

The Photoreduction of Carbonyl Compounds by Amines

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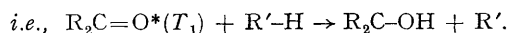
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THE photoreduction of carbonyl compounds by alcohols and alkanes¹ is well known, but the reduction by amines has only recently been studied. The photoreduction of benzophenone by primary, secondary, and tertiary aliphatic amines² and by tertiary *N*-alkyl arylamines has been reported.³ Here we report certain differences, found to occur between reductions by amines and those by alcohols and similar hydrogen donors.

We found that fluorenone, a ketone not reduced by alcohols⁴ or alkanes,⁵ is reduced by *NN*-dimethylaniline to give fluoropinacol (58% yield). Xanthone, a ketone reduced by alkanes⁶ but not by alcohols,⁷ is also reduced by *NN*-dimethylaniline to give xanthopinacol (56% yield). The reduction of benzophenone by some *N*-methyl- and *N*-benzyl-amines has been examined and the results are shown in the Table.

It was found that benzylic C-H bonds are slightly less reactive than methyl C-H bonds in

types of C-H bonds. One possible explanation of our result is that the nitrogen atom activates adjacent C-H bonds to such an extent that stabilization of the amine radical formed by a phenyl group in benzylic compounds is of little consequence. Also, if the C-H bonds adjacent to a nitrogen atom are extremely reactive, the reduction of fluorenone and xanthone is not so surprising. The reduction of 1-naphthaldehyde and 2-acetonaphthone by tri-*n*-butylstannane has been explained⁸ in a similar way, by saying that the tin hydride is a very good hydrogen donor. However, there is the possibility that the reduction by amines does not occur by the same mechanism as the reduction by alcohols and alkanes,



Cohen and Cohen⁹ have suggested, as a result of

TABLE

The rates of photoreduction of 0.05M benzophenone by 0.1M amine in benzene solution^a

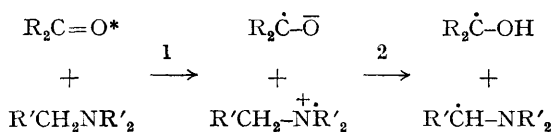
Amine	Rate of disappearance of benzophenone (min. ⁻¹)	Rate relative to reduction by 0.1M diphenylmethanol under the same conditions ^b	Reactivity per hydrogen ^c
<i>NN</i> -Dimethylaniline	0.072	1.54	0.26
<i>N</i> -Methyldiphenylamine	0.022	0.48	0.16
<i>N</i> -Benzoyldiphenylamine	0.0108	0.23	0.11
<i>N</i> -Methylcarbazole	0.0131	0.28	0.093
<i>N</i> -Benzylcarbazole	0.0073	0.15	0.078

^a 100w Medium-pressure "Hanovia" lamp. Volume irradiated, 150 ml; ^b Rate of reduction by diphenylmethanol 0.047 min.⁻¹; ^c Reactivity of the benzylic diphenylmethanol hydrogen taken as 1.

both the *N*-alkylated diphenylamine and carbazole systems. This result is in contrast to Walling and Gibian's observation⁵ that the triplet state of benzophenone shows extreme selectivity in abstracting hydrogen from alkanes which contain different

their finding that *p*-aminobenzophenone is reduced by certain aliphatic amines, that the reduction by amines might occur by initial transfer of an electron from the nitrogen atom to the electron-deficient oxygen atom of the excited carbonyl

group, which is followed by proton transfer and electron redistribution.



Our observation that *N*-benzylamines show a similar reactivity to the corresponding *N*-methyl compounds can be explained by this mechanism if step 2 is a particularly exothermic process.

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