·8 g.) during 30 min. at 60—70°. After a further 30 min., the alkaline solution was boiled for 5 min. and acidified. When the temperature had fallen to 60°, the precipitate (A) was collected, and the filtrate allowed to cool to room temperature, solid (B) precipitating. Ether-extraction of the cold filtrate gave solid (C). Crystallisation of (A) from 50% aqueous ethanol gave the methoxy-acid (36·9 g., 56%) as needles, m. p. 148—149° (lit.,[5] 146—147°); concentration of the mother liquor gave impure starting material (7 g., m. p. 169—171°); this was combined with fractions (B) (12 g.; m. p. 180°) and (C) (7·4 g.; m. p. 179—181°), and the whole re-methylated. Separation as above and final recycling of phenolic acid fractions gave the methoxy-acid in 83% overall yield.

5-Methoxy-2-methylbenzyl alcohol. A solution of the methoxy-acid (63·2 g.) in dry tetrahydrofuran (250 ml.) was added dropwise during 6 hr. to a stirred suspension of lithium aluminium hydride (20 g.) in dry ether (300 ml.) in a 2 l. flask fitted with a double-surface condenser. The exothermic reaction was attended by frothing. When the reaction had moderated, the mixture was refluxed for 1 hr. and cooled in ice, and ethyl acetate added dropwise to destroy excess of reagent. The mixture was poured into water (500 ml.) acidified with hydrochloric acid, the organic layer separated, and the aqueous layer extracted with ether (200 ml.). The combined extracts were washed with sodium hydrogen carbonate solution and water, dried (Na_2SO_4), evaporated, and distilled, giving the alcohol (49 g., 85%), b. p. 136°/8 mm. (lit.,[6] 104—106°/0·6 mm.), n_D^{20} 1·5443 (Found: C, 71·0; H, 8·0. Calc. for $C_9H_{12}O_2$: C, 71·1; H, 7·9%).

[8] Cf. Oddo, *Gazzetta*, 1914, **44**, 277.
[9] Fieser and Fieser, "Steroids," Reinhold, New York, 1959, p. 287.

The alcohol (1·1 g.) and phthalic anhydride (1·0 g.) in dry pyridine (5 ml.) were heated on a steam-bath for 1 hr. The solution was poured on to crushed ice, acidified with hydrochloric acid, and extracted with chloroform (3 × 15 ml.). The extract was washed with water, dried, and evaporated; the residual oil was dissolved in a little ether, and crystallisation (at the interface) induced by addition of water. The *hydrogen phthalate* (1·2 g.) formed cubes, m. p. 98° (from aqueous ethanol) (Found: C, 67·7; H, 5·2. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%).

5-Methoxy-2-methylbenzyl chloride. A solution of 5-methoxy-2-methylbenzyl alcohol (20 g.) in dry ether (50 ml.) and light petroleum (100 ml.) was saturated with dry hydrogen chloride during 2 hr. at room temperature. Hydrogen chloride was passed intermittently through the solution during the next 5 days to maintain saturation. A lower aqueous layer slowly formed. The organic phase was separated, washed with water, 5% sodium carbonate solution, and water, and dried (Na_2SO_4). Concentration to *ca.* 20 ml. and cooling gave colourless plates, m. p. 39—40°. The pure chloride (19·8 g., 88%) had m. p. 43—44° (from light petroleum) (lit.,[6] 44—45°) (Found: C, 63·1; H, 6·4; Cl, 20·65. Calc. for $C_9H_{11}ClO$: C, 63·4; H, 6·4; Cl, 20·85%).

5,5′-Dimethoxy-2,2′-dimethylbibenzyl. Magnesium turnings (1·42 g.) and a crystal of iodine in a 500 ml. flask were warmed to volatilise the iodine and so etch the metal surface. A solution of 5-methoxy-2-methylbenzyl chloride (19·8 g.) in dry ether (90 ml.) was added dropwise to the cooled activated magnesium, whereupon formation of the Grignard reagent commenced immediately, and the reacting mixture required external cooling. When the reaction was complete, anhydrous ferric chloride (1 g.) was added to the grey solution. An intense red colour developed, fading rapidly to pale yellow as a white sediment was formed. The suspension was boiled for 3 hr., cooled, and an excess of aqueous ammonium chloride solution was added. The ethereal solution was separated, the aqueous phase was extracted with ether (30 ml.), and the combined ether extracts were washed, dried ($MgSO_4$), and evaporated. The residual oil was concentrated until all material of b. p. <140°/10 mm. had been removed. The undistilled residue solidified on cooling. The *bibenzyl* (9·2 g., 59%) formed needles, m. p. 78—79° (from light petroleum) (Found: C, 79·7; H, 8·2. $C_{18}H_{22}O_2$ requires C, 80·0; H, 8·2%). The mother-liquor afforded a second crop (2 g.), m. p. 70—75°.

5,5′-Dihydroxy-2,2′-dimethylbibenzyl. A mixture of 5,5′-dimethoxy-2,2′-dimethylbibenzyl (9·2 g.), freshly distilled hydriodic acid (90 ml.), and glacial acetic acid (100 ml.) was refluxed for 3 hr., cooled, and poured on to crushed ice. The suspension was decolorised by addition sodium sulphite, basified with sodium hydroxide solution, filtered, and acidified with concentrated hydrochloric acid. The precipitate was collected, washed, and dried. Crystallisation from chloroform gave *5,5′-dihydroxy-2,2′-dimethylbibenzyl* (7·24 g., 88%) as needles, m. p. 164° (Found: C, 79·2; H, 7·6. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·4%).

A solution of bromine (2·65 g.) in glacial acetic acid (50 ml.) was added during 30 min. to a stirred solution of the above diol (1·0 g.) in acetic acid (50 ml.). After 30 min., the solution was poured into water (200 ml.), and the precipitate collected, washed, and dried. From chloroform, *4,4′,6,6′-tetrabromo-5,5′-dihydroxy-2,2′-dimethylbibenzyl* (1·44 g., 63%), separated as needles, m. p. 200° (Found: C, 34·5; H, 2·7. $C_{16}H_{14}Br_4O_2$ requires C, 34·4; H, 2·5%).

