

Dehydrodimerisation of Ketones by Nickel Peroxide

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1,4-Diketones are produced on treatment of monoketones with nickel peroxide; reaction occurs more readily with cyclic than with acyclic ketones, except in the case of activated (*e.g.* benzylic) ketones, and less readily at a branched site. Cyclohexanone gives, in addition to bicyclohexyl-2,2'-dione, variable amounts of 2-(cyclohex-1-enyloxy)cyclohexanone *via* the enol form of the ketone.

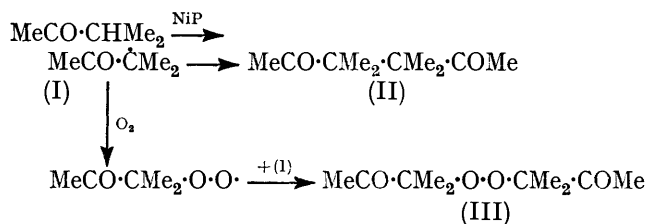
CONSIDERABLE attention has been given recently to the use of nickel peroxide for the oxidation of organic substrates, *e.g.* of alcohols to carbonyl compounds¹⁻⁴ or acids;^{1,4,5} of aldehydes to acids;^{1,6} of aldehydes to amides and nitriles;⁷ of $\alpha\beta$ -diols and α -hydroxy-acids to cleavage products;⁸ of phenols to quinones, ethers, and polymers;⁹⁻¹² of primary amines to azo-compounds or nitriles;¹³ of secondary aromatic amines to imines and hydrazines;^{11,14} of hydroxylamines to nitrones and nitroso- and azoxy-compounds;¹⁵ of hydrazones to diazo-compounds;¹⁶ of phenylhydrazones¹¹ and carbazoles¹⁷ to dehydrodimers; of phenothiazines to their S-oxides;¹⁸ of aromatic Schiff bases to benzoxazoles;¹⁹ of arylacetonitriles to dehydrodimers;^{20,21} and of cyanoacetyl compounds to their oxidative cyclisation products.²² By e.s.r. studies of the intermediates, in the presence of nitroso spin traps,^{21,23} it has been shown that such oxidations proceed *via* the radicals produced by hydrogen abstraction from the substrate.

However, reported work on the reaction of nickel peroxide with ketones appears to be limited to claims in a patent²⁴ where the quoted examples, involving α -alkyl- or α -aryl-substituted aldehydes or ketones, include only one reference to nickel peroxide (with 2-methylbutyraldehyde) the remainder illustrating the use of manganese dioxide as oxidant.

In the present work the reactions of nickel peroxide with a number of ketones have been examined, and it has been shown that the dehydrodimers (*i.e.* 1,4-diketones) formed have structures in agreement with a

mechanism involving the corresponding α -oxo(cyclo)alkyl radicals. With monocyclic ketones this reaction was rapid and exothermic, and for neat cyclohexanone was almost complete at the end of the addition of the nickel peroxide. The highest selectivity in production of the 1,4-diketones was achieved by limiting monoketone conversion to <30%; increased proportions of oxidant to substrate led to production of higher molecular-weight products (*e.g.* C₁₈ dehydrotrimers from cyclohexanone).

In comparison with cycloalkanones, acyclic ketones (*e.g.* butan-2-one) generally reacted less readily and gave lower yields of diketones except when an activating group (*e.g.* as in benzyl methyl ketone) was present. Although, as with other radical reactions, hydrogen abstraction from a methine group may be that of preference, steric hindrance plays an important role in deciding the point of attack. From the (slow) reaction of 3-methylbutan-2-one with nickel peroxide (NiP) was obtained the expected 3,3,4,4-tetramethylhexane-2,5-dione (II) [identified by mass spectroscopy, *m/e* 43 (MeC:O), 85 (β -cleavage ion), and 86 (McLafferty re-



¹² G.E.C., U.S.P. 3,390,125.

¹³ K. Nakagawa and T. Tsujii, *Chem. and Pharm. Bull. (Japan)*, 1963, **11**, 296.

¹⁴ J. Sugita, *Nippon Kagaku Zasshi*, 1967, **88**, 1235.

¹⁵ K. Nakagawa, H. Onoue, and K. Minami, *Chem. and Pharm. Bull. (Japan)*, 1969, **17**, 835, 1522.

¹⁶ K. Nakagawa, H. Onoue, and K. Minami, *Chem. Comm.*, 1966, 730.

¹⁷ J. Sugita, *Nippon Kagaku Zasshi*, 1967, **88**, 659.

¹⁸ J. Sugita and Y. Tsujino, *Nippon Kagaku Zasshi*, 1968, **89**, 309.

