

31. Radical Mechanisms in Saturated and Olefinic Systems. Part III. The Reaction of Hydroxyl Radicals with Olefins.

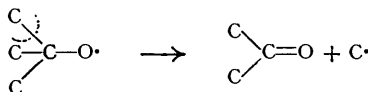
By E. H. FARMER and C. G. MOORE.

The hydroxyl radicals and *tert.*-butoxy-radicals formed by the thermal decomposition of *tert.*-butyl hydroperoxide have been brought into reaction with *cyclohexene* and with 1-methyl*cyclohexene* at 140° in order to determine the characteristic reactivities towards olefinic carbon chains of the hydroxyl radicals.

The olefins are dehydrogenated at their α -methylene groups, and the olefin radicals so formed pass into dehydro-dimeric and to some extent into higher dehydro-polymeric forms which are mostly oxygenated. The bulk, but not quite all, of the dehydrogenation is accomplished by the *tert.*-butoxy-radicals, the hydroxyl radicals being mostly expended in oxygenating the monomeric and polymeric olefin forms. Considerable yields of α -hydroxy- and α -keto-*cyclohexenes* and α -*dicyclohexenyls* are formed from *cyclohexene*, together with higher oxygenated polymeric forms, and comparable products are obtained from 1-methyl*cyclohexene*, although here the unsymmetrical character of the resonating olefin radicals causes isomerism. The mechanism of hydroxylic and double hydroxylic substitution at α -methylenic positions is discussed. Only to a relatively small extent are hydroxyl radicals added (in pairs) at olefinic double bonds to give 1 : 2-diols, and it is notable that to no observable extent do they react additively with such double bonds to give epoxide groupings.

THE thermal decomposition of a saturated alkyl hydroperoxide ($R-OOH \longrightarrow R-O\cdot + \cdot OH$) may be expected to yield a pair of radicals of very dissimilar reactivity. Thus when *tert.*-butyl hydroperoxide is decomposed in presence of an olefin the dehydrogenating action which characterises the moderately stabilised (not intensely electrophilic) *tert.*-butoxy-radical to almost complete exclusion of other reactivities is hardly likely to apply with equal exclusiveness to the little stabilised (highly electrophilic) hydroxyl radical. It was interesting, therefore, to discover to what extent (if any) the hydroxyl radical from *tert.*-butyl hydroperoxide is capable of reacting with a simple olefin in the various ways which may (with more or less justification) be suspected to be open to it. These are: (1) Dehydrogenation at α -methylene groups to give olefin radicals: $RH + \cdot OH \longrightarrow R\cdot + H_2O$. (2) Union with α -methylenic olefin radicals to give alcohols: $R\cdot + \cdot OH \longrightarrow R\cdot OH$. (3) Addition to double bonds in pairs to give saturated glycols: $C=C + 2 \cdot OH \longrightarrow C(OH)-C(OH)$. (4) Re-hydroxylation of $>CH(OH)$ groups to give ketones $>CH-OH \xrightarrow{(a)} >\dot{C}(OH) \xrightarrow{(b)} >C(OH)_2$. (5) Addition to double bonds singly to give epoxides. The first of these ways appears from all present information to be open to all radicals except those of the most outstanding stability, and the second is a feasible second stage for a process of substitutive hydroxylation.* The third, fourth, and fifth ways appear to be possible in view of the frequent formation of glycols, ketones, and epoxides during the autoxidation of olefins.

Careful investigation of the decomposition of *tert.*-butyl hydroperoxide (1 mol.) in presence of a large excess of *cyclohexene* (6 mols.) gives results which are entirely compatible with the simultaneous reaction on the olefin of *tert.*-alkoxy and hydroxyl radicals. The *tert.*-alkoxy-group clearly acts as a dehydrogenating agent, since it reappears as *tert.*-butanol, only under-



going thermal breakdown to acetone to a minute extent. The full list of products identified, and their yields, are given in the table.

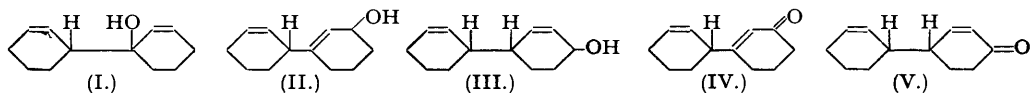
* Such substitutive hydroxylation is probably not the main path to the formation of olefinic alcohols in olefin autoxidation, in which the thermal scission of hydroperoxides ($R-O-OH$) may be followed by hydrogenation of the alkoxy-group and conceivably also by the substitution $RO\cdot + \cdot OH \longrightarrow ROH + \cdot O$.