We thank the Department of Scientific and Industrial Research for a maintenance grant (to J. M. W.), Imperial Chemical Industries Limited (Dyestuffs Division) for a gift of chemicals, and Dr. G. A. Hughes for helpful discussion.

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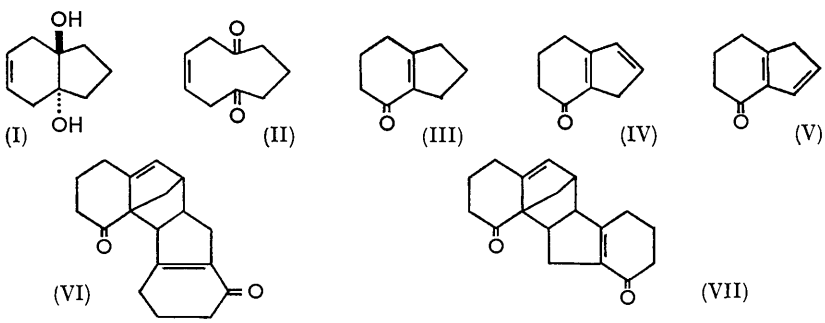
879. *Cyclononane Derivatives.*

By G. L. Buchanan, J. G. Hamilton, and R. A. Raphael.

As an approach to certain required substituted cyclononanes, the use of the *trans*-diol (I), readily obtainable [1] from indane, suggested itself. Fission of this diol by lead tetra-acetate produced the crystalline *cis*-cyclonon-3-en-1,6-dione (II) which showed ultraviolet absorption appropriate [2] to a $\beta\gamma$-unsaturated ketone [$\lambda_{max.}$ (in EtOH) 292 mμ (ε 1200)] and equally consistent absorption in the infrared region [$\nu_{max.}$ (in CCl_4) 1703 (C=O), (thin film) 776 (C=C) cm.$^{-1}$]. The presence of a nine-membered carbocycle in this product was confirmed by hydride reduction followed by catalytic hydrogenation to a mixture of *cis*- and *trans*-cyclononane-1,5-diols; these were separated and characterised by comparison with authentic samples.[3] Cataytic hydrogenation of the dione (II) itself was accompanied by transannular aldolisation of the expected cyclononane-1,5-dione to form the known tetrahydroindanone [3] (III).

In an attempt to induce double-bond rearrangement to the conjugated isomer the ketone (II) was treated with ethanolic potassium acetate (more drastic conditions caused extensive decomposition). The solid ketonic product (A) thus obtained seemed, on the basis of analysis and mass-spectrometric molecular weight (134), to possess the composition $C_9H_{10}O$. This formula was consistent with a not-unexpected transannular aldolisation of the diketone (II) or its conjugated isomer to produce one of the isomeric dienones (IV) and



(V). However, neither of these alternatives was consistent with the spectral properties of material (A) [$\lambda_{max.}$ (in EtOH) 249 mμ (ε 9400); $\nu_{max.}$ (in CCl_4) 1705m, 1680s, 1635w cm.$^{-1}$]. Again the borohydride reduction product of this material (A) showed no ultraviolet absorption above 220 mμ; dienones (IV) and (V) would have produced a conjugated dienol on this treatment. This anomaly was clarified by determining the molecular weight ebullioscopically; the result (236) indicated a dimeric formulation $(C_9H_{10}O)_2$ for compound (A). We thus suppose that the compound dissociated into two equal halves in the electron-beam of the mass-spectrometer. Such a dissociation appeared to be induced even by heating since a redistilled sample solidified only slowly even on being seeded. These findings suggested that compound (A) was a Diels–Alder dimer of (IV) or (V). It is noteworthy that the borohydride reduction product gave the expected mass-spectrometric molecular weight (272).

A detailed examination of the infrared spectrum of compound (A) in a number of solvents (see Experimental section) showed that the correct formulation must accommodate both saturated and conjugated carbonyl groups; the ultraviolet absorption demanded that the latter

[1] Giovannini and Wegmüller, *Helv. Chim. Acta*, 1958, **41**, 933.
[2] Cookson and Wariyar, *J.*, 1956, 2302.
[3] Prelog, Schenker, and Küng, *Helv. Chim. Acta*, 1953, **36**, 471.

carbonyl be in conjugation with a fully substituted double bond. Consideration of all possible Diels–Alder dimers theoretically obtainable from (IV) and (V) leaves only two possible structures, (VI) and (VII), both derived from (IV), which satisfy the light-absorption properties. We conclude, therefore, that acetate treatment of the enedione (II) converts it into (IV) which then dimerises to (VI) or (VII).

Experimental.—cis-*Cyclonon-3-en-1,6-dione* (II). Grob and Schiess's technique [4] gave the best results. The diol (I) (10 g.) and trichloroacetic acid (30 g.) in dry methanol (220 ml.), cooled to −10°, were treated portionwise, by stirring with finely powdered lead tetra-acetate (50 g.) which was continued for 1 hr. at −10°, and for a further 2 hr. at 15°. Most of the solvent was removed at room temperature under a vacuum. To the residue were added water (700 ml.) and chloroform (2 l.), and the mixture was stirred and made faintly alkaline with dilute aqueous sodium carbonate. The choroform layer was separated and the aqueous layer and the precipitated lead salts were re-extracted with chloroform. The united extracts were washed with dilute aqueous sodium carbonate, then with water, dried, and concentrated under a vacuum, yielding the crude semi-solid product (8·7 g.). Two low-temperature crystallisations from ether gave the pure *dione* (4·2 g., 45%), m. p. 25° (Found: C, 70·8; H, 8·2. $C_9H_{12}O_2$ requires C, 71·0; H, 7·95%).

The *bis*-2,4-*dinitrophenylhydrazone* was unstable to heat and to prolonged contact with mineral acid. The temperature had to be kept below 10° during its preparation, and the precipitate filtered off after 1 min. and washed well with methanol. The derivative crystallised from ethyl acetate in yellow needles, m. p. 201° (Found: C, 49·0; H, 4·3; N, 21·9. $C_{21}H_{20}N_8O_8$ requires C, 49·2; H, 3·9; N, 21·9%).

