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Photochemistry of 1,2,3-Benzotriazin-4-one in Matrices. A New Photochromic System Including Triazinone-Azoazetinone Photointerconvertion

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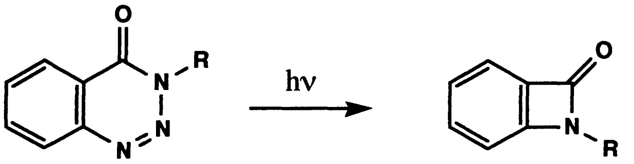
Irradiation (λ>300 nm) of 3-methoxy-1,2,3-benzotriazin-4-one (**3**) matrix isolated in Ar at 10 K resulted in the formation of E- and Z-1-(methoxyazo)benzazetinones which reproduced **3** upon irradiation of light of λ>350 nm, thus constituting a new photochromic system consisting of ternary components.

Compounds containing azo functionalities are often suitable candidates for fragmentation reactions. Departure of the thermodynamically stable, nonreactive nitrogen molecule can often be induced whereby generating a biradical species which destroys itself by ring closure.[1)] For example, photolysis of 1-pyrazoline results in the formation of cyclopropane as a result of nitrogen loss and coupling of a 1,3-biradical, which has been characterized by using matrix isolation techniques.[1d)] The reaction has been applied to 1,2,3-benzotriazine-4-ones (**1**, R=Ph, PhCO), which produce benzazetinones derivatives (**2**) upon photolysis.[2)] In order to obtain information concerning intermediates involved in the reaction, we studied photochemical reaction of the title triazinone under matrix conditions and found that this triazinone did afford benzazetinone, but without loss of molecular nitrogen.



1 **2**

Irradiation (λ>300 nm) of 3-methoxy-1,2,3-benzotriazin-4-one (**3**)[3)] matrix-isolated in Ar at 10K was monitored by infrared spectroscopy, which revealed a gradual decrease in starting material carbonyl stretching absorption bands (1723 cm^{-1}) and concurrent growth of new carbonyl absorption band appearing at 1823 and 1806 cm^{-1} (Fig. 1). By analogy with the absorption of the carbonyl stretch of analogous benzazetinone, [2,4,5)] one may assign the resulting photoproduct as 1-methoxybenzazetione (**2**, R=OMe) formed as a result of nitrogen loss followed by coupling of a 1,4-biradical. This possibility was, however, soon eliminated by the following observations.

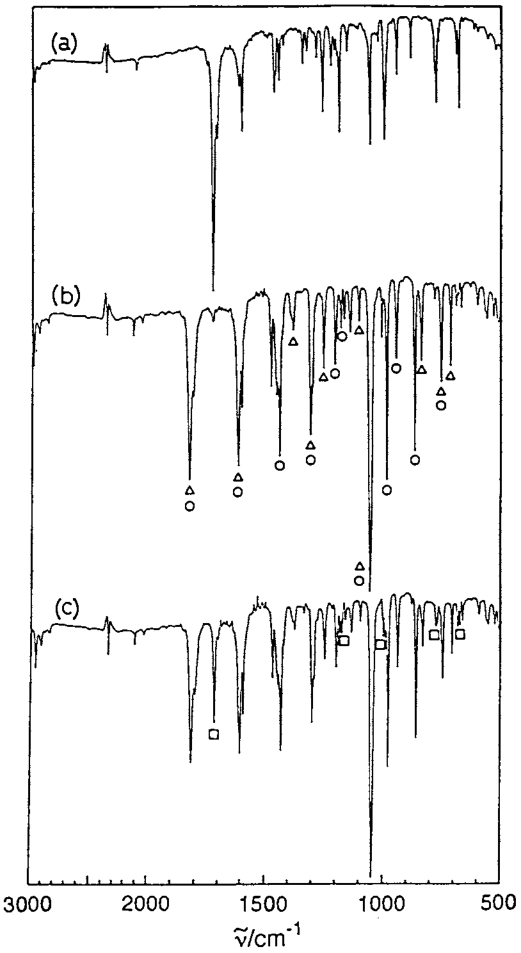


Fig. 1. (a) IR spectrum of 3-methoxy-1,2,3-benzotriazin-4-one (**3**) matrix-isolated in Ar at 10K. (b) Same sample after 2.5-h irradiation at >300 nm. Bands marked O are due to the initial photoproduct and bands marked Δ are due to the second one. (c) Same sample after 16-h additional irradiation at >350 nm. Bands marked □ are due to the starting triazinone **3**.

Firtst, the photoproduct (**4**) showed an intense blue color showing UV/visible absorptions at λmax 288 and 631nm (Fig.2). Such absorptions extending to visible region are obviously not expected for simple azetinone like **2** (R=OMe).[4,5] Second, a continued irradiation (λ>300 nm) of the initial photoproduct (**4**) produced a second photoproduct having very similar IR and UV/visible (λmax 273, 281, 578 nm) absorptions with **4**. Geometrical isomeric relationship between the two products was soon confirmed by the finding that both products were interconvertible under irradiation. Again, such isomerism is not attained in **2** (R=OMe) . Finally, irradiation of the product mixtures with light of λ>350 nm resulted in a reproduction of the starting triazinone (**3**), suggesting that nitrogens are not completely eliminated as nitrogen molecule since the photochemical reaction of **2** and molecular nitrogen reproducing **3** is highly unlikely.[6]

What are the structures of the photoproducts, then? The finding that the three nitrogens are not completely eliminated from the photoproducts coupled with the presence of chromophoric functional group in the photoproducts deducible from its intense blue color suggest the presence of azo groups in both products.[7)] Taking into account the presence of carbonyl absorption assignable to azetinone, 1-(methoxyazo)benzazetinones (**4**) are proposed as most reasonable structures which explain the available data best.