¹⁹ K. Nakagawa, H. Onoue, and J. Sugita, *Chem. and Pharm. Bull. (Japan)*, 1964, **12**, 1135.

²⁰ J. Sugita, *Nippon Kagaku Zasshi*, 1967, **88**, 668.

²¹ S. Terabe and R. Konaka, *J. Amer. Chem. Soc.*, 1969, **91**, 5655.

²² B. T. Golding and D. R. Hall, *Chem. Comm.*, 1970, 1574.

²³ S. Terabe and R. Konaka, *J.C.S. Perkin II*, 1972, 2163.

²⁴ Reynolds Tobacco Co., B.P. 1,209,493.

¹ K. Nakagawa, R. Konaka, and T. Nakata, *J. Org. Chem.*, 1962, **27**, 1597.

² Shionogi & Co. Ltd., G.P. 1,249,249.

³ I. Ichimoto, T. Washino, K. Fujii, and C. Tatsumi, *Nippon Nogei Kagaku Kaishi*, 1967, **41**, 317.

⁴ J. S. Belew and T.-L. Chwang, *Chem. Comm.*, 1967, 1100.

⁵ R. N. Warrener and E. N. Cain, *Austral. J. Chem.*, 1971, **24**, 785.

⁶ Farbwerke Hoechst A.G., G.P. 1,244,768.

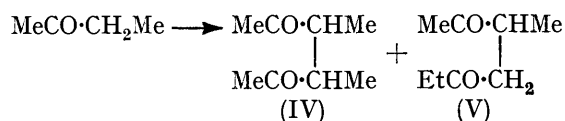
⁷ K. Nakagawa, H. Onoue, and K. Minami, *Chem. Comm.*, 1966, **17**; Shionogi & Co. Ltd., Fr.P. 1,503,195.

⁸ K. Nakagawa, K. Igano, and J. Sugita, *Chem. and Pharm. Bull. (Japan)*, 1964, **12**, 403.

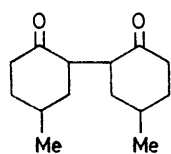
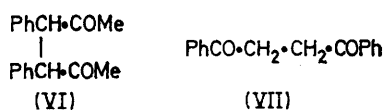
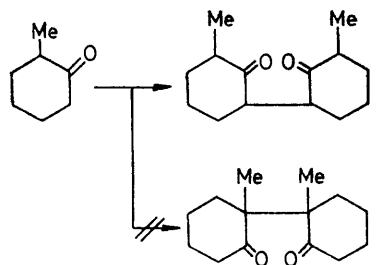
⁹ J. Sugita, *Nippon Kagaku Zasshi*, 1966, **87**, 603, 607, 741, 1082.

¹⁰ H.-D. Becker, *J. Org. Chem.*, 1967, **32**, 2943.

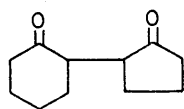
¹¹ K. S. Balachandran, I. Bhatnagar, and M. V. George, *J. Org. Chem.*, 1968, **33**, 3891.



arrangement ion)] together with a small quantity of a solid peroxide, of probable structure (III), derived from the same radical (I) via autoxidation.



(VIII)



(IX)

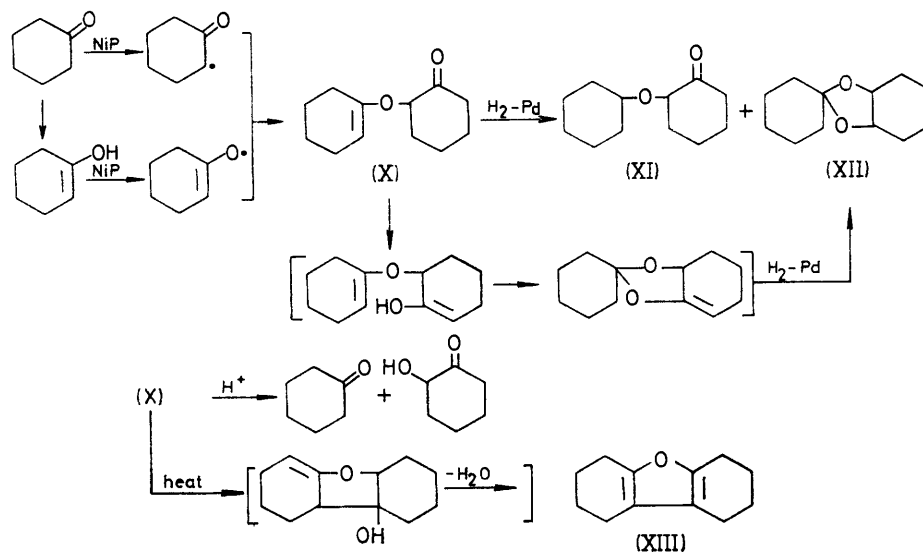
The diketone obtained from butan-2-one was largely that [(IV), mixture of *meso* and (\pm)-isomers] derived

provided evidence for the presence of some of the secondary-primary linked compound (V) [m/e 142 (*M*), 113 (*M* - Et), and 57 (EtC:O)]. However, the n.m.r. spectrum (with evidence for CH_2CH_3 coupling) of the product derived from 2-methylcyclohexanone indicated that the rings were linked at the secondary rather than the tertiary positions.