Reductions of the dione. (*a*) To a solution of the dione (3 g.) in anhydrous ether (20 ml.) was added lithium aluminium hydride (2 g.). The mixture was vigorously stirred and refluxed for 4 hr., then stirred overnight at room temperature. The excess of hydride was destroyed with ethyl acetate, and saturated aqueous sodium sulphate was added, with shaking, until the inorganic salts aggregated into a crystalline mass. This was filtered off and extracted with ether. The combined filtrate and ether extracts afforded a crude oil which was reduced catalytically in methanol (100 ml.) in the presence of 10% palladium–charcoal (0·5 g.). In 5 hr. 0·8 mol. of hydrogen was absorbed and the usual working up gave a viscous oil which was chromatographed in benzene–ether on basic alumina. Elution with benzene–ether afforded a solid, m. p. 61—64° (from light petroleum), which gave a *p*-nitrobenzoate, m. p. 150—152°, identical (mixed m. p.) with the *p*-nitrobenzoate of one of the cyclononane-1,5-diols of Prelog *et al.*[3] Further elution with ether yielded an oil, whose *p*-nitrobenzoate, m. p. 178—180° (from chloroform–methanol), was identical (mixed m. p.) with that obtained from the epimeric diol described by Prelog *et al.*[3]

(*b*) The dione (II) (3 g.) in ethanol (100 ml.) was hydrogenated in the presence of 10% palladium–charcoal (1·5 g.), 1·2 mols. of hydrogen being taken up in 5 min. The catalyst was filtered off and the solvent removed under a vacuum, leaving an oil which showed C=O absorption at 1680 cm.$^{-1}$. It afforded a semicarbazone, m. p. 253—254° (from methanol), and a 2,4-dinitrophenylhydrazone, m. p. 247—249° (from chloroform–methanol), which gave no depression in m. p. when admixed with the corresponding derivatives of 4,5,6,7-tetrahydroindan-4-one [3] (III).

	ν (cm.$^{-1}$) ($\Delta\frac{1}{2}a$)		
Solvent	(a)	(b)	(c)
Hexane	1710 (4·3)	1680 (3·5)	1635 (6)
Carbon tetrachloride	1705 (8)	1672 (11)	1633 (8)
Chloroform	1700 (12)	1658 (10)	1631 (9)

Reaction of the dione (II) *with potassium acetate.* A solution of the dione (5 g.) and anhydrous potassium acetate (10 g.) in ethanol (100 ml.) was stirred at 30° for 2 hr. and the solvent then removed *in vacuo* at that temperature. A mixture of water (100 ml.) and chloroform (100 ml.) was added, the mixture was made just acid with dilute hydrochloric acid, and the organic layer was separated, washed, dried, and concentrated. The resulting resin distilled at 100°/0·1 mm.

[4] Grob and Schiess, *Helv. Chim. Acta*, 1960, **43**, 1546.

as a pale amber, mobile liquid which slowly crystallised. The solid *product* (A) (VI) or (VII) (0·6 g.) was twice recrystallised from methanol and then had m. p. 110° [Found: C, 80·35; H, 7·2%; *M* (mass-spectroscopy) 134, (ebullioscopic) 236. $C_9H_{10}O$ requires C, 80·6; H, 7·5%; *M*, 134].

From an examination of the infrared spectral shifts in various solvents (see Table) it may be deduced [5] that bands a and b represent carbonyl functions whilst band c represents a carbon–carbon double bond. Borohydride reduction afforded a crude solid which, crystallised from chloroform–methanol, had m. p. 120—135°: attempted purification by fractional crystallisation or chromatography was unsuccessful. Its infrared spectrum showed a strong OH band but no C=O absorption [Found: *M* (mass-spectroscopy), 272]. On re-oxidation with potassium dichromate this product afforded the ketone (A), demonstrating that no anomalous reduction [6] had occurred.

The authors are indebted to D.S.I.R. for a maintenance grant (to J. G. H.), to Mr. J. M. L. Cameron, B.Sc., and his staff for micro-analyses, to Mrs. F. Lawrie for determining the infrared spectra and to Dr. R. I. Reed and his associates for the mass spectra. They also thank Professor V. Prelog for supplying samples for comparison.

CHEMISTRY DEPARTMENT, THE UNIVERSITY, GLASGOW, W.2. [*Received, March 16th*, 1963.]

[5] Bellamy and Rogasch, *Spectrochim. Acta*, 1960, **16**, 30.
[6] Goering, Greiner, and Sloan, *J. Amer. Chem. Soc.*, 1961, **83**, 1391; Atwater, *ibid.*, p. 3071.

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880. *Planar–Tetrahedral Isomerism of Bis-(N-n-alkylsalicylideneaminato)nickel(II) Complexes in Pure Liquid Phases.*

By L. SACCONI.

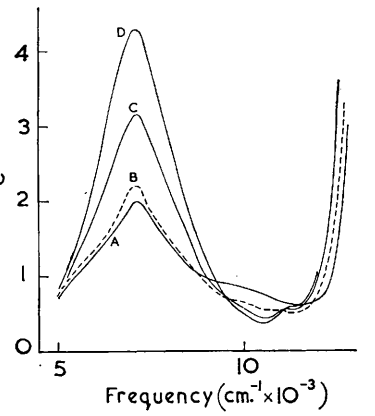
THE nickel(II) complexes with *N*-n-alkylsalicylideneamines, from the ethyl to the n-decyl derivative, dissolved in inert solvents, were found to be essentially diamagnetic and non-polar at room temperature, and therefore *trans*-planar.[1] Above 100° the μ_{eff} values of such compounds, in solution in dibutyl phthalate as well as in the molten state, increase steadily with temperature from about 0·8 B.M. at 100—120° to 1·1—1·2 B.M. at 200°.[2,3] The corresponding percentages of paramagnetic forms, calculated from the formula, % param. $= \mu_{eff}^2/3{\cdot}3^2 \times 100$, are 6% and 11—13%, respectively.

