Autoxidation of Ketimines

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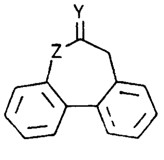
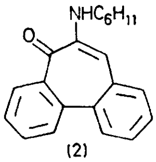
Summary Autoxidation transformed the *N*-cyclohexylimine derivative of dibenzyl ketone and of 3,4:5,6-dibenzocyclohepta-3,5-dienone into the corresponding α-ketoketimine (or tautomer) and degraded the intermediate *N*-cyclohexylimine of benzyl benzoyl ketone into benzoic acid, cyclohexyl isocyanide, cyclohexylamine, and dibenzyl ketone.

An uncatalysed ground state autoxidation of the *N*-cyclohexylimines (**3**) and (**4**) of dibenzyl ketone and 3,4:5,6-dibenzocyclohept-3,5-dienone (**1**) respectively into intermediate α-ketoimines is explained by a free-radical chain process similar to the one previously proposed for the formation of unsaturated 1,4-diones by autoxidation of Schiff's bases.[1] Autoxidation of imines has also produced amino peroxides.[2] The imine (**12**) of benzyl benzoyl ketone produces, after autoxidation and degradation, $C_6H_{11}NC$, $C_6H_{11}NH_2$, $(PhCH_2)_2CO$, $PhCO_2H$, and presumably, PhCHO, and the ketoimine from (**4**) is stabilized as 7-cyclohexylamino-2,3:4,5-dibenzotropone (**2**).



(1); $Z = CH_2, Y = O$
(4); $Z = CH_2, Y = NC_6H_{11}$
(5); $Z = C{=}NOH, Y = NOH$



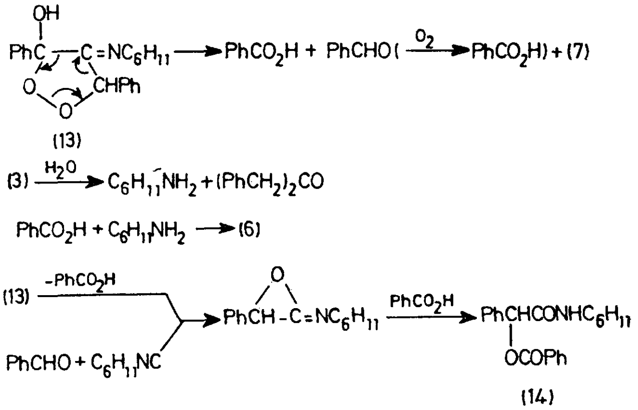
(2)

$(PhCH_2)_2C=NC_6H_{11}$
(3)

$PhCO_2^{-}\overset{+}{N}H_3C_6H_{11}$ (6)

$C_6H_{11}NC$ (7)

$Et_2C=NC_6H_{11}$ (8)



An equimolar mixture of the ketone (**1**)[3] and $C_6H_{11}NH_2$ was refluxed for 3 h in MeOH containing a few drops of HCl to give the tropone (**2**) (42%), m.p. 118—119 °C [dioxime (**5**), m.p. 218—219 °C], presumably *via* the imine (**4**) as an intermediate.† Autoxidation of (**3**)[4] was effected by passing air or oxygen through the neat liquid for 48 h. Cyclohexylammonium benzoate (**6**) (38%), m.p. 172—173 °C, precipitated and gave *N*-cyclohexylbenzamide, m.p. 148—149 °C,[5] on heating at 200 °C. Cyclohexyl isocyanide (**7**)[6] (8%) was obtained by chromatography (silica–hexane) from the liquid portion of the reaction mixture. Further elution with hexane and benzene gave $(PhCH_2)_2CO$ (19%) and intractable mixtures. The products (**6**) and (**7**) were also obtained from similar treatment of a mixture of $(PhCH_2)_2CO$ and $C_6H_{11}NH_2$. The ketone alone was not attacked by oxygen.[7] The neat *N*-cyclohexylimine (**8**) of diethyl ketone was unreactive to a stream of oxygen for 100 h.

Stabilization of the benzylic carbanion portion of the zwitterionic form (**9**) of the enamine tautomer enhanced autoxidation, initiated by an electron transfer. The hydroperoxide (**11**) gave the diketone monoimine (**12**) on dehydration. A hydroperoxide derivative of the enamine tautomer of (**12**), in equilibrium with the cyclic peroxide (**13**) fragmented into $PhCO_2H$, PhCHO (not detected), and (**7**). Hydrolysis accounted for the formation of the $C_6H_{11}NH_2$ and $(PhCH_2)_2CO$.

Since autoxidation of PhCHO precluded its participation in the Passerini reaction with $PhCO_2H$ and (**7**) to give the ester (**14**),[8] the isomerisation (**13**) → (**14**) was not detected.

Financial assistance from the N.S.F. and the P.R.F. is gratefully acknowledged.

(*Received*, 17*th July* 1975; *Com.* 815.)

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† Each compound was identified by comparison with an authentic sample or by satisfactory elemental and i.r. and n.m.r. spectroscopic analysis.

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