Benzyl methyl ketone, acetophenone, and 4-methylcyclohexanone, treated with nickel peroxide, gave rise to the expected symmetrical diketones (VI)—(VIII), respectively.

G.l.c. examination of a number of the 1,4-diketones produced by this reaction showed that they consisted of isomeric mixtures, and the diketone (VI) was isolated in both crystalline (\pm)- and *meso*-forms;²⁵ the oxidation of a mixture of cyclopentanone and cyclohexanone led to a product containing two isomers each of bicyclohexyl-2,2'-dione, bicyclopentyl-2,2'-dione, and the unsymmetrical diketone (IX).

The rapid reaction between cyclohexanone and nickel peroxide (neat or in an inert solvent, *e.g.* benzene) occurred even at moderate temperatures ($<70^\circ$) and gave bicyclohexyldione in selectivities of up to 75% based on ketone and *ca.* 50% based on the active oxygen content of the nickel peroxide. Unlike the product from the very slow reaction between lead dioxide and cyclohexanone,²⁶ which contained a high proportion of cyclohexenylcyclohexanone compared with bicyclohexyldione, that from the nickel peroxide treatment had little of this self-condensation product and the major impurity was a compound (concentrated by fractional distillation) having the molecular formula $\text{C}_{12}\text{H}_{18}\text{O}_2$ (mass spectrum). This compound had an i.r. spectrum



SCHEME

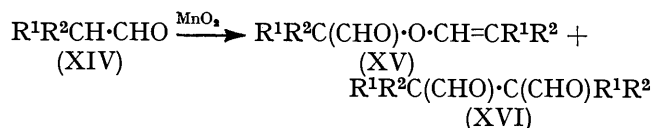
from attack at the secondary position, but n.m.r. and combined g.l.c.-mass spectroscopy of the crude product

²⁵ M. S. Kharasch, H. C. McBay, and W. H. Urry, *J. Amer. Chem. Soc.*, 1948, **70**, 1269.

²⁶ A. Wolf, G.P. 876,237.

giving evidence for unsaturation and ketone and ether groups, it gave a semicarbazone with all protons assignable by n.m.r., with acidic 2,4-dinitrophenylhydrazine it provided the bisdinitrophenylhydrazone of cyclohexane-1,2-dione, and it partially decomposed

during g.l.c. examination into cyclohexanone, 2-hydroxy-cyclohexanone, and octahydrodibenzofuran (XIII). These results could be accommodated by the structure (X) for the by-product which, on catalytic hydrogenation, gave a mixture of the corresponding saturated alkoxy-ketone (XI) and the dioxolan (XII), both synthesised for comparison. The formation and reactions of (X) are in accord with the illustrated Scheme. Alkenyloxy-aldehydes (XV), presumably produced by a similar mechanism, have been shown to be present, together with the dialdehydes (XVI), in the products of reaction of aldehydes (XIV) with manganese dioxide.²⁴



The conditions necessary for decreasing the proportion of (X) relative to bicyclohexyl-2,2'-dione were not examined, but the use of nickel peroxide and anhydrous solvents appeared to be important factors.

EXPERIMENTAL

Low-resolution 70 eV mass spectra of single compounds were obtained at an accelerating voltage of 8 kV, a trap current of 100 μA , and a source temperature of 200° with an A.E.I. MS9 or MS12 spectrometer. Mass measurements were carried out with the MS9 instrument. Low-resolution mass spectra of the components of mixtures were obtained with the MS12 instrument coupled *via* a two-stage jet-type carrier gas separator to a Pye series 104 gas chromatograph.

nickel peroxide, but subsequently the reagent was prepared from nickel sulphate and sodium hypochlorite by the reported technique;¹ the active oxygen equivalent was determined iodometrically as for an organic peroxide.

Reaction of Nickel Peroxide with Cyclohexanone.—

(i) Nickel peroxide (20 g; active O equiv. 262) was added in portions to a stirred mixture of cyclohexanone (30 g) and acetonitrile (30 cm³) at <45°; after 0.5 h the reaction was complete (green nickel hydroxide formed), the solution was filtered, and the filtrate was distilled. Removal of the acetonitrile and unchanged cyclohexanone left the product (4.6 g), b.p. 160–200° at 15 mmHg, shown by g.l.c. analysis to contain cyclohexanone (12.2%) and bicyclohexyl-2,2'-dione (mixed isomers; 72.8%).