This paramagnetism is not fully accounted for by the assumption of an equilibrium between diamagnetic and paramagnetic planar forms. The decrease in the singlet–triplet separation, ΔE, at temperatures above 100—120°, which would correspond to an increase with temperature in the axial perturbation on the ligand field by the liquid,[4] is difficult to explain satisfactorily. Similarly, the hypothesis of formation of paramagnetic associated species, as assumed for the paramagnetic solid *N*-methyl nickel(II) complex [5] and then for the solutions of the initially diamagnetic isomer,[6] can be safely discarded. All the representative compounds of this series so far investigated are practically monomeric in both freezing and boiling benzene.[6,7] Furthermore, the logarithms of the viscosity of the melts of the n-nonyl and n-decyl derivatives, measured between 100° and 180°,

[1] Sacconi, Paoletti, and Del Re, *J. Amer. Chem. Soc.*, 1957, **79**, 4062.
[2] Sacconi, Cini, and Maggio, *J. Amer. Chem. Soc.*, 1957, **79**, 3933.
[3] Sacconi, Cini, Ciampolini, and Maggio, *J. Amer. Chem. Soc.*, 1960, **82**, 3487.
[4] Liehr and Ballhausen, *J. Amer. Chem. Soc.*, 1959, **81**, 538; Maki, *J. Chem. Phys.*, 1959, **29**, 1129.
[5] Sacconi, Paoletti, and Cini, Internl. Symposium on Co-ordination Chemistry, Rome, 1957, *Ricerca Sci.*, 1958, **28** *Suppl.*; *J. Inorg. Nuclear Chem.*, 1958, **8**, 492; *J. Amer. Chem. Soc.*, 1958, **80**, 538.
[6] Holm, *J. Amer. Chem. Soc.*, 1961, **83**, 4683.
[7] Sacconi, Orioli, Paoletti, and Ciampolini, *Proc. Chem. Soc.*, 1962, 255; Sacconi, Paoletti, and Ciampolini, *J. Amer. Chem. Soc.*, 1963, **85**, 411.

were found to be linear with $1/T$. This indicates that the molecular complexity of these compounds in the molten state does not vary over this range of temperature.[3]

The discovery of the existence of tetrahedral co-ordination in s-alkyl nickel(II) complexes [7] led to further investigations on the analogous *N*-n-alkyl compounds. In this case no conclusive information on the stereochemistry of these complexes in the molten state was obtained from spectrophotometric measurements in the 5000—12,000 cm.$^{-1}$ region.



Temperature-dependence of the ligand-field spectrum of molten bis-(*N*-n-decylsalicylideneaminato)nickel(II). A, 100°; B, 130°; C, 170°; D, 200°.

While no absorption band is observed in benzene solutions at room temperature, at 80—100° the spectra of all the complexes show two incipient bands at 7150—7300 and 11,100—11,200 cm.$^{-1}$ whose intensities increase sharply with temperature. A representative absorption curve, that for the molten n-decyl compound, is shown in the Figure.* The first maximum may be considered as a ν_2 band corresponding to a $^3T_1 \longrightarrow {}^3A_2$ transition; the other weak band may be assigned to spin-forbidden transition to upper states arising from the ^1D state of the free ion. These two maxima were found to be diagnostic of the tetrahedral forms of the salicylideneaminatonickel(II) chelates.[7] This leads to the conclusion that, both in the melts and in the bibenzyl solutions of these *N*-n-alkyl compounds, at temperatures above 100°, a conformational equilibrium between diamagnetic planar and paramagnetic tetrahedral isomers exists which is displaced to the right with increasing temperature.

From a comparison of the spectral and dielectric polarisation data for the benzene solutions of the t-butyl complex,[7] a value of *ca.* 42 can be obtained by extrapolation for the molar absorbance at the ν_2 maximum of the pure tetrahedral forms of the *N*-alkylsalicylideneaminatonickel(II) chelates. If we divide the molar absorbance at 200° of this peak of the n-decyl complex, about 4·3, by such a value, a proportion of *ca.* 10% of tetrahedral species is found to be present in the melts of the n-decyl derivative at such a temperature. This value is very close to the 11% of paramagnetic forms calculated from the magnetic data at the same temperature. This demonstrates that the presence of tetrahedral species is predominantly, if not wholly, responsible for the paramagnetism of these liquids above 100°.

Following the discovery of tetrahedral forms of *N*-s-alkyl-[7] and *N*-aryl-salicylideneaminatonickel(II) complexes [8] in the solid phase or in solution, this is the third example found so far of tetrahedral co-ordination of nickel(II) complexes with Schiff bases. This indicates that the occurrence of tetrahedral species of such complexes, especially in liquid

* Since some absorption maxima of the ligand salicylideneimines fall in this region, the corresponding Schiff bases were used as blanks.

[8] Sacconi and Ciampolini, *J. Amer. Chem. Soc.*, 1963, **85**, 1750.

phases at elevated temperatures, is not as rare as has been thought. Evidently the energy difference between the tetrahedral and the planar arrangement is so small that a sufficient increase in temperature leads to the formation, in solution as well as in the melt, of an appreciable proportion of tetrahedral forms. At a given temperature the percentage of tetrahedral species of n-alkyl derivatives is lower than for the α-branched salicylideneaminatonickel(II) complexes. This shows that steric and electronic factors do not favour the attainment of such a configuration for the n-alkyl over the α-branched derivatives.

Experimental.—The *N*-n-alkylsalicylideneaminatonickel(II) complexes were prepared as previously described.[1,3] The absorption spectra were recorded with a Beckman DK2 spectrophotometer equipped with a thermostat-controlled cell housing. Temperatures from 100° to 200° were obtained by circulating liquid paraffin from a thermostat regulating to ±0·5°. The light-paths of the stoppered silica cells were 1·00 cm. for the measurements on the solutions and 0·10 cm. for the measurements on the melts. In calculating extinction coefficients, allowance was made for the variation of the density of the solution and the melt with the temperature. Bibenzyl was purified by repeated crystallization from light petroleum.

Thanks are due to C.N.R. and C.N.E.N. for support and to Dr. N. Nardi for the spectrophotometric measurements.

