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# THE REACTIVITY OF DIAZO KETONES. III.[1]
# THE THERMAL OR PHOTOCHEMICAL REACTION OF AZIBENZIL WITH MOLECULAR OXYGEN

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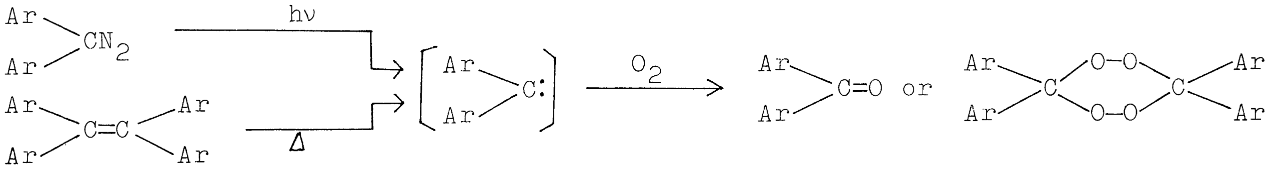
Thermal or photochemical reaction of azibenzil (I) with molecular oxygen in benzene gave tetraphenylglycolide (II), instead of benzil or a cyclic peroxide, together with bis-benzilketazine (III) and diphenylketene (IV). The formation of II did not occur from III or IV, suggesting that phenyl benzoyl carbene reacted with molecular oxygen followed by phenyl migration.

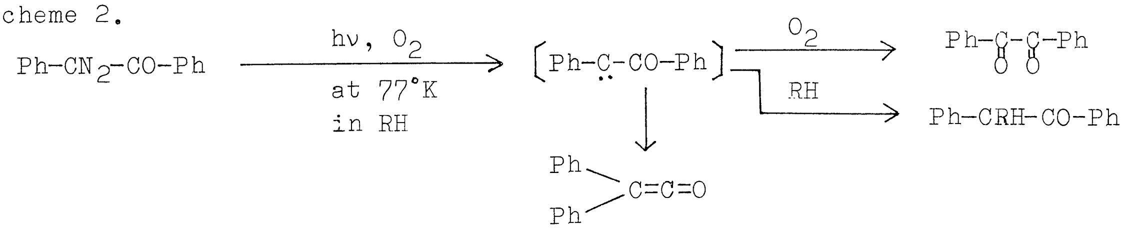
A number of reports on the photochemical reaction[2] of diphenyldiazomethane and the thermal reactions[3] of tetraarylethylene with molecular oxygen have been published. These reactions are explained by the addition of diaryl carbenes to molecular oxygen[2,3](Scheme 1).

Scheme 1.



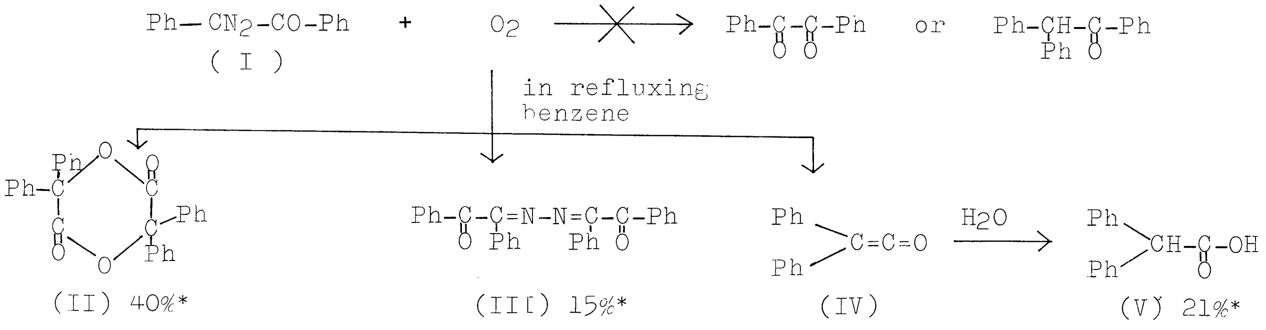
On the other hand, an indirect information[4] of the addition of a ketocarbene to molecular oxygen has been obtained from the photolysis of azibenzil in organic glass at around 77°K. The reaction gave a very small amount of benzil and a high yield of solvent substituted deoxybenzoin along with a ketene (Scheme 2).

Scheme 2.



We now wish to report the thermal or photochemical reaction of azibenzil (I) with molecular oxygen in benzene to give tetraphenylglycolide (II) together with bis-benzilketazine (III) and a ketene (IV), instead of benzil or solvent substituted deoxybenzoin (Scheme 3).

