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A NEW EVIDENCE FOR ACID-CATALYTIC ACTION OF SINGLET EXCITED 2-NAPHTHOL ON THE GROUND STATE REACTION

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A new evidence to demonstrate acid-catalytic action of excited 2-naphthol on the ground state reaction is presented for the production of acetals from irradiation of alkanals in alcohols in the presence of 2-naphthol.

2-Naphthol is known to exhibit higher acidity at the excited singlet state (pKa~3) than at the ground state (pKa~10).[1)] Recently, Saeva and Olin found that sodium 2-naphthol-6-sulphonate (I), on irradiation in neutral aqueous solution in the presence of sodium nitrite, was nitrosated and postulated that facile deprotonation of (I) in its singlet excited state would initiate a sequence of ground state reactions through protonation of nitrite ions to give nitrous acid which subsequently nitrosate (I).[2)] Soon afterwards, Chandross criticized this postulation, however, without giving explanation on the observed effect of the naphthol,[3)] and the nature of the observed role of the naphthol still remains unsolved from quantitative view point. We now wish to add a new evidence clearly demonstrating singlet excited naphthol to act as an acid catalyst on the ground state chemical reaction, which proceeds between aldehydes and alcoholic solvents resulting in acetals.

Irradiation of butanal (0.1 M) in ethanol or in 2-propanol under nitrogen atmosphere with a high pressure mercury lamp did not cause any detectable change, contrasting to benzaldehyde[4)] which is facilely photoreduced into 1,2-diphenylethane-1,2-diol; however, on addition of 2-naphthol (0.02 M), irradiation of butanal in ethanol or in 2-propanol gave rise to 1,1-diethoxybutane (in 16 % on the aldehyde employed) or 1,1-bis(1-methylethoxy)-butane (10 %), respectively, together with recovered butanal. The acetals were not produced without irradiation. In the presence of 1,3-pentadiene (0.2 M), the irradiation gave only negligible amount of the acetal, and the effect of 1,3-pentadiene is taken to quench the singlet excited state of 2-naphthol on the basis of a finding that 1,3-pentadiene strongly quenched the fluorescence from 2-naphthol. This result indicates that the reaction surely proceeds through participation of photo-excited state of 2-naphthol. Likewise, irradiation of hexanal in methanol gave its dimethyl acetal, 1,1-dimethoxyhexane, in 3 % yield in the absence of 2-naphthol, but its yield was increased to 11 % in the presence of 2-naphthol (0.05 M), and the aldehyde consumed was quantitatively converted into the acetal, and 2-naphthol was almost quantitatively (more than 96 %) recovered. Similar photochemical effect of 2-naphthol to catalyze the production of acetals was observed for several aldehydes examined as follows: 2-methylpropanal in methanol, 2-phenylpropanal in methanol, and 3-phenylpropanal in ethanol; the yields of their corresponding acetals were 32, 15 and 64 %, respectively, in the presence of 2-naphthol (0.1 M), whereas, in the absence of 2-naphthol, their yields were nil or negligible.

Production of acetals from irradiation of carbonyl compounds in alcohols have previously been reported in a few cases, but the reactions seem to proceed not through photochemical excitation of carbonyl compounds but through catalysis by acidic matter adventitiously present or produced during the irradiation. Thus, it was reported that irradiation of 3-(2-methylene-1-methylcyclohexyl)propanal in unpurified methanol gave its dimethyl acetal but did not give the acetal in methanol freshly distilled from sodium carbonate, which shows that the production of acetal under irradiation is due to the catalysis by acidic matter produced from unpurified alcohol.[5] Also the formation of ketal from irradiation of nortricyclanone in ethanol was attributed to catalysis by acidic matter resulted during the irradiation.[6]

The present reaction is not due to the catalysis by acidic matter produced during the irradiation, because this possibility is excluded from the following observations. In the first place, the acetals were produced even in 2-propanol which would not facilely give acidic matter through eventual oxidation during the irradiation. Secondly, alcoholic solvents were pre-irradiated, then aldehydes were added there and kept in the dark, but acetals were not produced. Thirdly, 2-naphthol was irradiated in alcohols wherein were added aldehydes and kept in the dark without producing acetals. Fourthly, aldehydes were irradiated in alcohols in the presence of 2-naphthol, in which was added an amount of fresh aldehyde and kept in the dark, but the added aldehyde was not converted into acetal. The all above cases would produce acetals if acidic matters were produced during the irradiation.

Therefore, in view that the singlet excited 2-naphthol easily transfers protons to acceptors,[1] it seems reasonable to imply that the present reaction starts from the proton transfer from the excited naphthol to aldehyde followed by ground state reactions. The detailed mechanism will be presented in a full paper.

References

1) As reviews: A. Weller, "Progress in Reactions Kinetics", 1, 189 (1961); J. F. Ireland and P. A. Wyatt, "Advances in Physical Organic Chemistry", ed. by V. Gold and D. Bethell, 12, 131 (1976), Academic Press.
2) F. D. Saeva and G. Olin, J. Am. Chem. Soc., 97, 5631 (1975).
3) E. A. Chandross, J. Am. Chem. Soc., 98, 1053 (1976).
4) G. Ciamician and P. Silber, Ber., 34, 1530 (1901).
5) J. A. Marshall and J. P. Arrington, J. Org. Chem., 36, 214 (1971).
6) P. Yates. J. Photochem., 5, 91 (1976).

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