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881. *Reductive Cyclisations by Means of Sodium Borohydride and Palladium–Charcoal.*

By R. T. COUTTS and D. G. WIBBERLEY.

CYCLIC hydroxamic acids related to quinoline show antibacterial activity,[1] but no general method exists for their preparation in good yield. Our previous attempts to prepare them by reductive cyclisation of *o*-nitro-esters have met with only limited success,[2,3] owing to side reactions or reduction of the nitro-group beyond the required hydroxyamino-stage. Neilson, Wood, and Wylie [4] have recently described the use of sodium borohydride catalysed by palladium–charcoal for the preparation of amines from aromatic nitro-compounds. Although these authors were unable to isolate any intermediate compounds their reactions were carried out in alkaline solution, a factor which should favour cyclic hydroxamic acid formation. We have now demonstrated that *o*-nitro-esters, in which the ester group is suitably orientated with respect to the *o*-nitrophenyl group, give good yields of cyclic hydroxamic acids on treatment with sodium borohydride in the presence of palladium–charcoal. Thus, methyl *o*-nitrobenzoylacetate yielded 1,2-dihydro-1,4-dihydroxy-2-oxoquinoline, and methyl α-cyano-α-*o*-nitrobenzoylacetate gave 3-cyano-1,2-dihydro-1,4-dihydroxy-2-oxoquinoline. Ethyl *o*-nitrobenzylidenemalonate, which has one ethoxycarbonyl group in the *cis*-position, gave 3-ethoxycarbonyl-1,2-dihydro-1-hydroxy-2-oxoquinoline whereas reduction of methyl *trans*-*o*-nitrocinnamate yielded 1,2-dihydro-2-oxoquinoline. In the latter reaction there was evidence of the formation of methyl *o*-aminocinnamate, but no hydroxamic acid was produced. Ethyl α-cyano-α-*o*-nitrobenzylideneacetate also exists in the ethyl *trans*-*o*-nitrocinnamate form, and previous reductions [5]

[1] Newbold and Spring, *J.*, 1948, 1864; Cunningham, Newbold, Spring, and Stark, *J.*, 1949, 2091.
[2] Coutts, Hooper, and Wibberley, *J.*, 1961, 5058.
[3] Coutts and Wibberley, *J.*, 1962, 2518.
[4] Neilson, Wood, and Wylie, *J.*, 1962, 371.
[5] Bauer, *Ber.*, 1938, **71**, 2226.

of this compound have involved addition at the nitrile group with formation of 2-amino-3-ethoxycarbonylquinoline. With sodium borohydride and palladium–charcoal, however, 3-cyano-1,2-dihydro-2-oxoquinoline was the major product.

Hydroxylamines condense most readily with ketones and with esters but not with acids. It would therefore be expected that, in this type of reductive cyclisation, suitable nitro-ketones would yield cyclic *N*-oxides, nitro-esters would give cyclic hydroxamic acids, and nitro-acids, which would not cyclise at the hydroxyamino-stage, would be further reduced to amino-acids, capable of lactamisation. These conjectures were borne out in practice; not only did *o*-nitrobenzoylacetone give an excellent yield of 4-hydroxy-2-methylquinoline 1-oxide, but also methyl *o*-nitrobenzoylacetoacetate gave 4-hydroxy-3-methoxycarbonyl-2-methylquinoline 1-oxide and not the 3-acetylquinoline hydroxamic acid. Free acids on reduction did not give hydroxamic acids; *o*-nitrobenzoylacetic acid, for example, yielded 1,2-dihydro-4-hydroxy-2-oxoquinoline. 1-Hydroxyindole-2-carboxylic acid was the sole acidic reduction product from both *o*-nitrophenylpyruvic acid and its methyl ester.

Reductive cyclisation with sodium borohydride in the presence of palladium–charcoal has also proved successful for the preparation of other heterocyclic hydroxamic acids. We have obtained 1-hydroxyoxindole on reduction of ethyl *o*-nitrophenylacetate, and have shown that methyl 5-methyl-3-*o*-nitrophenylpyrazole-4-carboxylate yielded 4,5-dihydro-5-hydroxy-3-methyl-4-oxo-1*H*-pyrazolo[4,3-*c*]quinoline. The corresponding acid, however, as expected, yielded 4,5-dihydro-3-methyl-4-oxo-1*H*-pyrazolo[4,3-*c*]quinoline. Reductive cyclisation of methyl (*o*-nitrophenylthio)acetate also proceeded normally to give 3,4-dihydro-4-hydroxy-3-oxo-1,4-benzothiazine. Similarly, methyl (*o*-nitrobenzenesulphonyl)acetate gave 3,4-dihydro-4-hydroxy-3-oxo-1,4-benzodiazine 1,1-dioxide.

All the cyclic hydroxamic acids described above were soluble in aqueous sodium hydrogen carbonate solution and, with the exception of 1-hydroxyoxindole which gave a deep blue colour,[6] all gave the characteristic wine-red colour with aqueous ferric chloride solution.

Experimental.—General method of reductive cyclisation. A solution of the nitro-compound (0·01 mole) in either sodium hydroxide or methanol was added during 5 min. to a suspension of palladium–charcoal (0·05 g.) in aqueous sodium borohydride (0·02 mole) solution. A slow stream of nitrogen was passed through the stirred mixture during the addition and for a further 15 min., the charcoal removed, and the product liberated by addition of acid, followed by removal of the methanol, if necessary.

1,2-Dihydro-1,4-dihydroxy-2-oxoquinoline [2] (61%), m. p. 275—276°, was obtained by reduction of methyl *o*-nitrobenzoylacetate.

3-Cyano-1,2-dihydro-1,4-dihydroxy-2-oxoquinoline (99%), m. p. 228—229° (decomp.) (from ethanol), was obtained from methyl α-cyano-α-*o*-nitrobenzoylacetate (Found: C, 59·35; H, 3·0; N, 13·9. $C_{10}H_6N_2O_3$ requires C, 59·4; H, 3·0; N, 13·9%); $\nu_{max.}$ 2260s (CN).