Scheme 3.



* The yields were calculated in mole % based on one mole of I for IV and V, and based on a half mole of I for II and III.

The reaction of I with molecular oxygen gas in benzene did not proceed at room temperature, but did readily by the thermal or photochemical decomposition of I. The thermal reaction was carried out at around the decomposition point (78°C) of I. When molecular oxygen gas, ca. 340 l, was passed through a benzene (85ml) solution of I, 8.5g, at the refluxing temperature, the color of the solution changed from orange to yellow gradually during 4.5 hours. The absorption of a diazo group was absent in the infrared spectrum of the reaction mixture. Into the reaction mixture, water (40ml) and ether (40ml) were added. From the organic layer, benzene and ether were removed under reduced pressure. Methanol (100ml) was added into the residue.

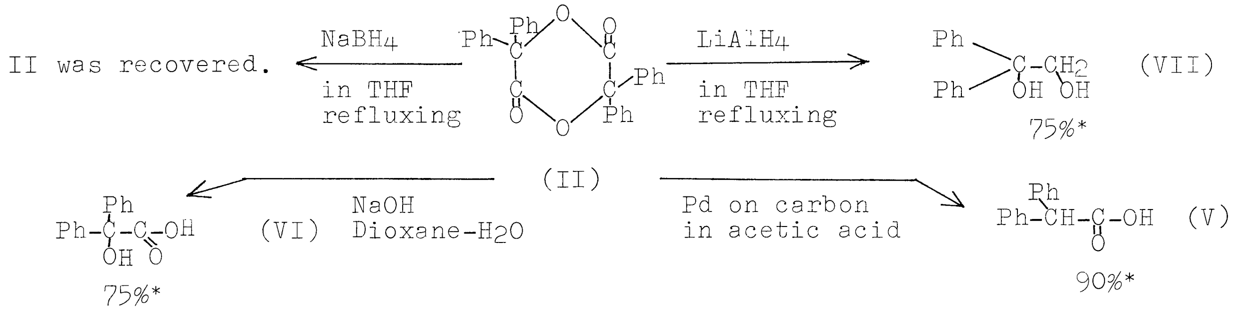
On cooling the methanol solution, white powders precipitated. From the methanol solution, III and V were obtained in the yield of 15% and 21%, respectively. The benzene (20ml) solution of the white powders was subjected to chromatography on silica gel. Elution with benzene gave II in the yield of 40%, which was recrystallized from ethyl acetate to give II.

The confirmation of tetraphenylglycolide (II), mp190~193°C, was made from IR and NMR spectra, elemental analysis, molecular weight determination, its derivatives by reduction and hydrolysis and mixed mp ,189~192°C, with the authentic sample[5]. IR(Nujol): 1760$cm^{-1}$ ; NMR($CDCl_3$):$\tau$, 2.6~3.4 .

The hydrolysis of II with aqueous sodium hydroxide in 1:1 water-dioxane gave benzilic acid (VI). The reduction of II with lithium aluminum hydride in tetrahydrofuran afforded α,α-diphenylethyleneglycol (VII). The reduction of II with sodium borohydride under the same condition as with lithium aluminum hydride, however, did not occur, and II was recovered in 92% yield. Moreover, the reduction of II with palladium on carbon in acetic acid gave V as shown in Scheme 4.

The identification of III, V, VI and VII was made by comparison of their IR spectra with those of the authentic samples[6,7,8,9] and mixed mp methods.