Interaction of cyclohexene (328 g., 4.0 g.-mols.) with *tert.*-butyl hydroperoxide (60 g., 0.67 g.-mol.) (140°; 24 hours).

Products.	G.	G.-mols.	Products.	G.	G.-mols.
<i>tert.</i> -Butanol	46.7	0.62	<i>trans</i> -cycloHexane-1 : 2-diol ...	1.25	0.011
Water	3.4	0.19	<i>cyclo</i> Hexenylcyclohexenol(s) ...	>5.2	>0.03
Acetone	0.05	0.0386	<i>cyclo</i> Hexenylcyclohexenone(s)	>0.92	>0.0252
<i>cyclo</i> Hex-2-enol	ca. 17.4	~0.18	Tercyclohexenyl (s)	ca. 2.7	~0.011
<i>cyclo</i> Hex-2-enone	ca. 3.1	~0.032	Residue	5.1	—
Dicyclohexenyl	>28.25	>0.175			

In considering the origin of the various products it is impossible to distinguish between the dehydrogenation effected by the *tert.*-butoxy- and by the hydroxyl radicals, but there can be no doubt that some part of the dehydrogenation of the olefin (reaction 1, above) must have been accomplished by the hydroxyl radicals since the yield of water formed in the reaction is appreciable—considerably higher, indeed, than can be accounted for by mere elimination of water during ketone formation [*i.e.*, at stage 4(b) of the reaction paths listed above]. Most of the dehydrogenation, however, must be attributed to the *tert.*-butoxy-radicals which pass thereby into *tert.*-butanol, since, not only is the degree of recovery of the latter actually achieved high (95%), but the degree to which the *tert.*-butoxy-radicals have been expended in thermal decomposition (to give acetone) is trivial and that of their coupling with olefin radicals to give ethers, comparable with reaction $2(R\cdot + \text{Bu}^t\text{O}\cdot \longrightarrow \text{R-OBu}^t)$, insignificant. The dehydrogenation has been followed by extensive coupling of the resulting olefin radicals to give first di- and then *ter*-cyclohexenyl, etc. Correspondingly, most of the hydroxyl radicals appear to have been used in oxygenation of the olefin—principally in converting olefin radicals into olefinic alcohols and thence (in part) into $\alpha\beta$ -unsaturated ketones: indeed, only to a relatively small extent have they been expended in direct addition to double bonds to give (saturated) cyclohexane-1 : 2-diol, and to no recognisable extent at all have they contributed to the formation of epoxides. The apparent entire absence of cyclohexene epoxide from the reaction product suggests that the epoxides which are so frequently formed in the autoxidation of olefinic materials cannot result from any very simple interaction of hydroxyl radicals with double bonds, and may in fact depend for their formation on the transient liberation of atomic oxygen from decomposing $-\text{OOH}$ groups or $-\text{OO}\cdot$ radicals.

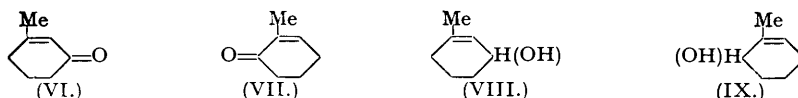
The capacity for advanced oxygenation (*e.g.*, beyond simple substitutive hydroxylation) shown by the hydroxyl groups is confined to ketone formation, the fairly abundant cyclohex-2-enol in the reaction product being accompanied by a moderate yield of the corresponding ketone, cyclohex-2-enone. With respect to the dimer alcohols and ketones formed, which probably spring in the main from the already dehydro-dimerised olefin, no allocation of specific formulæ can be made, since the separation and identification of the individual isomers was not attempted. Previous results in this series (see Part I), however, indicate that substitution at the tertiary carbon atoms in dicyclohexenyl may be sufficiently hindered sterically to permit reaction to occur in quite important degree at secondary as well as tertiary α -methylene positions. Such substitutive hydroxylation, together with the occurrence of allylic resonance



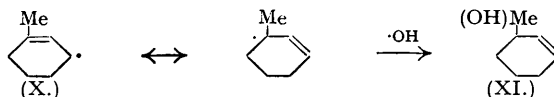
in the tertiary radicals, will be likely to give the alcohols (I—III) and the ketones (IV and V). Corresponding, but less abundant, hydroxy- and keto-derivatives of “trimeric” (and possibly higher) olefinic forms were probably present in the highest-boiling portion of the product, but were not isolated.