3-*Ethoxycarbonyl*-1,2-*dihydro*-1-*hydroxy*-2-*oxoquinoline* [7] (59%), m. p. 168—169°, was obtained from ethyl *o*-nitrobenzylidenemalonate. The corresponding quinoline acid (m. p. 258—259°) and its acetyl derivative (m. p. 203—204°) were prepared.[7]

3-Cyano-1,2-dihydro-2-oxoquinoline (80%), m. p. 154—155°, was isolated as its hydrate from the reduction of ethyl α-cyano-α-*o*-nitrobenzylideneacetate (Found: C, 63·8; H, 4·0; N, 15·1. $C_{10}H_8N_2O_2$ requires C, 63·8; H, 4·3; N, 14·9%). The hydrate gave no wine-red colour with ferric chloride. On treatment with acetic anhydride, the anhydrous product,[8] m. p. 330—332°, was formed (Found: C, 70·7; H, 3·95; N, 16·1. Calc. for $C_{10}H_6N_2O$: C, 70·6; H, 3·5; N, 16·5%).

4-Hydroxy-2-methylquinoline 1-oxide [3] (86%), m. p. 247—248° (decomp.), was obtained from *o*-nitrobenzoylacetone.

[6] Reissert, *Ber.*, 1908, **41**, 3921.
[7] Loudon and Wellings, *J.*, 1960, 3462.
[8] Guareschi, *Chem. Zentr.*, 1894, **65**, II, 211.

4-Hydroxy-3-methoxycarbonyl-2-methylquinoline 1-oxide (98%), m. p. 192—193° (from ethanol), was obtained from methyl *o*-nitrobenzoylacetoacetate (Found: C, 62·1; H, 4·8; N, 5·9. $C_{12}H_{11}NO_4$ requires C, 61·8; H, 4·7; N, 6·0%).

1,2-Dihydro-4-hydroxy-2-oxoquinoline [9] (31%), m. p. 344—345°, was the sole acidic product obtained from *o*-nitrobenzoylacetic acid. The filtrate gave a positive reaction for primary aromatic amines.

1-Hydroxyindole-2-carboxylic acid,[10] m. p. 166—167° (decomp.), resulted from the reduction of both *o*-nitrophenylpyruvic acid (40%) and its methyl ester (64%).

1-Hydroxyoxindole [11] (40%), m. p. 197—198°, was obtained from ethyl *o*-nitrophenylacetate.

Methyl 5-methyl-3-o-nitrophenylpyrazole-4-carboxylate. In a large-scale preparation of 1,2-dihydro-1,4-dihydroxy-2-oxoquinoline by the action of hydrazine hydrate and palladium–charcoal on methyl *o*-nitrobenzoylacetoacetate [2] the filtrate on concentration and dilution with water yielded the *pyrazole* (30%), m. p. 150—151° (from water) (Found: C, 55·7; H, 4·2; N, 15·8. $C_{12}H_{11}N_3O_4$ requires C, 55·2; H, 4·2; N, 16·1%). Treatment with sodium borohydride and palladium–charcoal yielded *4,5-dihydro-5-hydroxy-3-methyl-4-oxo-1H-pyrazolo-[4,3-c]quinoline* (98%), which separated from ethanol in needles, m. p. >300° (decomp.) (Found: C, 61·8; H, 4·1; N, 19·5. $C_{11}H_9N_3O_2$ requires C, 61·5; H, 4·2; N, 19·5%). The corresponding *pyrazole-4-carboxylic acid*, obtained in quantitative yield by hydrolysis of the ester, separated from acetic acid in prisms, m. p. 293—294° (decomp.) (Found: C, 53·55; H, 3·85; N, 16·8. $C_{11}H_9N_3O_4$ requires C, 53·4; H, 3·65; N, 17·0%); on reduction it yielded *4,5-dihydro-3-methyl-4-oxo-1H-pyrazolo[4,3-c]quinoline* (95%), m. p. >350° (from methanol) (Found: C, 66·2; H, 4·6; N, 21·1. $C_{11}H_9N_3O$ requires C, 66·3; H, 4·6; N, 21·1%).

Methyl (o-nitrophenylthio)acetate, prepared by the action of diazomethane on a solution of the corresponding acid in ether–methanol, formed yellow needles, m. p. 89—90° (from ethanol) (Found: C, 48·0; H, 3·9; N, 6·1; S, 14·1. $C_9H_9NO_4S$ requires C, 47·6; H, 4·0; N, 6·2; S, 14·1%). Reduction yielded *3,4-dihydro-4-hydroxy-3-oxo-1,4-benzothiazine* (47%), m. p. 151—152° (from aqueous ethanol) (Found: C, 53·2; H, 4·0; N, 7·8; S, 17·6. $C_8H_7NO_2S$ requires C, 53·1; H, 3·9; N, 7·7; S, 17·7%).

Methyl (o-nitrobenzenesulphonyl)acetate, similarly prepared from the corresponding acid, formed prisms, m. p. 119—120° (from ethanol) (Found: C, 42·1; H, 3·6; N, 5·4; S, 12·3. $C_9H_9NO_6S$ requires C, 41·7; H, 3·5; N, 5·4; S, 12·35%). Reduction yielded *3,4-dihydro-4-hydroxy-3-oxo-1,4-benzothiazine 1,1-dioxide* (80%), m. p. 149—150° (from ethyl acetate) (Found: C, 45·3; H, 3·6; N, 6·8; S, 15·5. $C_8H_7NO_4S$ requires C, 45·1; H, 3·3; N, 6·6; S, 15·0%).

We thank Mr. D. Noble for the preparation of the sulphur-containing hydroxamic acids.

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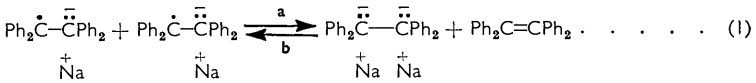
[*Received, April 1st*, 1963.]

[9] Bischoff, *Annalen*, 1889, **251**, 376.
[10] Reissert, *Ber.*, 1896, **29**, 646.
[11] Wright and Collins, *J. Amer. Chem. Soc.*, 1956, **78**, 221.

