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PHOTOLYTIC AND THERMAL DECOMPOSITIONS OF 2-DIAZOPHENOL. FORMATION OF FULVENE DERIVATIVES

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Photolytic decomposition of 2-diazophenol in methanol afforded 6-hydroxy-6-methoxy-2-(2-hydroxyphenylazo)fulvene, guaiol, phenol, and dimer of methyl cyclopentadienecarboxylate. The decomposition in water gave 6,6-dihydroxyfulvene derivative. Thermal decomposition of 2-diazophenol gave fulvenylidenebenzo-1,3-dioxole. Structure and mechanism of the formation of these products are discussed.

The photolytic and thermal decompositions of diazooxides have been known to form 6-oxofulvenes (fulven-6-one) as unstable intermediate, from which dimer of cyclopentadienecarboxylic acid or indenecarboxylic acid has been obtained.[1, 2] Recently, the pyrolyses of o-phenylene carbonate,[3] salicylic acid esters,[4] and 3-bromotropolone[5] were also found to give 6-oxofulvene as intermediate.

In the connection with the studies of reactivity of cyclic unsaturated ketenes related to 8-oxoheptafulvene (heptafulven-8-one),[6] we have planned to investigate a reactivity of 6-oxofulvene and have obtained a further evidence for existence of the fulvene in the decomposition of 2-diazophenol and also several interesting results concerning to the fulvene chemistry, the results of which will be reported in this paper.

Photolytic decomposition[7] of 2-diazophenol (6-diazo-2,4-cyclohexadien-1-one) (1) or its hydrochloride in methanol afforded guaiol (2), phenol (3), dimer of methyl cyclopentadienecarboxylate (4), and a reddish pigment (5), $C_{13}H_{12}O_3N_2$, mp 156°C (decomp.), in about 50, 2, 30, and 15% yields, respectively. The compound (5) shows UV, λ_{max}^{MeOH} 244.5 nm (log ε, 4.29), 280 (3.83), 436 (4.23), and 464 (4.23); $\lambda_{max}^{MeOH\text{-}NaOH}$ 262 (4.34), 270^{sh}(4.28), 376 (3.73), 490^{sh}(4.35), and 508 (4.37); NMR ($CDCl_3$), δ 3.90 ppm (s, OCH_3), 6.42 (d,d, J=5.0, 3.6 Hz, Hb), 6.66 (d,d, J=5.0, 2.0 Hz, Ha), 6.76~7.10 (m, 4H), 7.54 (d,d, J=3.6, 2.0 Hz, Hc), 10.10 (s, He), and 14.44 (bs, Hd). The signal at 10.10 easily disappears by deuterium exchange with D_2O, but the signal at 14.44 does not change at all by shaking with D_2O.[8]

Acetylation of 5 with acetyl chloride and pyridine afforded monoacetate (6), reddish needles, mp 118~119°C, UV, λ_{max}^{MeOH} 243.5 (4.34), 260^{sh}(3.94), 285^{sh}(4.47), 410 (4.28), and 450 (4.17).

UV spectra of 5 and 6 were similar to those of 6-hydroxy-6-methyl-2-phenylazofulvene[9] formed by diazocoupling of diacetylferrocene or of 6-acetoxy-6-methylfulvene.

When 2-diazophenol was photolytically decomposed in ethanol and isopropyl alcohol, the corresponding reddish pigments (7), mp 115~116°C, and (8), mp 125.5~126.5°C, were obtained respectively.

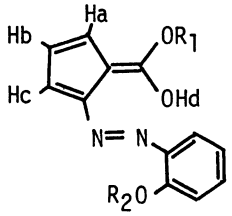
When a methanolic solution of the compound (5) was catalytically hydrogenated in the presence of 5% Pd-C, 2 moles of hydrogen were taken up and color of the solution disappeared, but during a chromatographic purification of the products on silica gel, color changed to red and bright red crystals (9), $C_{13}H_{14}O_3N_2$, mp 106~107°C, were obtained besides a very minute amount of o-aminophenol. The compound (9) shows UV, λ_{max}^{MeOH} 250 (3.92), 344 (4.13), and 528 (3.80); NMR ($CDCl_3$) δ 2.05 (quintet, 2H), 2.93 (t, 4H), 3.89 (s, OCH_3), 6.9~7.8 (m, 4H), and 14.67 (s, OH), from which a structure shown in the scheme was assigned, and the initially formed colorless product may be a tetrahydro derivative (10).[10]

