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# INTERMEDIATES IN THE PHOTOCHEMICAL REACTIONS OF CAMPHORQUINONE WITH ALIPHATIC ALDEHYDES

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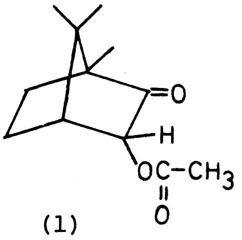
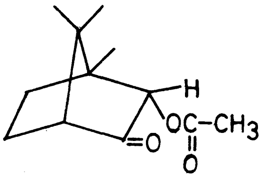
The dynamic aspects of photochemical reactions of camphorquinone with aliphatic aldehydes were investigated by means of CIDNP. Besides that the two types of stable products (1)-(3) could be produced through ionic rearrangement of unstable intermediates (6), (7) arose from radical pair (5), the reverse hydrogen atom abstraction reaction was found to occur between the two radicals resulted from the reaction of photo-excited camphorquinone and aldehyde.

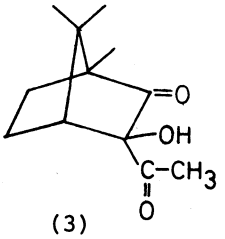
Photochemical hydrogen atom abstraction of camphorquinone(CQ) has been extensively studied by several workers.[1)] Owing to the complexity of the products, however, the reaction is still attracting the attension of investigators. According to M.Rubin and his co-worker[2)] in the photoreaction with aliphatic aldehydes CQ gave two endo-α-ketoesters(1),(2) and one endo-β-diketone(3), but they were unsuccessful to isolate the another possible isomer(4). Stereochemistry of these products were unambiguously determined by them. The reaction is assumed to involve hydrogen atom transfer from aldehyde to the photo-excited CQ and subsequent combination of the resulting radicals.



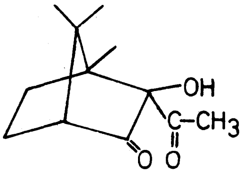
(1)



(2)

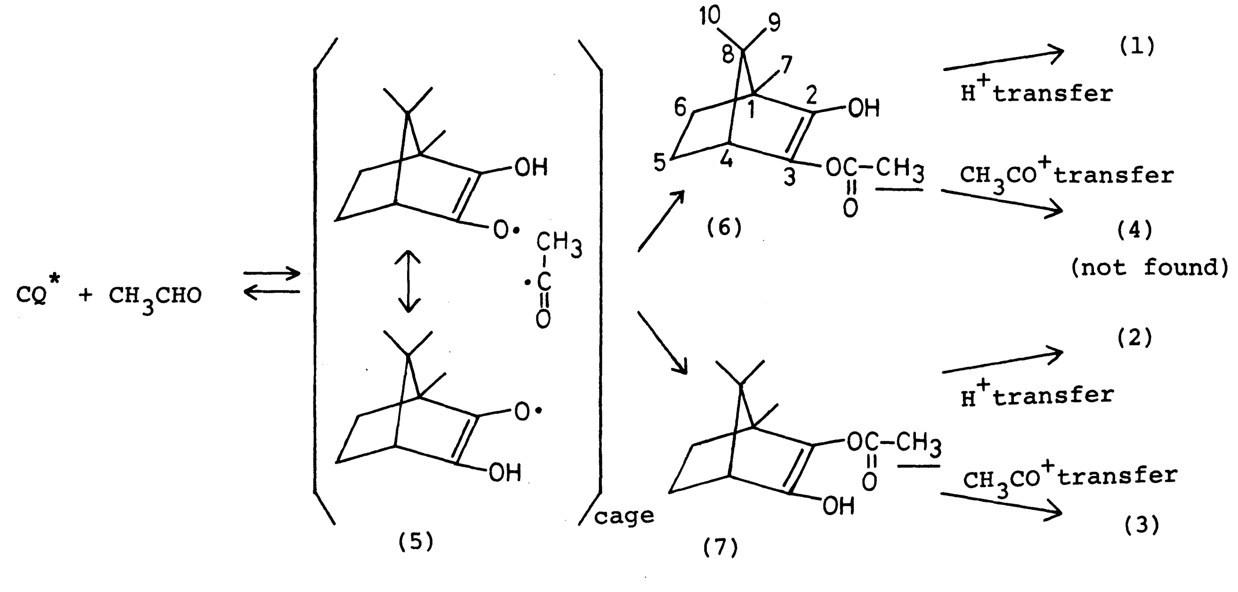


(3)



(4)

The reaction was reinvestigated by using CIDNP technique.[3)] As Fig.1 shows, in the photochemical reaction of CQ with acetaldehyde a strongly polarized pmr absorption signal due to methyl protons appeared in the region corresponding to enol ester methyl protons, the chemical shift of the polarized methyl protons did correspond to that of neither of the isolated products (1)-(3), which were obtained by the reaction in a macro scale.[4)] Reactions with aliphatic aldehydes(RCHO: R=$C_2H_5$, n-$C_3H_7$, i-$C_3H_7$, n-$C_4H_9$, and i-$C_4H_9$) showed quite similar phenomena. Since according to the CKO theory[5)] the polarized pmr signal should be observed for the product formed via a radical process, these experimental results suggest that an unstable intermediate exhibiting polarized pmr signal is formed at first and subsequently rearranges to the isolated stable products. Assuming two possible endiol monoesters (6) and (7) as the unstable intermediates, one can ingeniously explain the experimental results as are shown in the following scheme.



Reaction Scheme

Endiol monoesters(6),(7) formed via radical pair (5) may affect on the methyl protons to give polarized pmr signal, and the monoesters could rearrange to (1)-(4) by ionic process. A possible acetyl group transfer in (6) to (4) is unfavorable because of the steric repulsion with bridgehead methyl group(7-$CH_3$). This may be the reason that (4) is not isolated in the reaction. Two methyl groups of the endiol monoesters would show their pmr signals at the same chemical shift.