882. *The Catalytic Action of Anionic Catalysts. Part IV.*[1] *The Importance of the Positive Counterion.*

By ALWYN G. EVANS and B. J. TABNER.

WHEN a tetrahydrofuran solution of tetraphenylethylene is allowed to come into brief contact with a sodium film and then filtered, the following disproportionation equilibrium is set up:



(1)

The positions of the electrons shown on these ions are formal and do not indicate their actual location. Electron spin resonance (e.s.r.) and visible absorption measurements of this system at various temperatures give the results shown in the Table.[1]

Counter-ion	$\lambda_{max.}$, di-ion (mμ)	$\lambda_{max.}$, radical ion (mμ)	E.s.r. signal (20°)	ΔH_{1a} (kcal. mole^{-1})	K_1 (30°)	$\Delta G°_{1a}$ (kcal. mole^{-1}) (30°)	$\Delta S°_{1a}$ (cal. deg.$^{-1}$ mole^{-1}) (30°)
Lithium.....	485	645	Strong	15·8	$4·1 \times 10^2$	−3·6	64
Sodium	466	675	Strong	11·0	$2·8 \times 10^3$	−4·8	52
Potassium...	465	—	Weak	0—1	—	—	—
Casesium ...	470	—	Nil	Zero or negative	—	—	—

We have now used lithium, potassium, and cæsium as electron-donors to the olefin and hence as counterions in equilibrium (1). In the case of lithium we find that the e.s.r. spectrum for lithium tetraphenylethylene is the same as for sodium tetraphenylethylene, but that equilibrium (1) lies further to the left, and that the increase in radical-ion concentration with decrease in temperature is more marked than in the case of sodium.

When potassium is used as counterion, however, a very small e.s.r. signal is obtained at room temperature, and the increase of this signal with decrease in temperature, and of the visible absorption corresponding to the radical ion, is much smaller than in the case of sodium. With cæsium as counterion, no e.s.r. signal is obtained, and no development of radical-ion absorption can be detected with decrease in temperature. The results are summarised in the Table for systems in which the concentration of the alkali-metal ions is approximately equal to the concentration of total olefin.

Using lithium, potassium, and cæsium as counterions, we have studied the change in the visible spectrum of the system with change of temperature (as we did earlier for sodium [1]). In the case of lithium, the extinction coefficient of the tetraphenylethylene di-ion was determined as $2·7 \times 10^4$ by leaving a tetrahydrofuran solution of the tetraphenylethylene in contact with lithium until no further increase in optical density occurred. Neutral olefin was added to a tetrahydrofuran solution of di-ion, and the extinction coefficient of the radical ion determined as $3·1 \times 10^4$. By using these values, K_1 was determined from 50° to 0°, and log K_1 was then plotted against $1/T$. This gave $\Delta H_{1a} = 15·8$ kcal. mole^{-1}.

The results (see Table) show that as we change the counterion from cæsium through potassium and sodium to lithium, the radical ions are made increasingly more stable with respect to the di-ion. We believe this to be because the radical-ion ion-pairs will be more easy to solvate than will the di-ion ion-pairs, since the charges are so close together in the

[1] Part III, Bennett, Evans, Evans, Owen, and Tabner, *J.*, 1963, 3954.

latter. Thus, as the importance of solvation increases from cæsium to lithium, so will the stability of the radical ions with respect to the di-ion.

This interpretation is supported by the fact that although equilibrium (1) is exothermic in the direction of formation of radical ions, only a small proportion of the olefin is present as radical ions at ordinary temperatures because of the large drop in entropy associated with the change from di-ion plus olefin to radical ions. Furthermore, this drop in entropy is increased on changing from sodium to lithium.

We thank the University of Wales for a Research Studentship (to B. J. T.) and D.S.I.R. for a grant to purchase the e.s.r. spectrometer.

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883. *The Rearrangement of* 1-*Bromopentan*-2-*one.*

By M. D. MEHTA, D. MILLER, and D. J. D. TIDY.

THE rearrangement of α-bromo-ketones to their isomers under the influence of hydrogen bromide has been observed in the case of derivatives of β-diketones,[1] β-keto-esters,[2] and steroidal ketones.[3] The isomerisations of 1-bromo-1,1-diphenylpropan-2-one and 1-bromo-3-phenylpropan-2-one have also been studied [4] but no rearrangement of a simple aliphatic α-bromo-ketone has hitherto been reported.

We have observed the rearrangement of 1-bromopentan-2-one (I) [5,6] to the isomeric 3-bromopentan-2-one (III).[6] This reaction occurred slowly under the influence of hydrogen bromide in ether at room temperature, or more rapidly with 48% aqueous hydrobromic acid in glacial acetic acid under reflux. In each experiment, a small quantity of 1-bromo-ketone remained, as shown by gas chromatography, together with several unidentified minor products. When 3-bromopentan-2-one was treated with ethereal hydrogen bromide, a small amount of the 1-bromo-isomer was formed. These results indicate that an equilibrium is set up between the isomeric ketones, lying very much in favour of the more stable 3-bromo-ketone.

$$\underset{\text{(I)}}{Br{\cdot}CH_2{\cdot}COPr^n} \overset{HBr}{\rightleftharpoons} \underset{\text{(II)}}{CH_3{\cdot}COPr^n} + Br_2 \overset{HBr}{\rightleftharpoons} \underset{\text{(III)}}{CH_3{\cdot}CO{\cdot}CHEtBr}$$

Of the various mechanisms put forward, the most favoured has been the one involving debromination and rebromination under the influence of hydrogen bromide, with the intermediate formation of a dehalogenated ketone and free bromine.[7] Evidence that the rearrangement of 1-bromopentan-2-one proceeds at least partially by this mechanism was obtained by carrying out an experiment in ethereal hydrogen bromide containing 1 mol. of 2-naphthol; this should compete with the intermediate pentan-2-one (II) for