From these facts, it must be clear that the compounds (5), (7), and (8) are 6-hydroxy-6-methoxy-2-(2-hydroxyphenylazo)fulvene and its ethyl and isopropyl homologues. This is furthermore confirmed by the reaction of sodium methoxycarbonylcyclopentadienide and 1 to afford the compound (5) in a moderate yield.[11]

When the decomposition of 1 was performed in water, a dimer of cyclopentadienecarboxylic acid (11), and a reddish pigment (12), mp ca 150°C (decomp.), were obtained in 8.9 and 72%, respectively. The compound (12) shows UV, λ_{max}^{MeOH} 243 (4.00), 276 (3.78), 434 (4.12), and 462^{sh}(4.07); $\lambda_{max}^{MeOH-NaOH}$ 255 (4.14), 280 (3.70), 438 (4.51), and 458 (4.14); NMR (DMSO-d_6), δ 4.90 (bs, Hf), 6.40 (d,d, J=4.8, 3.0 Hz, Hb), 6.72 (d,d, J=4.8, 2.0 Hz, Ha), 6.8~6.9 (m, 3H), 7.55 (d,d, J=3.0, 2.0 Hz, Hc), 7.63 (m, 1H), 7.73 (s, He), and 15.62 (bs, Hd). The compound (12) was assumed to be 6,6-dihydroxy-2-(2-hydroxyphenylazo)fulvene from the spectroscopic data and the reaction mode.

On the other hand, a heating of 1 in boiling xylene afforded a pale yellow product (13), mp 255°C (decomp.), $C_{12}H_8O_2$, in 11.7%, which was formulated as fulvenylidenebenzo-1,3-dioxole on the basis of the spectroscopic data; UV, $\lambda_{max}^{isooctane}$ 274^{sh}(3.80), 286^{sh}(4.02), 310.5 (4.60), and 322.5 (4.68); NMR ($CDCl_3$) δ 6.40 (m, 2H), 6.75 (m, 2H), and 7.20 (s, 4H).

Among the tautomeric structures, fulvene (5a), 6-azafulvene (5b), and cyclopentadiene (5c), which may be considered for the compound (5), the fulvene (5a) containing seven-membered cyclic structure through a hydrogen bonding is considered to be the most appropriate structure as observed in 1,2-diacylcyclopentadiene[12, 13] from the facts that no carbonyl band was observed in its IR and that a very strong hydrogen bonding was observed in the NMR, and in addition from the fact that a



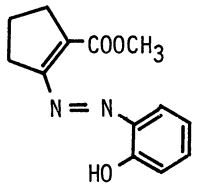
(5) $R_1 = CH_3$, R_2 = He

(6) $R_1 = CH_3$, $R_2 = COCH_3$

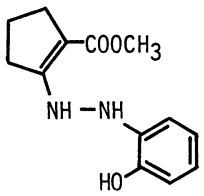
(7) $R_1 = C_2H_5$, R_2 = H

(8) R_1 = isoPr, R_2 = H

(12) R_1 = Hf, R_2 = He



(9)



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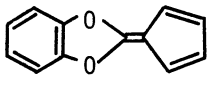

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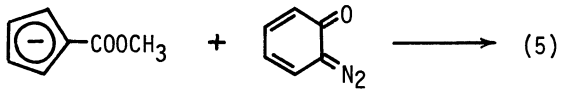
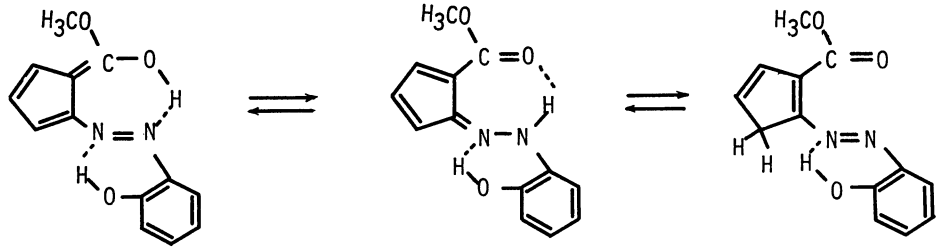


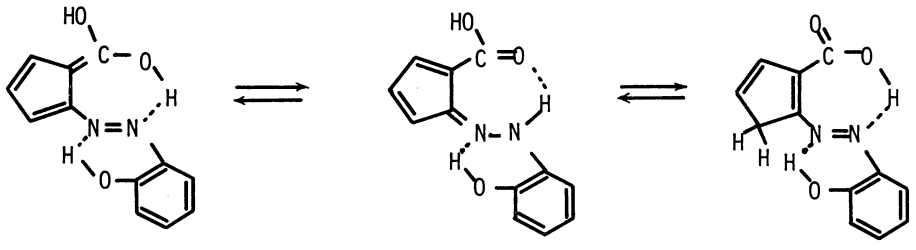
(1)

phenolic hydroxy proton appeared at very low field, δ 10.10, to suggest that the proton must form a hydrogen bonding with another nitrogen atom.