(ii) Nickel peroxide (40 g; active O equiv. 255) was stirred with cyclohexanone (30 g) and benzene (100 cm³) at <45° for 2.5 h; the product, worked up as before, gave a fraction (8.6 g) containing cyclohexanone (13.8%) and bicyclohexyl-2,2'-dione (69.8%), and a residue (0.9 g).

(iii) From cyclohexanone (100 g), acetonitrile (10 cm³), and nickel peroxide (80 g; active O equiv. 330) at <65° for 0.25 h were obtained a similar fraction (14.3 g) containing cyclohexanone (7.7%), bicyclohexyl-2,2'-dione (71.8%), and octahydrodibenzofuran (1.8%), and a residue (0.9 g).

A number of experiments similar to (i) but carried out in the presence of other solvents (ethyl acetate, benzonitrile) gave similar yields of diketone.

(iv) To stirred cyclohexanone (200 g) was added nickel peroxide (140 g) at such a rate that the temperature did not exceed 70°; the crude diketone fraction (*ca.* 35 g) was fractionated through a heated, helices-packed column at 15 mmHg to give five fractions: (i) (5.7 g), b.p. 48–135°; (ii) (4.8 g), b.p. 135–150°; (iii) (4.9 g), b.p. 150–168°;

	% (i) (ii) (iii) (iv) (v)					Nature
	(i)	(ii)	(iii)	(iv)	(v)	
Peak I	61.3	4.9	1.3	0.2	0.4	Cyclohexanone
Peaks II–V	3.6	1.7	0.4	0.2	0.2	
Peak VI	3.2	4.9	2.9	<0.1	<0.1	C ₁₂ H ₁₈ O ₂ (unidentified)
Peak VII	20.0	35.7	10.5	0.5	0.3	C ₁₂ H ₁₈ O ₂
Peaks VIII–IX	9.4	41.0	29.2	1.4	1.6	Octahydrodibenzofuran isomers
Peak X	0.6	2.4	1.4	0.1	0.2	Cyclohexenylcyclohexanone
Peaks XI–XII	0.3	2.4	2.6	1.0	0.5	
Peaks XIII–XIV	1.2	6.4	50.1	88.4	58.1	Bicyclohexyl-2,2'-dione isomers
Later peaks		0.5	0.9	7.8	38.2	

Full mass spectra of the compounds discussed in this paper have been submitted to the Mass Spectrometry Data Centre, A.W.R.E., Aldermaston. ¹H N.m.r. spectra (60 MHz) were recorded with a Perkin-Elmer R-10 spectrometer and natural abundance ¹³C n.m.r. spectra with a Bruker HFX-90 spectrometer using pulsed Fourier transform operation (5 kHz spectral window). ¹³C N.m.r. peak assignments were based on the shift data summarised by Stothers²⁷ and confirmed by off-resonance proton-decoupling experiments. All chemical shifts are reported as p.p.m. downfield from tetramethylsilane. I.r. spectra of single compounds were recorded with a Perkin-Elmer 457 spectrometer, and vapour-phase i.r. spectra of components of mixtures with a Grubb-Parsons Spectromaster connected directly to the output of a Pye series 104 gas chromatograph.²⁸ G.l.c. analyses are based on area percent measurements of the required peaks.

Preliminary oxidations were carried out with B.D.H.

²⁷ J. B. Stothers, 'Carbon-13 N.M.R. Spectroscopy,' Academic Press, New York, 1972.

(iv) (11.5 g), b.p. 168–178°; (v) (2.1 g), b.p. 178–185°; and a residue (0.5 g). The results of g.l.c.–mass spectrometric analysis are shown in the Table. Fraction (iv) crystallised in the receiver, and, from aqueous methanol, afforded bicyclohexyl-2,2'-dione, m.p. 72–74° (lit.,²⁹ 70°; lit.,²⁵ 70–71°; lit.,³⁰ 73.4°) [ν_{max} (KBr) 1685 cm⁻¹ (C=O); δ_{H} (CDCl₃) 1.0–3.22 (complex); δ_{C} (CDCl₃) 25.7 (CH₂; C-4 and C-4'), 28.2 (CH₂; C-5 and C-5'), 30.3 (CH₂; C-3 and C-3'), 42.4 (CH₂; C-6 and C-6'), 49.2 (CH; C-2 and C-2'), and 211.5 (C=O; C-1 and C-1)']; *m/e* 194 (*M*, 26.0%), 137 (18.7), 98 (100.0), 97 (68.7), and 96 (20.7)]; when heated with methylamine in acetic acid it yielded 9-methyloctahydrocarbazole, m.p. 89–91° (lit.,²⁵ 94–95°). The isomeric bicyclohexyl-2,2'-dione, obtained as a separate g.l.c. peak, could not be obtained crystalline [ν_{max} (film) 1690 cm⁻¹ (C=O); δ_{H} (CCl₄) 1.0–2.10 (max. 1.82) (CH₂,

²⁸ J. E. Crooks, D. L. Gerrard, and W. F. Maddams, *Analyt. Chem.*, in the press.