[1] Tavares, O'Sullivan, and Hauser, *J. Org. Chem.*, 1962, **27**, 1251.
[2] Hantzsch, *Ber.*, 1894, **27**, 3168; Hirst and Macbeth, *J.*, 1922, **121**, 2169.
[3] Heilbron, Jones, and Spring, *J.*, 1937, 801; Jones and Wluka, *ibid.*, 1959, 907, 911; Fishman, *J. Org. Chem.*, 1962, **27**, 1745.
[4] Stevens and Lenk, *J. Org. Chem.*, 1954, **19**, 538; Smith and Wilson, *J.*, 1955, 1342; Smith, Wilson, and Woodger, *Chem. and Ind.*, 1954, 309.
[5] Catch, Elliott, Hey, and Jones, *J.*, 1948, 278.
[6] Catch, Hey, Jones, and Wilson, *J.*, 1948, 276.
[7] Crowne, Evans, Green, and Long, *J.*, 1956, 4351, and references therein.

any bromine formed, with the consequent accumulation of (II). From the products, a small quantity of 1-bromo-2-naphthol was isolated and pentan-2-one was identified and estimated by gas chromatography. Neither of these products was detected in a control experiment without the hydrogen bromide. Isomerisation of 1-bromopentan-2-one also occurred in ethereal hydrogen chloride [8] although the rate of conversion was slower and several unidentified products were formed.

Treatment of 1-chlorobutan-2-one with ethereal hydrogen chloride, or concentrated hydrochloric acid in glacial acetic acid under reflux, did not cause any rearrangement. This result is in agreement with the general stability of chloro-ketones towards hydrogen chloride [8] or bromide,[9] although Blaise [10] showed that, under the latter conditions, a slow conversion of 1,1-dichlorobutan-2-one into 1,3-dichlorobutan-2-one occurred.

The conditions which bring about the rearrangement of 1-bromopentan-2-one are those under which bromomethyl ketones are prepared from diazo-ketones. Hence, consideration should always be given to the possibility of rearrangement during such preparations.

Experimental.—Gas chromatograms were obtained on a column (2 m. × 5 mm.) packed with 85—100 mesh firebrick coated with 10 parts (w/w) of ethylene glycol polyadipate at 100°; the carrier gas was hydrogen–nitrogen (3 : 1), 40 ml. per min.; a flame ionisation detector was used.

1-Bromopentan-2-one (purity 98%), b. p. 62—64°/12 mm., n_D^{21} 1·4657, and 3-bromopentan-2-one (purity 100%), b. p. 77—78°/44 mm., $n_D^{21\cdot5}$ 1·4593, were prepared by published methods,[5,6] purified by fractionation, and assayed by gas chromatography. Reaction products were assayed with methyl oxalate as an internal standard. The relative retention time of the 1-bromo-ketone with respect to methyl oxalate (retention times being measured from the time of injection) was 1·16, whilst that of the 3-bromo-ketone was 0·58.

Rearrangement of 1-bromopentan-2-one. (*a*) *With ethereal hydrogen bromide.* 1-Bromopentan-2-one (1 g.) was dissolved in ethereal hydrogen bromide (25 ml., 0·42 g./ml.) and kept at room temperature for 4 days. The mixture was washed with water (20 ml.) and saturated sodium hydrogen carbonate solution (2 × 30 ml.), and dried (Na_2SO_4). Removal of solvent left a pale yellow oil (0·56 g.), shown by gas chromatography to contain 3-bromopentan-2-one (58%), 1-bromopentan-2-one (1·5%), and several impurities.

(*b*) *With 48% aqueous hydrobromic acid in glacial acetic acid.* 1-Bromopentan-2-one (5 g.) was dissolved in a mixture of 48% aqueous hydrobromic acid (20 ml.) and glacial acetic acid (30 ml.), and heated at 100° for 2 hr. After cooling, water (50 ml.) was added, and the solution treated with 10% sodium carbonate solution (pH 8). The liberated oil was extracted with ether (4 × 150 ml.), and the solution dried (Na_2SO_4). Removal of solvent left a yellow oil (3·0 g.) which contained 3-bromopentan-2-one (68%), 1-bromopentan-2-one (5·2%), and several unidentified products.

(*c*) *With ethereal hydrogen chloride.* 1-Bromopentan-2-one (1 g.) in ethereal hydrogen chloride (25 ml., 0·18 g./ml.) was kept at room temperature for 5 days. Working up as in (*a*) gave a yellow oil (0·83 g.) which contained 3-bromopentan-2-one (21%), 1-bromopentan-2-one (17%), and several unidentified products.

(*d*) *With ethereal hydrogen bromide in the presence of 2-naphthol.* 1-Bromopentan-2-one (4·3 g.) and 2-naphthol (3·75 g.) in ethereal hydrogen bromide (75 ml., 0·19 g./ml.) were kept at room temperature for 7 days. The solution was washed with water (50 ml.) and 10% sodium hydroxide (3 × 25 ml.), and dried ($MgSO_4$). Removal of solvent left an oil (1·35 g.) which was assayed by using decane as internal standard. It contained pentan-2-one (9·7%), 3-bromopentan-2-one, and unidentified products. The sodium hydroxide washings were acidified and the liberated oil was extracted with ether (4 × 50 ml.). After drying ($MgSO_4$), removal of solvent left an oily solid (3·43 g.) which, on fractional crystallisation from light petroleum, gave 1-bromo-2-naphthol (0·27 g., 5%), m. p. and mixed m. p. 77—78°.

Rearrangement of 3-bromopentan-2-one. 3-Bromopentan-2-one (1 g.) in ethereal hydrogen

[8] Cf. Beereboom and Djerassi, *J. Org. Chem.*, 1954, **19**, 1196.
[9] Ellis and Petrow, *J.*, 1953, 3869.
[10] Blaise, *Bull. Soc. chim. France*, 1914, **15**, 728.

bromide (25 ml., 0·42 g./ml.) was kept at room temperature for 4 days. Working up as in (*a*) gave an oil (0·88 g.) which contained unchanged 3-bromopentan-2-one (98%) and 1-bromopentan-2-one (1·5%).

We thank Mr. A. E. Bird of the Physical Department for the gas-chromatographic determinations, and Professor E. R. H. Jones, F.R.S., for his interest in this work.

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