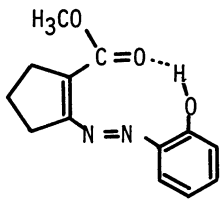
The structure of 12 is very interesting because it has unique dihydroxyvinylidene group which corresponds to a hydration product at carbonyl group of ketene. For the compound (12), various tautomers having fulvene or cyclopentadiene sketeton maintaining hydrogen bondings with nitrogen atoms are possibly considered. Although cyclopentadienecarboxylic acid itself is known to



(5a) (5b) (5c)



(12a) (12b) (12c)

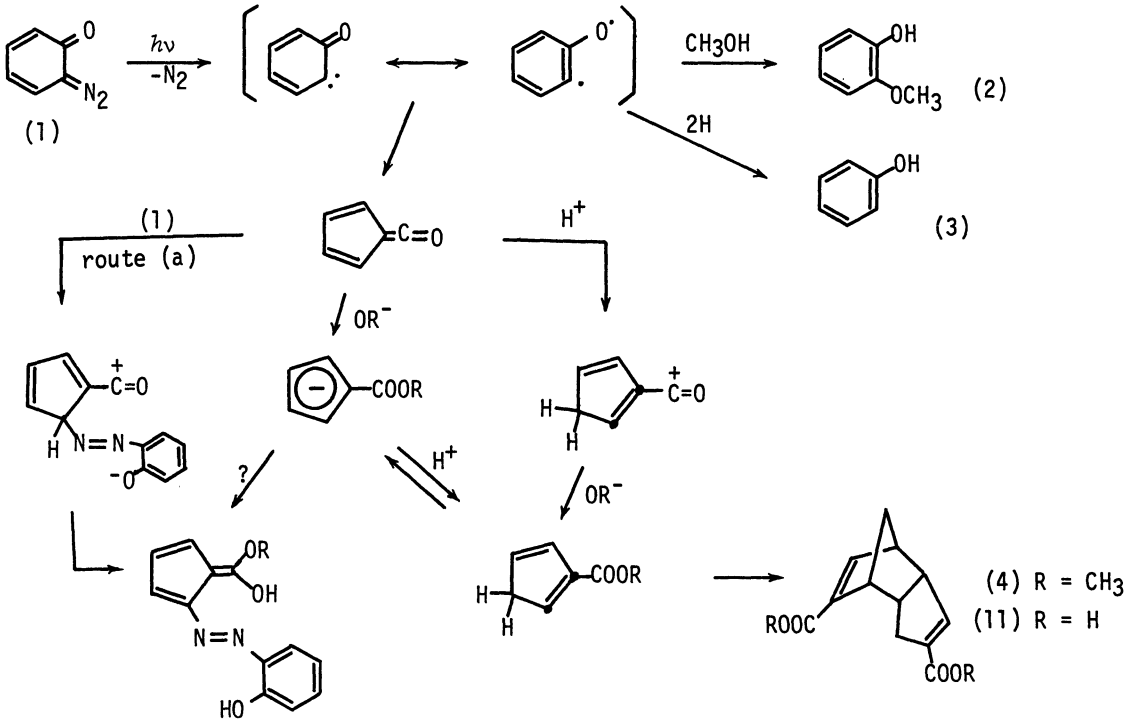


(9a)

completely exist in a cyclopentadiene structure, any cyclopentadiene structure can not be recognized for 12 from its NMR and no carbnoyl band is observed in the IR, therefore, it must be clear that 12 exists in 6,6-dihydroxyfulvene structure by consisting a fully conjugated 10-membered bicyclic structure (12a).

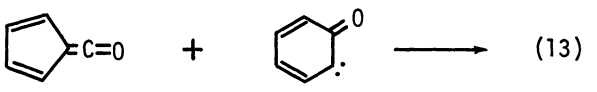
The fact that a phenolic hydroxy proton of 9 appears at very low field , δ 14.67 ppm, indicates that a hydrogen bonding with carbonyl group must be formed by consisting a planar 10-membered cyclic structure (9a).

The mechanism of the formation of products by photolytic decomposition of 2-diazophenol can be illustrated as follows;



Methyl cyclopentadienecarboxylate slowly reacts with 2-diazophenol in methanol to give 5 in a low yields, and the decomposition of 1 in ether-MeOD afforded 5 which does not contain any deuterium atom, and dimer of mono- and/or dideuterated methyl cyclopentadienecarboxylate.[14] Furthermore, the photolytic decomposition of 1 in dilute hydrochloric acid (pH 2) still afforded 5 in a moderate yield. These facts suggest that the pigments may be formed by direct attack of diazophenol to the intermediate, 6-oxofulvene, followed by attack of the solvents (route a).