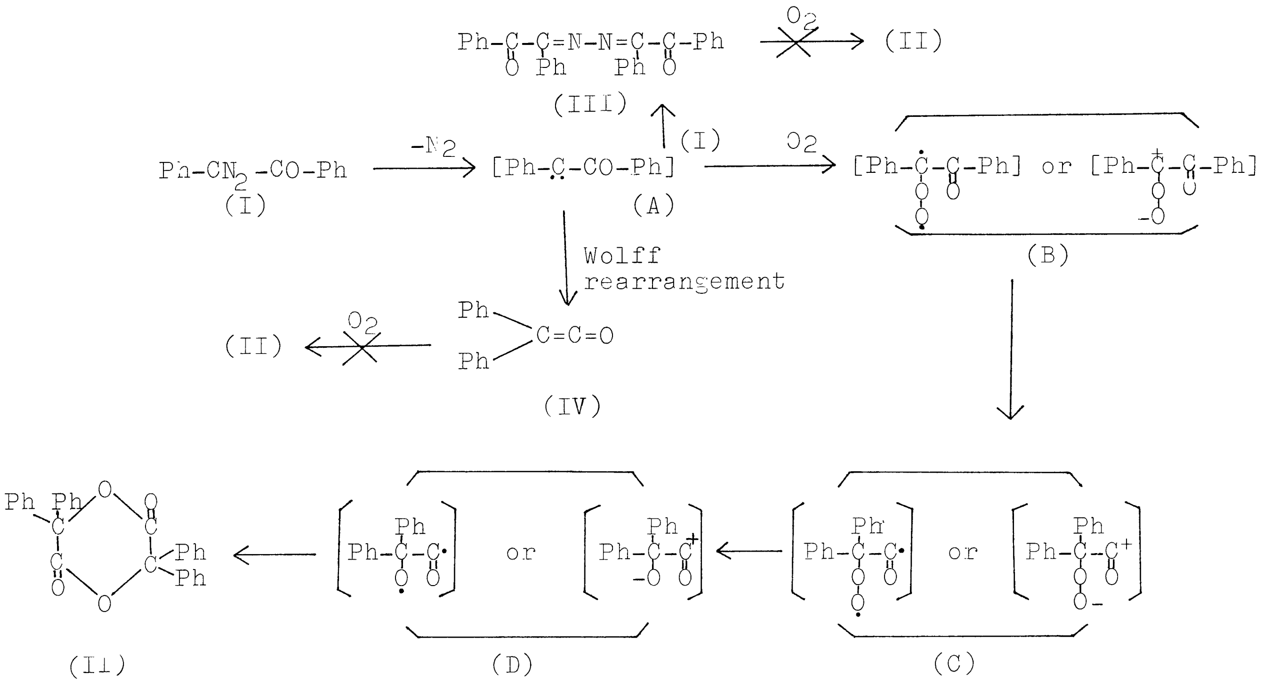
Scheme 4.



* The yields were calculated in mole % based on twice mole of II for V, VI and VII.

The thermal reaction of bis-benzilketazine (III) or diphenylketene (IV) with molecular oxygen under the same condition did not occur and the starting material (III or IV) was recovered.

Scheme 5.



Thus, phenyl benzoyl carbene (A) formed by the decomposition of I is considered to react with molecular oxygen in competition with the Wolff rearrangement, and carbonyl oxide[10] (B) seems to be the reaction intermediate, which is followed by phenyl migration, as shown in Scheme 5. The deoxygenation in the reaction path from (C) to (D) can not be discussed in detail[11].

A photochemical reaction of I with molecular oxygen in benzene was also carried out under irradiation by a high-pressure mercury lamp for 6 hours at 15~20°C, giving II in the yield of 41% in addition to V (17%) and III (trace).

## References

1. a) T. Nagai, M. Tanaka, and N. Tokura, Tetrahedron Lett., 6293 (1968).
   b) M. Tanaka, T. Nagai, and N. Tokura, In contribution for J. Org. Chem. (1972).
2. a) H. Staudinger, E. Anthes, and F. Pfenninger, Ber., 49, 1928 (1916).
   b) W. Kirmse, L. Horner, and H. Hoffman, Ann. Chem., 619, 19 (1958).
   c) P. D. Bartlett and T. G. Traylor, J. Amer. Chem. Soc., 84, 3408 (1962).
   d) W. B. De Moore, H. O. Pritchared, and N. Cavidoon, J. Amer. Chem. Soc., 81, 5874 (1959).
   e) R. W. Murray and A. M. Trozzole, J. Org. Chem., 26, 3109 (1961).
3. V. Franzen and H. I. Joschek, Ann. Chem., 633, 7 (1960).
4. A. M. Trozzolo, Accounts Chem. Res., 1, 329 (1968).
5. H. Staudinger, Ber., 44, 543 (1911).
6. R. Adams and C. Marvel, "Organic Syntheses," Coll. Vol I, p89 (1941).
7. C. Pall and E. Weidenkall, Ber., 39, 2063 (1906).
8. J. Ritter and M. Wiedemen, J. Amer. Chem. Soc., 51, 3583 (1929).
9. C. Marvel, D. Hager, and C. Caudle, "Organic Syntheses," Coll. Vol III, p45 (1955).
10. A "Carbonyl oxide" was suggested[2c] as the primary product in the photoxidation of diphenyldiazomethane.
11. In the formation of benzophenone from the related carbonyl oxide, the mechanism of the deoxygenation was not made clear[2c].

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