²⁹ R. Criegee and H. G. Reinhardt, *Chem. Ber.*, 1968, **101**, 102.

³⁰ C. G. Moore, *J. Chem. Soc.*, 1951, 236.

cyclic) and 2.10—3.00 (max. 2.20) ($\text{CH}_2\text{C}=\text{O}$ and $\text{CH}\cdot\text{C}=\text{O}$); δ_{C} (CDCl_3) 25.1 (CH_2 ; C-4 and C-4'), 26.7 (CH_2 ; C-5 and C-5'), 29.2 (CH_2 ; C-3 and C-3'), 41.9 (CH_2 ; C-6 and C-6'), 50.4 (CH ; C-2 and C-2'), and 210.6 ($\text{C}=\text{O}$; C-1 and C-1'); mass spectrum identical with that of the solid isomer].

Direct examination of fraction (ii) by i.r. spectroscopy [ν_{max} (film) 1715 ($\text{C}=\text{O}$), 1667 ($\text{C}=\text{C}$), 1600 ($\text{C}=\text{C}=\text{C}$), and ca. 1120 cm^{-1} ($\text{C}-\text{O}$)] showed that it contained ca. 10% octahydrodibenzofuran; the remainder (indicated by g.l.c. analysis) presumably arose through instantaneous decomposition of a component of the fraction on chromatographic injection. Peak VII [ν_{max} (vapour) 1720 ($\text{C}=\text{O}$) and 1232 cm^{-1} ($\text{C}-\text{O}$); m/e 194 (M , 12.7%), 98 (23.0), 97 (40.0), 96 (100.0), and 55 (93.3)] was trapped and rechromatographed—only 37.8% survived and the remainder decomposed to cyclohexanone (39.3%) and compounds (a) (1.8%), (b) (10.5%), and (c) (2.3%; $\text{C}_6\text{H}_8\text{O}_2$); (a) and (b) were shown to be 2-hydroxycyclohexanone and cyclohexane-1,2-dione, respectively, by comparison (g.l.c.—mass spectroscopy) with authentic compounds. Fraction (ii) {semicarbazone, m.p. 160—161° (from benzene—petroleum) (Found: C, 61.7; H, 8.5; N, 16.35. $\text{C}_{13}\text{H}_{21}\text{N}_3\text{O}_2$ requires C, 62.2; H, 8.4; N, 16.7%); δ_{H} [$(\text{CD}_3)_2\text{SO}$] 1.0—2.0 (max. 1.68) (CH_2 , cyclic), 2.0—2.6 ($\text{CH}_2\cdot\text{C}$), 4.64 and 5.00 (d, $\text{CH}-\text{O}$), 6.40 (NH_2), 8.46 ($\text{CH}=\text{C}$), and 9.40 (NH); m/e 251 (M , 11.8%), 154 ($\text{C}_7\text{H}_{12}\text{N}_3\text{O}$, 77.1), and 111 ($\text{C}_6\text{H}_{11}\text{N}_2$, 100.0)} with acidified 2,4-dinitrophenylhydrazine provided the bis-dinitrophenylhydrazone of cyclohexane-1,2-dione, m.p. and mixed m.p. 229—231° (from ethyl acetate), and on hydrogenation (Pd—charcoal catalyst) in ethanol gave a crude product which afforded a semicarbazone, m.p. 190—191° (from ethanol) [(Found: C, 61.1; H, 9.45; N, 16.6. $\text{C}_{13}\text{H}_{23}\text{N}_3\text{O}_2$ requires C, 61.7; H, 9.1; N, 16.6%); δ_{H} [$(\text{CD}_3)_2\text{SO}$] 0.82—2.30 (CH_2), 4.05 ($\text{CH}-\text{O}$), 6.32 (NH_2), and 9.40 (NH); m/e 155 ($\text{C}_7\text{H}_{13}\text{N}_3\text{O}$, 100.0%) and 112 (32.9)], identical with a synthetic sample (see later). G.l.c.—mass spectrometry of this hydrogenated material showed it to contain, in addition to 2-cyclohexyloxycyclohexanone (XI) (11.0%), the dioxolan (XII) (62.7%), bicyclohexanone (5.5%), and minor components; the dioxolan was identified by comparison with synthetic material (see later).