Mechanism of the formation of the product (13) by thermal decomposition is considered as follows as postulated in the case of the decomposition of diazonaphthol.[2]



References

1) O. Süs, Ann, 556, 65, 85 (1944); 579, 133 (1953); O. Süs, M. Glos, K. Möller, and H. D. Eberhard, ibid., 583, 150 (1953); O. Süs and K. Möller, ibid., 593, 91 (1955); O. Süs, K. Möller, and H. Heiss, ibid., 598, 123 (1956); O. Süs and K. Möller, ibid., 599, 233 (1956); J. de Jonge and R. Dijkstra, Rec. trav. Chim., 67, 328 (1948); 68, 426 (1949); J. de Jonge, R. J. H. Alink, and R. Dijkstra, ibid., 69, 1448 (1950).

2) P. Yates and E. W. Robb, J. Amer. Chem. Soc., 79, 5760 (1957).

3) D. C. Dejongh and D. A. Brent, J. Org. Chem., 35, 4240 (1970).

4) H. F. Grützmacher and J. Hübner, Ann., 748, 154 (1971).

5) H. F. Grützmacher and J. Hübner, Tetnahedron Lett., 1971, 1455.

6) T. Asao, N. Morita, and Y. Kitahara, J. Amer. Chem. Soc., 94, 3655 (1972); N. Morita, Y. Kitahara, and T. Asao, Tetrahedron Lett., 1972, 869; T. Asao, N. Morita, and Y. Kitahara, Synthetic Commun., 2, 353 (1972); T. Asao, N. Morita, C. Kabuto, and Y. Kitahara, Tetrahedron Lett., 1972, 4379; N. Morita, T. Asao, N. Iwagame, and Y. Kitahara, Chem. Lett., 1973, 67; N. Morita, T. Asao, and Y. Kitahara, Tetrahedron Lett., 1974, 2083.

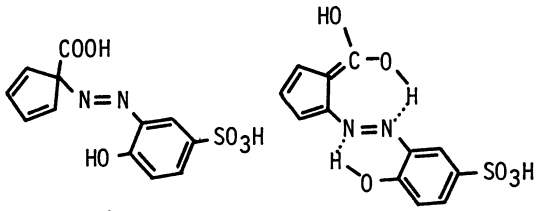
7) Photolytic decompositions were performed with Ushio 100 watts high pressure mercury lamp.

8) The hydroxy proton (Hd) is exchanged with deuterium by refluxing a solution of 5 in ether containing D_2O.

9) a) A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, N. A. Simukova, and O. V. Starovski, Izvest, Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 638 (1957); A. N. Nesmeyanov, E. G. Perevalova, N. A. Simukova, Y. N. Sheikerm, and M. D. Reshetova, Doklad. Akad. Nauk S.S.S.R., 133, 851 (1960); b) R. E. Bozak and K. L. Rinehart, Jr., J. Amer. Chem. Soc., 84, 1589 (1962).

10) The catalytic hydrogenation of 6-hydroxy-6-methyl-2-phenylazofulvene has been reported to give N-phenylimmidazol derivative, see ref. 9).

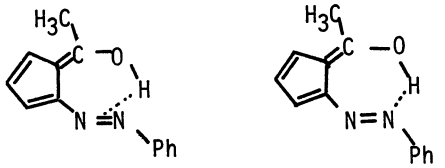
11) Süs had reported the reaction of carboxycyclopentadienide and 2-diazophenol-4-sulfonic acid afforded an azo compound, for which the structure (A) has been assigned; O. Süs, Ann., 556, 85 (1944). However, it is considered that the structure should be revised as (B).



(A) (B)

12) W. J. Linn and W. H. Sharkey, J. Amer. Chem. Soc., 79, 4970 (1957); K. Hafner, K. H. Vöpel, G. Ploss, and C. König, Ann., 661, 52 (1963); D. Lloyd and N. W. Preston, J. Chem. Soc., (C), 1969, 2464, and references cited therein.

13) A structure (C) which contains a hydrogen bonding between hydroxy proton and π-electron of N=N bond, has been assigned for 6-hydroxy-6-methyl-2-phenylazofulvene,[9b] however, we now propose a structure (D) for the compound.



(C) (D)

14) Existence or absence of deuterium in these products has been examined by their mass spectra.

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