Finally, no significant amount of oxygenation carried to the stage of chain scission has occurred in the cyclohexene ring—produced, for example, by the further attack of hydroxyl radicals at the α -methylene groups or the double bonds of first-formed ketones. This feature, however, appears to be due only to the insufficiency of reagent radicals, since supplementary experiments in which cyclohexanol (1 mol.) and cyclohex-2-enol (0.41 mol.) were in turn heated with *tert.*-butyl hydroperoxide (1 mol.) at 130° gave in both cases much of the corresponding (saturated or unsaturated) ketone, and an appreciable amount of carboxylic acid. The acid from cyclohexanol was found to be adipic acid, thus emphasizing that substitutive attack by hydroxyl groups occurs very readily at the α -carbon atoms of saturated secondary alcohols, and then at the α -methylene groups of the resulting ketones.

A similar, but less complete examination of the action of thermally decomposing *tert.*-butyl hydroperoxide on 1-methylcyclohexene at 140° was carried out. In this example the presence of the methyl group in the olefin molecule produced, owing to its destruction of the molecular



symmetry, appropriate isomerism among the hydroxy- and keto-derivatives of the olefins, and doubtless (although this was not investigated) also among the "dimeric" and higher "polymeric" olefins themselves. Amongst the simple products, the isomeric cyclic ketones (VI) and (VII) were easily identified, as also the corresponding, more abundant, alcohols (VIII) and (IX), which passed on oxidation into (VI) and (VII). The third theoretically possible



(tertiary) cyclohexenol (XI) and/or derivatives thereof may well have been present, but were not actually sought.

EXPERIMENTAL.

(Microanalyses by Dr. W. T. Chambers, Miss E. Farquhar, and Mrs. H. Hughes. Spectrographic observations by Dr. H. P. Koch.)

Reaction of tert.-Butyl Hydroperoxide with cycloHexene.—*tert.*-Butyl hydroperoxide was prepared according to Milas and Surgenor (*J. Amer. Chem. Soc.*, 1946, **68**, 205). The final product, after drying ($MgClO_4$), had b. p. 37.5–38.0°/20 mm., n_D^{20} 1.4004, n_D^{25} 1.3980 (Milas and Surgenor, *loc. cit.*, give n_D^{20} 1.4013, and Milas and Perry, *loc. cit.*, give b. p. 33–34°/17 mm., n_D^{20} 1.3983).

A mixture of cyclohexene (328 g., 4 mols.) and the hydroperoxide (60 g., 0.67 mol.) was heated at 140° ($\pm 1^\circ$) for 24 hours in nitrogen-filled Carius tubes. The product (386.2 g.) separated into two layers, a small aqueous lower one and a large yellow upper one. Both layers were submitted to fractional distillation in nitrogen. A large volatile fraction (i) b. p. 66.0–82.5°/750 mm. (257.2 g.) first distilled, and a second volatile fraction (ii), consisting of cyclohexene (n_D^{20} 1.4460; 47.0 g.), was removed from the residue by spontaneous distillation at 10 mm. pressure into a liquid-air trap. The residual fraction (iii) was a light yellow oxygen-containing liquor (78.4 g.) [Found: C, 81.25; H, 11.05; O (by diff.), 7.7; OH (Zerewitinoff), 6.75, 6.85, 6.95; O (as OH), 6.35–6.54%]. Distillation of fraction (iii), in nitrogen, gave the fractions (iv), b. p. 53–62.5° (mainly 62.0–62.5°)/10 mm., n_D^{20} 1.4740 (23.2 g.); (v) b. p. 62.5°/10 mm.—63°/0.6 mm., n_D^{20} 1.4798 (5.05 g.); (vi) b. p. 63–68°/0.6–0.7 mm., n_D^{20} 1.5000 (29.5 g.), and (vii) a residual viscous yellow liquid (16.7 g.). Redistillation of fraction (vii) from a smaller still gave (viii) b. p. 72–106°/1 mm., n_D^{20} 1.5080 (0.68 g.); (ix) b. p. 106–132°/1 mm., n_D^{20} 1.5210 (6.55 g.); (x) b. p. 132–142°/1 mm., n_D^{20} 1.5319 (2.7 g.); and (xi) a residual viscous orange liquid, undistillable at 200° (both temp./10 mm., n_D^{20} 1.5455 (5.1 g.).