2-Cyclohexyloxycyclohexanone (XI).—Cyclohexanol (100 g), containing dissolved sodium (0.5 g) was refluxed with 1,2-epoxycyclohexane (32 g) for 17 h; distillation provided, in addition to cyclohexanol and polymeric material, a fraction (12.8 g), b.p. 140—160° at 15 mmHg, shown by g.l.c.—mass spectrometry to contain 2-cyclohexyloxycyclohexanol (81.1%). Oxidation of this with chromium trioxide in acetic acid yielded a product, b.p. 136—152° at 15 mmHg, containing 2-cyclohexyloxycyclohexanone (24.8%) [ν_{max} (film) 1710; ν_{max} (vapour) 1734 cm^{-1} ($\text{C}=\text{O}$); δ_{H} (CDCl_3) 2.00—2.70 (max. 2.20) ($\text{CH}_2\cdot\text{C}=\text{O}$); m/e 196 (M , 0.3%), 100 (26.8), 98 (77.2), and 55 (100.0)], as well as the unchanged alcohol (54%), with semicarbazone, m.p. 190—191° (from methanol) (Found: C, 61.55; H, 9.45; N, 16.7%).

Perhydro-1,3-benzodioxole-2-spirocyclohexane (XII).—Cyclohexanone (12 g) and cyclohexane-1,2-diol (10 g) were heated in benzene containing toluene-*p*-sulphonic acid under a Dean-Stark head until no further water was produced. Distillation provided a major fraction (13.4 g), b.p. 120—130° at 15 mmHg, from which traces of unchanged glycol were removed by cooling a solution in petroleum. The final product (98.5% pure by g.l.c.) was crystallised from petroleum; m.p. 35—36° [ν_{max} (film)

1025, 1080, 1112, and 1163; ν_{max} (vapour) 1036, 1089, 1122, and 1170 cm^{-1} ($\text{C}-\text{O}$, acetal); δ_{H} (CCl_4) 1.00—1.95 (max. 1.51) (CH_2 , cyclic) and 2.86—3.38 (max. 3.08) ($\text{CH}-\text{O}$); m/e 196 (M , 21.2%), 153 (69.0), 81 (38.3), and 55 (100.0)].

Reactions of Nickel Peroxide with Other Ketones.—

(i) Cyclopentanone. Cyclopentanone (30 g) was treated at <45° with nickel peroxide (20 g; active O equiv. 282), and the stirred mixture was finally heated at 60—65° for 0.5 h. Distillation of the filtered solution gave a fraction (2.5 g), b.p. 140—170° at 15 mmHg, and a residue (0.8 g); g.l.c. showed the distillate to contain cyclopentanone (3.4%), cyclopentenylcyclopentanone (0.2%), and two isomers of bicyclopentyl-2,2'-dione (79.8%), and provided crystalline bicyclopentyl-2,2'-dione, m.p. 66—68° (from petroleum) (lit.,³¹ 67—69°; lit.,³² 67—68°) [ν_{max} (KBr) 1725 cm^{-1} ($\text{C}=\text{O}$); δ_{H} (CCl_4) 1.20—2.25 (max. 2.02) (CH_2 , cyclic) and 2.25—2.80 ($\text{CH}_2\cdot\text{C}=\text{O}$ and $\text{CH}\cdot\text{C}=\text{O}$); m/e 166 ($\text{C}_{10}\text{H}_{14}\text{O}_2$, 47.2%), 123 (16.7), 110 (37.0), 84 ($\text{C}_5\text{H}_8\text{O}$; 100.0), and 83 (95.7)].

(ii) Mixture of cyclopentanone and cyclohexanone. The procedure was as in (i), with cyclopentanone (15 g), cyclohexanone (15 g), acetonitrile (5 cm^3), and nickel peroxide (20 g). G.l.c.—mass spectrometric analysis of the product (2.7 g), b.p. 145—180° at 15 mmHg, showed the presence of two isomers each of bicyclopentyl-2,2'-dione (22.8%), of bicyclohexyldione (14.7%) and of 2-oxocyclopentylcyclohexan-2-one (36.1%) [m/e 180 (M , 55.2%), 98 (100.0), 97 (93.7), 84 (80.2), and 83 (58.3)].