Furthermore, CIDNP examination, though it is qualitative, indicates clearly the existence of hydrogen back donation from semidione radical to acyl radical. As Fig.3 shows, pmr signal due to formyl proton is emission polarized during the

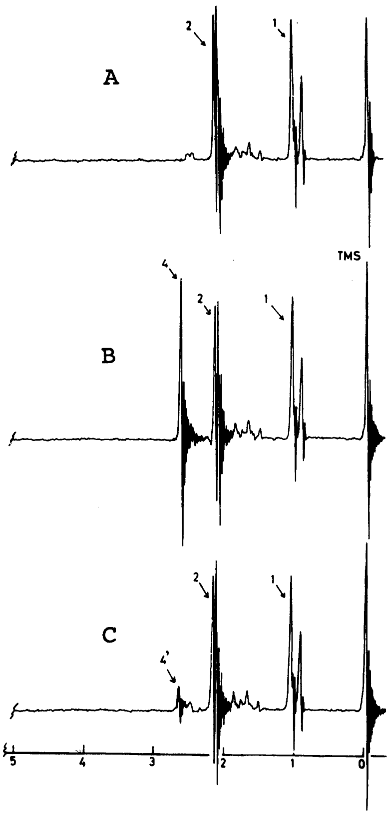


Fig.1

Fig.2

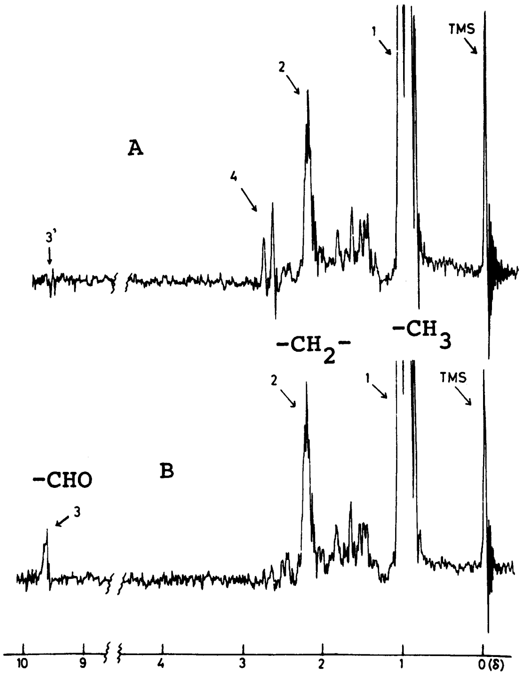


Fig.3

Fig.1 Pmr Signals observed in the Reaction of CQ with Acetaldehyde(solvent:$CCl_4$). A:before, B:during, and C:after of irradiation (Ca.10 seconds). 1:methyl protons of CQ, 2:methyl protons of acetaldehyde, and 4: polarized methyl protons of unstable intermediates(δ :2.63).

Fig.2 Comparison of Pmr Signals of Products.

A: pmr signal of mixture of β-diketones.
B: pmr signal of α-ketoester(3).

C: pmr signal observed during irradiation of CQ and acetaldehyde.

Fig.3 Pmr Signals observed in the Reaction of CQ with i-Valeraldehyde.

A:during irradiation; formyl proton (signal 3') is emission polarized. Signal 4 is absorption polarized signal due to methylene protons of unstable intermediates.

B:before irradiation.

course of the photochemical reaction, but it does not show any change without CQ under the same condition.6) This is a decisive evidence of actaldehyde reproduction.7) The hydrogen back donation from semidione radical to acyl radical was assumed by M.Rubin and his co-worker on the basis of kinetic approach to the reaction.8)

## Referrences

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2) M.B.Rubin and J.M.Ben-Bassat, Tetrahedron, 26, 3579(1970)
3) 100 MHz pmr spectrometer manufactured by JEOL and 300 W Hg-arc lamp were used.
4) (1) and (2) were obtained as yellow oil in a mixture after usual work-up. Every efforts to separate them were unsuccessful, but they could be identified by pmr spetrum; (1) showed doublet at $\delta$:5.30 due to exo-3-H and (2) showed singlet at $\delta$:5.30 due to exo-2-H. Ester methyl protons of (1) and (2) were appeared at $\delta$:2.07. Ir; $\nu_{C=O}$:1750 $cm^{-1}$(mixture), and no $\nu_{OH}$.
   (3) was isolated as white crystal, mp 142.5-143.0 °C, ir; $\nu_{C=O}$:1755,1685 $cm^{-1}$, $\nu_{OH}$:3400 $cm^{-1}$. Pmr; $\delta$:4.17(s, OH), 2.18(s, $-COCH_3$).
5) G.L.Closs, J. Amer. Chem. Soc., 91, 4552(1969); G.L.Closs and A.D.Trifunac, ibid., 91, 4554(1969); 92, 2183, 2186(1970)
   R.Kaptein and L.J.Oosterhoff, Chem. Phys. Lett., 195, 214 (1969)
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6) Recently photochemical reaction of acetaldehyde in liquid state has examined by CIDNP technique, and reported that some products showed polarized signals (H.E.Chen, S.H.Vaish, and M.Cocivera, J. Amer. Chem. Soc., 95 , 7586(1973)). But this condition is considerably different with ours, because under our condition photo-excitation of CQ is the initial stage of the reaction.
7) This photochemical reaction is quite clean, and there is little possibility of hydrogen atom abstraction by acetyl radical from acetaldehyde.
8) Private communication. The present authors are much indebted to them for sending of his data.

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