The fraction (i) consisted of a mixture of cyclohexene, *tert.*-butanol (*ca.* 46.7 g.; equiv. to 94.8% of hydroperoxide taken), acetone (0.05 g.), and water (3.4 g.). The *tert.*-butanol and acetone were identified and determined as previously described. An approximate estimate of the water formed in the reaction was made by shaking the bulk fraction with anhydrous potassium carbonate (30.0 g.); the increase in weight of the latter amounted to 3.4 g. The cyclohexene present in fractions (i) and (ii) was combined, dried ($CaCl_2$), and distilled over sodium, in nitrogen. It had b. p. 82.5°/750 mm., n_D^{20} 1.4461.

The fraction (iv), a colourless oily liquid, consisted of cyclohex-2-enol and a smaller amount of cyclohex-2-enone, together with a little olefinic material (probably dicyclohexenyl) which repeated refractionation failed to remove [Found: C, 74.6; H, 10.65; OH (Zerewitinoff), 13.0. Calc. for $C_6H_{10}O$: C, 73.4; H, 10.3; OH, 17.35%. Calc. for C_6H_8O : C, 75.0; H, 8.4%]. The cyclohex-2-enol was characterised by its α -naphthylurethane, m. p. and mixed m. p. 156° (Found: C, 76.05; H, 6.35; N, 5.15, 5.2. Calc. for $C_{17}H_{17}O_2N$: C, 76.4; H, 6.4; N, 5.25%). The cyclohex-2-enone was characterised by its 2:4-dinitrophenylhydrazone, which separated as deep red-orange needles from light petroleum (b. p. 100–120°). It had m. p. and mixed m. p. 162–163° (Found: C, 52.2; H, 4.45; N, 20.5. Calc. for $C_{12}H_{12}O_4N_4$: C, 52.2; H, 4.4; N, 20.3%). Quantitative determination of the ketone content of fraction (iv) by the method of Iddles, Low, Rosen, and Hart (*Ind. Eng. Chem. Anal.*, 1939, **11**, 102) indicated that 13.35% of it consisted of cyclohex-2-enone. The percentage of hydroxylic and carbonyl oxygen (12.23 + 2.33) derivable from the foregoing analyses of fraction (iv) shows a total OH + CO oxygen content therein of 14.46%. This total agrees well with the oxygen content of 14.75% (diff. value) obtained by elementary methods of analysis of the fraction, and so indicates that no substantial proportions of other oxygenated groups were present. Catalytic hydrogenation of a portion of (iv) with palladium-charcoal in absolute ethanol gave a product which by treatment with 2:4-dinitrophenylhydrazine yielded cyclohexanone 2:4-dinitrophenylhydrazone as orange-yellow plates from ethanol, m. p. and mixed m. p. 156–158° (Found: C, 52.15; H, 5.2. Calc. for $C_{12}H_{14}O_4N_4$: C, 51.8; H, 5.05%).

Ultra-violet spectrographic analysis of fraction (iv) showed an absorption maximum at λ 2250 \AA ., $\epsilon = 1350$, compatible with *ca.* 10–13% of *cyclohex-2-enone* (cf. Cooke and Macbeth, *J.*, 1938, 1408; Birch, *J.*, 1946, 593; Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123).