(iii) Cycloheptanone. Cycloheptanone (25 g) and nickel peroxide (20 g) were heated together under reflux for 0.25 h. Work-up gave a fraction (3.5 g), b.p. 180—210° at 15 mmHg, shown by g.l.c.—mass spectrometry to contain cycloheptanone (3.2%), bicycloheptyl-2,2'-dione (79.1%), an isomer ($\text{C}_{14}\text{H}_{22}\text{O}_2$; 6.5%), and a compound ($\text{C}_{16}\text{H}_{20}\text{O}$; 4.2%), probably a higher homologue of the furan (XIII). From this fraction was isolated bicycloheptyl-2,2'-dione, m.p. 93—95° (from aqueous methanol) (lit.,²⁹ 93°) [(Found: C, 75.9; H, 9.95. Calc. for $\text{C}_{14}\text{H}_{22}\text{O}_2$: C, 75.7; H, 9.9%); ν_{max} (KBr) 1684 cm^{-1} ($\text{C}=\text{O}$); δ_{H} (CCl_4) 0.85—2.13 (max. 1.48) (CH_2 , cyclic), 2.13—2.58 (max. 2.39) ($\text{CH}_2\cdot\text{C}=\text{O}$), and 2.58—2.97 (max. 2.72) ($\text{CH}\cdot\text{C}=\text{O}$); m/e 222 (M , 14.3%), 112 (54.3), 111 (21.4), 55 (54.3), and 41 (100.0)].

(iv) 4-Methylcyclohexanone. Reaction of 4-methylcyclohexanone (50 g) with nickel peroxide (33 g; active O equiv. 230) at <65° gave a product (9.0 g), b.p. 165—200° at 15 mmHg, from which was isolated 5,5'-dimethylbicyclohexyl-2,2'-dione, m.p. 63—65° (from aqueous methanol) [ν_{max} (film) 1706 cm^{-1} ($\text{C}=\text{O}$); m/e 222 (M , 34.0), 112 (100.0), 111 (89.8), 55 (50.8), and 41 (55.8)]; semicarbazone, m.p. 136—138° (from methanol—ethanol).

(v) 2-Methylcyclohexanone. A stirred mixture of 2-methylcyclohexanone (30 g) and nickel peroxide (20 g) was heated to 80—90° for 2 h, and provided a product (3.9 g), b.p. 160—205° at 15 mmHg [ν_{max} (film) 1705 cm^{-1} ($\text{C}=\text{O}$); δ_{H} (CDCl_3) 0.50—1.08 (m, max. 0.83) ($\text{CH}\cdot\text{CH}_2$), 1.08—1.95 (max. 1.52) (CH_2 , cyclic), and 1.95—3.10 (max. 2.08) ($\text{CH}\cdot\text{C}=\text{O}$ and $\text{CH}_2\cdot\text{C}=\text{O}$); m/e 222 (M , 24.2%), 112 (100.0), 111 (58.3), 55 (63.3), and 41 (95.0)].

(vi) Cyclododecanone. A mixture of cyclododecanone (10 g), benzene (20 cm^3), and nickel peroxide (9 g; active O equiv. 257.8) was heated under reflux for 7 h. Normal

³¹ B. J. F. Hudson and Sir Robert Robinson, *J. Chem. Soc.*, 1942, 691.

³² H. Paul, *Chem. Ber.*, 1960, 93, 2395.

work-up gave cyclododecanone (5.3 g), an intermediate fraction (0.4 g), a fraction (3.2 g), b.p. 280–300° at 15 mmHg, and a residue (0.6 g). From the main fraction was isolated *bicyclododecyl-2,2'-dione*, m.p. 178–181° (from benzene) [(Found: C, 79.1; H, 11.6. $C_{24}H_{42}O_2$ requires C, 79.55; H, 11.6%); ν_{\max} (KBr) 1693 cm^{-1} (C=O); m/e 362 (M , 24.7%), 334 (20.2), 182 (83.1), 181 (88.8), and 55 (100.0)].

(vii) *Butan-2-one*. Ethyl methyl ketone (30 g), benzene (50 cm^3) and nickel peroxide (12.5 g) were heated under reflux for 2 h. Distillation of the filtrate gave a fraction (1.4 g), b.p. 80–110° at 15 mmHg [ν_{\max} (film) 1710 cm^{-1} (C=O); δ_H (CCl_4) 1.02 (d, CH_2CH_3), 2.08 (s, Ac), and 2.5–3.0 (complex, COCH)] containing (by g.l.c.–mass spectrometry) isomers of 3,4-dimethylhexane-2,5-dione (IV) (37.8% and ca. 29%) [m/e 142 (M , 3.4%), 100 (17.6), 85 (27.4), and 43 (100.0)] and 3-methylheptane-2,5-dione (V) (ca. 14.5%) [m/e 142 (M , 11.3%), 113 (62.5), 85 (30.0), 57 (72.5), and 43 (100)]. Reaction of a portion of this fraction with ethanolic *p*-phenylenediamine provided 1-*p*-aminophenyl-2,3,4,5-tetramethylpyrrole, m.p. 169–172° (from ethanol) (lit.,³³ 174–175°) [(Found: N, 13.2. Calc. for $C_{14}H_{18}N_2$: N, 13.1%); ν_{\max} (KBr) 1619 (C=C), 3328, and 3408 cm^{-1} (NH); m/e 214 (M , 100.0%) and 199 (42.4)].

