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DIMERIC PHOTOREDUCTION IN 2-METHYLBENZOPHENONES(1)

Ned D. Heindel and E. W. Sarver
Chandler Laboratory of Chemistry
Lehigh University
Bethlehem, Penna. 18015

Michel A. Pfau
Laboratoire de Chimie
Ecole Normale Superieure
Paris (V^e), France

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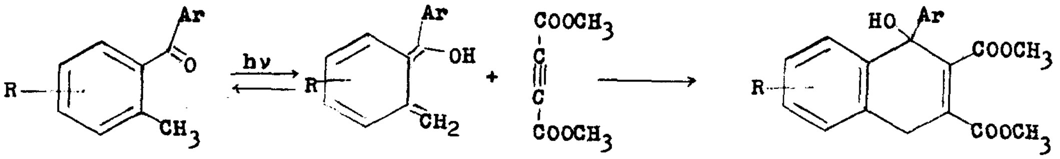
The concept of internal photoactivated hydrogen transfer (photoenolization) was originally postulated to explain the apparent lack of bimolecular photoreduction of 2-alkyl, 2-amino- and 2-hydroxybenzophenones(2). Yang and other workers have provided chemical and physical evidence to support the internal enolization process(3,4) and an enol of 2-methylbenzophenone has been "trapped" with dimethyl acetylenedicarboxylate(3). It therefore appeared, from efforts of previous workers, that the normal H atom abstraction from solvent which is a necessary prerequisite for photopinacolization(5) was circumvented by internal abstraction of the triplet state carbonyl in o-alkylketones(6). We have already demonstrated the synthetic generality of this photoenolization in a variety of o-methylbenzophenones(7).



We now wish to report that indeed a bimolecular photoreduction pathway is open to 2-methylbenzophenones in addition to the photoenolic process previously demonstrated. While testing other acetylenic and olefinic compounds (cyclohexene, dimethyl maleate, ethyl cinnamate, diphenylacetylene and phenylacetylene) as potential dienophiles for the photoenol of 2,4-dimethylbenzophenone, no trapped adducts were obtained but instead low yields (5-10%) of a dimeric substance were isolated. The dimer was identified by infrared, combustion, and mass spectral analysis as the corresponding pinacol and was subsequently independently synthesized by the Mg/I_2 reduction(8) of the parent benzophenone in 31% yield, m.p. 179-180°C.

The production of pinacol in such a poor H atom-donating medium as the benzene normally employed in photoenol trapping experiments encouraged us to investigate the photopinacolization of a series of 2-methylbenzophenones in 2-propanol. The ketones were irradiated as 0.05M solutions in the alcohol for a 10 hour period in a Rayonet reactor equipped with 3500 Å lamps. The results are reported in the Table.

TABLE

Ketone	Pinacol[a]		Trapped Enol[a]
	Yield	m.p.	
2-methylbenzophenone	33	144-145°	82[b]
2,4-dimethylbenzophenone	28	179-180°	81[b]
2,5-dimethylbenzophenone	50	142-143°	86[b]
2,3',4'-trimethylbenzophenone	33	139-141°	62[c]
3-methyl-4-benzoylpyridine	40	170-171°	--[d]

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a. Satisfactory combustion analyses were obtained for all products.
b. Yields based on analytically pure 1-aryl-2,3-dicarbomethoxy-1,4-dihydro-1-naphthol, see (7).
c. Not reported in (7), m.p. 126-127°C.
d. No trapped adduct could be obtained because the pyridine moiety of the ketone underwent a vigorous "dark reaction" with dimethyl acetylene-dicarboxylate presumably as described for pyridines in general in (9).

By utilization of a benzophenone actinometer the quantum yield for the photoreduction of 2,4-dimethylbenzophenone was calculated to be 0.03. The quantum yield for the photoenol trapping process on 2-methylbenzophenone was reported to be 0.5(3).

To investigate the competitive photoenolization-photoreduction processes under conditions in which both pathways would be stoichiometrically possible, equimolar (0.05 Molar) quantities of 2,4-dimethylbenzophenone, dimethyl acetylenedicarboxylate, and 2-propanol were irradiated in benzene solution for 10 hours. A 78% yield of the "trapped" enol, 1-phenyl-6-methyl-2,3-dicarbomethoxy-1,4-dihydro-1-naphthol, was isolated. Spectral examination of the mother liquors showed no evidence for the presence of pinacol.

However, when similar equimolar quantities of the 2,4-dimethylbenzophenone and dimethyl acetylenedicarboxylate were irradiated in 2-propanol medium, the only photoproduct was a 30% yield of the diol.

We are currently exploring the variation of reactant concentrations to establish conditions under which competitive quantum yields for the two processes can be measured.

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