The fraction (vi), a colourless oily liquid, deposited on cooling crystals of *trans-cyclohexane-1:2-diol*, m. p. 102–104° (1.25 g.) (Found: C, 62.25; H, 10.4. Calc. for $\text{C}_6\text{H}_{12}\text{O}_2$: C, 62.05; H, 10.4%). The liquid residue consisted of dicyclohexenyl, contaminated with a little oxygenated material (Found: C, 87.85; H, 11.3%). Repeated distillation of the impure olefin over sodium proved ineffective for removal of the contaminant; repeated extraction with water was more successful, giving a slightly impure olefin, b. p. 61–62°/0.5 mm., n_D^{20} 1.5082 (Found: C, 88.3; H, 11.3%); the best result was obtained by chromatography of a solution of the *cycloalkene* in light petroleum (b. p. 60–80°) through activated alumina, whereby an almost pure *cycloalkene*, b. p. 69–71°/1 mm., n_D^{20} 1.5099, was obtained [Found: C, 88.65, 88.25; H, 11.6, 11.3%; *M* (micro-Rast), 159, 160; $\bar{\nu}_{92}$ (by catalytic hydrogenation) Calc. for $\text{C}_{12}\text{H}_{18}$: C, 88.8; H, 11.2%; *M*, 162; $\bar{\nu}_{17}$]. The oxygenated impurity, obtained by elution of the chromatogram with absolute ethanol, proved to be *trans-cyclohexane-1:2-diol*, m. p. 104° (Found: C, 62.4; H, 10.15%). Addition of bromine to a representative sample of the *cycloalkene* in the way previously described gave the two known tetrabromides of dicyclohexenyl of m. p.s 159–160° (Found: C, 30.15; H, 3.75. Calc. for $\text{C}_{12}\text{H}_{18}\text{Br}_4$: C, 29.9; H, 3.75%) and 189–191° (Found: C, 29.6; H, 3.85%).

The fraction (ix) was a colourless viscous highly-oxygenated liquid (Found: C, 81.6; H, 10.3%). A portion of this (2.7 g.) gave on re-fractionation the following sub-fractions: (a) b. p. <87.5°/0.05 mm., n_D^{20} 1.5110 (0.4 g.); (b) b. p. 87.5–90.0°/0.04 mm., n_D^{20} 1.5160 (1.0 g.); (c) b. p. 90.0–105°/0.04 mm., n_D^{20} 1.5253 (1.0 g.). The fraction (b) contained, as indicated by the analytical data, *ca.* 80% of *cyclohexenylcyclohexenol*, $\text{C}_{12}\text{H}_{18}\text{O}$, and *ca.* 14% of *cyclohexenylcyclohexenone* [Found: C, 79.9; H, 10.25; OH (Zerewitinoff), 7.6. $\text{C}_{12}\text{H}_{18}\text{O}$ requires C, 80.85; H, 10.2; OH, 9.55%]; λ_{max} 2260 \AA ., $\epsilon = 1400$. A similar sample had b. p. 110–126°/1 mm., n_D^{20} 1.5160 [Found: C, 80.75; H, 10.05%; $\bar{\nu}_{17}$ (microhydrogenation)]. Fraction (c) was a mixture of the alcohol and ketone with a little higher-boiling olefin (Found: C, 81.6; H, 10.35%). Owing to the small amount of the alcohol-ketone mixture isolated, no structural investigation was possible.

Fraction (x) was shown to be mainly *tercyclohexenyl* with a little oxygenated material as impurity. On redistillation over sodium, a main fraction was obtained, b. p. 108–110°/0.5 mm., n_D^{20} 1.5328 (Found: C, 88.0; H, 10.85. Calc. for $\text{C}_{18}\text{H}_{26}$: C, 89.2; H, 10.8%).

The residue (xi), a mixture of high-boiling alcohols and olefins (Found: C, 85.1; H, 10.5%), was not further examined.

Reaction of tert.-Butyl Hydroperoxide with cycloHexanol.—*cycloHexanol*, b. p. 64°/17 mm. (10 g., 1 mol.) and the hydroperoxide (9.0 g., 1 mol.) were heated under reflux at 130° for 24 hours. On fractionation, the product gave (i) *tert.*-butanol, b. p. 80–83°/747 mm. (5.5 g., equivalent to 74.3% of the peroxide taken), (ii) a fraction, b. p. 140–156°/747 mm. (9.8 g.), containing *cyclohexanone* (19%), determined and identified as its 2:4-dinitrophenylhydrazone, m. p. and mixed m. p. 157–158° (Found: C, 52.0; H, 5.35. Calc. for $\text{C}_{12}\text{H}_{14}\text{O}_4\text{N}_4$: C, 51.8; H, 5.05%), and (iii) a residue (2.0 g.) containing a small amount of adipic acid which after crystallisation from ether had m. p. 147–148.5°.