(viii) *3-Methylbutan-2-one*. Isopropyl methyl ketone (30 g) and nickel peroxide (20 g; active O equiv. 335) were heated together at ca. 80° for 5 h. Distillation of the product afforded a fraction (0.5 g), b.p. 100–110° at 15 mmHg, from which was isolated *bis-1,1-dimethyl-2-oxopropyl peroxide* (III), m.p. 103–105° (from petroleum) [(Found: C, 58.95; H, 9.35%; peroxide equiv., 193. $C_{10}H_{18}O_4$ requires C, 59.4; H, 8.9%; peroxide equiv., 202); ν_{\max} (KBr) 1710 cm^{-1} (C=O); δ_H ($CDCl_3$) 1.36 (s, $C\cdot CH_3$) and 2.30 (s, Ac); m/e 159 ($C_8H_{15}O_3$, 0.1%), 59 (9.2), and 43 (100.0)]. The filtrate, containing 3,3,4,4-tetramethylhexane-2,5-dione (mass spectrum), yielded a bis-2,4-dinitrophenylhydrazone, m.p. 247–248° (from nitrobenzene) (Found: C, 49.75; H, 5.0; N, 20.85. Calc. for $C_{22}H_{26}N_8O_8$: C, 49.8; H, 4.9; N, 21.1%).

(ix) *Acetophenone*. Addition of nickel peroxide (20 g;

active O equiv. 262) to stirred acetophenone (30 g) led to a rise of the internal temperature to 67°; the reaction was completed by heating to 80° for 2 h. Distillation of the filtered product gave, in addition to unchanged ketone, a fraction (1.3 g), b.p. 240–260° at 15 mmHg, and a polymeric residue (1.8 g). The volatile fraction, which crystallised on storage, gave 1,2-dibenzoylthane, m.p. 142–145° (from methanol) (lit.,³⁴ 144–145°) [ν_{\max} (KBr) 1677 cm^{-1} (C=O); δ_H ($CDCl_3$) 3.47 (s, CH_2) and 7.25–8.44 (aromatic H); m/e 238 (M , 44.8%), 133 (22.0), 105 (100.0), and 77 (84.0)].

(x) *Benzyl methyl ketone*. Nickel peroxide (20 g; active O equiv. 273) was added gradually to stirred benzyl methyl ketone (30 g); the reaction was exothermic and rapid. Normal work-up gave a distillate (6.2 g), b.p. 190–220° at 15 mmHg, and a residue (6.3 g): from the distillate were isolated the isomeric diketones (VI), m.p. 205–207° (from benzene) (lit.,²⁵ 201–202°) [(Found: C, 81.0; H, 6.95. Calc. for $C_{18}H_{18}O_2$: C, 81.2; H, 6.75%); ν_{\max} (KBr) 1707 (C=O), 707, and 748 cm^{-1} (monosubstituted aromatic); δ_H (CCl_4 – $CDCl_3$) 1.83 (s, $CH_3\cdot C=O$), 4.55 (s, $PhCH\cdot C=O$), and 7.07–7.54 (aromatic H); m/e 266 (M , 2.5%), 224 (8.7), 181 ($C_{14}H_{13}$, 16.2), and 43 (100.0)]; and m.p. 103–105° (from petroleum) (lit.,²⁵ 98–100°) [(Found: C, 80.7; H, 6.9%); ν_{\max} (KBr) 1705 (C=O), 706, and 751 cm^{-1} (monosubstituted aromatic); δ_H (CCl_4 – $CDCl_3$) 2.09 (s, $CH_3\cdot C=O$), 4.32 (s, $PhCH\cdot C=O$), and 6.73–7.48 (aromatic H); m/e 266 (M , 6.9%), 224 (14.8), 181 (37.4), and 43 (100.0)].

We thank Mr. A. J. Plomer for experimental assistance, Dr. D. L. Gerrard for i.r. spectra, Dr. H. Pyszora for 1H n.m.r. spectra, Dr. S. A. Knight for ^{13}C n.m.r. spectra, Mr. D. F. Francis for g.l.c. analyses, and Mr. D. C. White for elemental analyses. Permission to publish this paper has been given by The British Petroleum Company Ltd.

[3/1853 Received, 6th September, 1973]

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³⁴ S. Kapf and C. Paal, *Ber.*, 1888, **21**, 3053.