Reaction of tert.-Butyl Hydroperoxide with cycloHex-2-enol.—The alcohol (b. p. 162–165°/752 mm.; *a*-naphthylurethane, m. p. 156°; 4.0 g.) and hydroperoxide (9.0 g.) were heated under reflux at 130° for 24 hours. Fractionation of the product gave (i) *tert.*-butanol (3.3 g., equivalent to 44.6% of the peroxide taken), (ii) unchanged peroxide (3.6 g.), (iii) a fraction, b. p. 150–163° (3.55 g.), containing *ca.* 18% of *cyclohex-2-enone*, determined and identified as its 2:4-dinitrophenylhydrazone, m. p. and mixed m. p. 158–160° (Found: C, 52.3; H, 4.5. Calc. for $\text{C}_{12}\text{H}_{12}\text{O}_4\text{N}_4$: C, 52.2; H, 4.4%).

Reaction of tert.-Butyl Hydroperoxide with 1-Methylcyclohexene.—A mixture of the olefin (144 g., 1.5 mols.) and the hydroperoxide (45 g., 0.5 mol.) was heated at 140° for 24 hours in nitrogen-filled Carius tubes. The product (187.2 g.) was a bright yellow liquid which on fractionation gave the following fractions: (i) b. p. 78–112°/735 mm. (104.7 g.), containing a small aqueous layer; (ii) evaporated spontaneously into a liquid-air trap at 13 mm. (7.0 g.); (iii) b. p. <53°/13 mm., n_D^{20} 1.4520 (20.5 g.); (iv) b. p. 53–77° (mainly 67–77°)/13 mm. (14.2 g.); and (v) a yellow viscous residue, not further investigated.

The fraction (i) contained water-soluble and water-insoluble portions. The former (37.1 g.) consisted mainly of *tert.*-butanol, together with a small amount of water and a trace of acetone; the latter, like fractions (ii) and (iii), consisted of unchanged *cycloalkene*, and these when combined, dried (CaCl_2), and distilled in nitrogen over sodium gave a main fraction, b. p. 107–108°, n_D^{20} 1.4501 (73.6 g.).

The fraction (iv), a colourless oily liquid, was a mixture of methyl *cyclohexenols* and methyl *cyclohexenones* (Found: C, 76.1; H, 10.55. Calc. for $\text{C}_7\text{H}_{12}\text{O}$: C, 74.95; H, 10.7%). Ultra-violet spectrographic analysis disclosed a selective absorption band at λ 2310 \AA ., $\epsilon = 1200$, consistent with the presence of ~12% of conjugated methyl *cyclohexenones*.

Treatment of a portion (0.5 g.) of this fraction with 2:4-dinitrophenylhydrazine in absolute ethanol gave a mixture of deep red dinitrophenylhydrazones (0.25 g.); these (25 mg.), dissolved in light petroleum (b. p. 40–60°) (150 c.c.), were chromatographed on a column of alumina (30 g.; 600 \times 9 mm.), and became adsorbed in two distinct bands. The upper band consisted of 3-methyl *cyclohex-2-enone* dinitrophenylhydrazone (4.4 mg.), m. p. 168–170°, and the lower band contained 2-methyl *cyclohex-2-enone* dinitrophenylhydrazone (9.7 mg.), m. p. 198–200°, mixed m. p. 199–201°.

To a further portion (6.0 g.) of (iv) in glacial acetic acid (10 c.c.) there was added with cooling a solution of chromic anhydride acid (4.0 g.) in 75% aqueous acetic acid (10 c.c.). The oxidation was completed by warming the mixture on the water-bath for 30 minutes. The ketonic portion was extracted with ether (200 c.c.), and the ethereal layer neutralised with saturated sodium hydrogen carbonate

solution and then dried (CaCl_2). After removal of the solvent the product was distilled, giving a fraction (i) b. p. $62-70^\circ/13$ mm., n_D^{20} 1.4672 (2.2 g.), and a higher-boiling residue (ii) (1.2 g.). The ketone content of fraction (i), determined as its dinitrophenylhydrazone, was 64%. Chromatographic separation of the mixed dinitrophenylhydrazones (30 mg.) as described above gave the dinitrophenylhydrazones of 2-methylcyclohex-2-enone (12.1 mg.) and 3-methylcyclohex-2-enone (5.0 mg.).

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