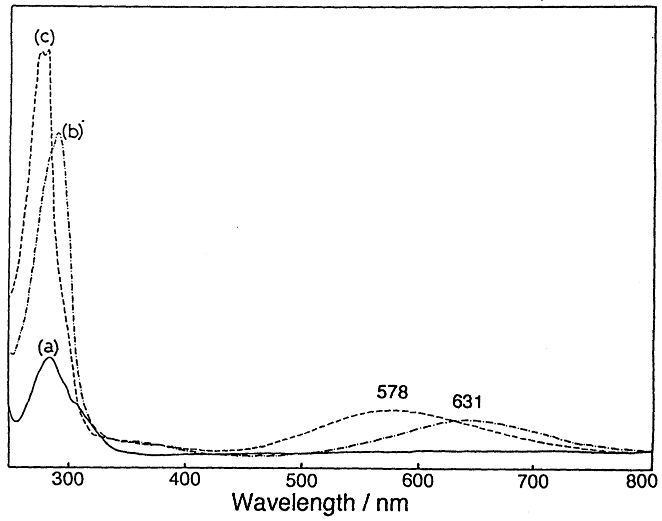
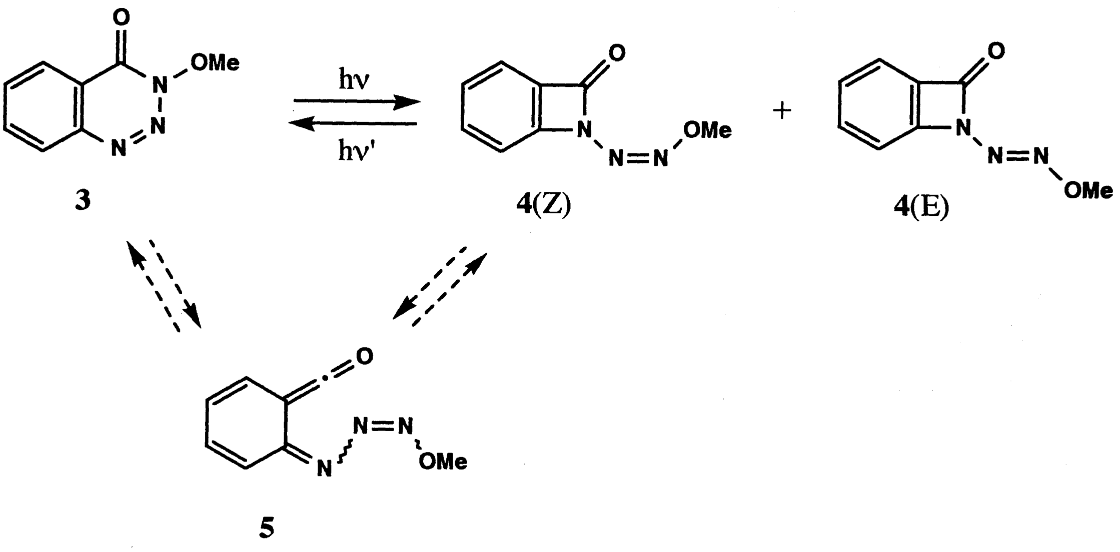


Fig. 2. (a) UV/VIS spectrum of **3** matrix-isolated in Ar at 10 K. (b) Same sample after 18.5-min irradiation at >300 nm. (c) Same sample after 3-h additional irradiation at >300 nm.



What is the mechanism for the present photointerconversion between3 and **4**, then? Conceivably it is possible that the triazinone undergoes photochemical electrocyclic ring-opening to form carbonyl (azoimino)cyclohexadienylidenes (**5**) which subsequently cyclize to the azetinones. Exactly the reverse pathway may be applied to explain the reproduction of the starting triazinone. Actually we observed a ketene absorption band at 2118 cm^{-1} during the irradiation. However, the ketene bands were very weak, and, more importantly, remained unchanged during the interconversion between **3** and **4**. An alternative, and more plausible pathway is, then, 1,3-sigmatropic shift initiated by photocleavage of CO-N bond. Thus, photoexcitation of **1** resulted in CO-N bond fission to result in 1,3-supra-supra sigmatropic energy surface leading to the azoazetinone, which can be reverted to the starting material upon excitaion to the same energy surface.

The present findings reveal that, contorary to the well-accepted observations with other benzotriazinone at ambient temperature, the triazinone (**3**) undergoes photoreversible sigmatropic conversion without elimination of thermodynamically stable molecular nitrogen under matrix conditions, thus providing a new photochromic system. The similar reactions were observed with 3-n-butoxy-1,2,3-benzotriazin-4-one (**1**, R=OBu^n), but not with 3-methyl derivative (**1**, R=Me), which was essentially unchanged even under prolonged irradiation, thus suggesting that the alkoxy group at 3-position should exert a special effect on the reaction course. Further investigations including theoretical calculations are in progress.8)

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References

1) See for example; a) R.M. Kellogg, "Photochemistry of Heterocyclic Compounds," ed by O. Buchardt, Wiley, New York(1976), pp. 368-413; b) R.S. Gevens, "Organic Photochemistry," ed by A. Padwa, Marcel Dekker, New York and Basel(1981), Vol.5, pp. 227-273; c) P. Beak and W.R. Messer, "Organic Photochemistry," ed by A. Padwa, Marcel Dekker, New York and Basel(1967), Vol.2, pp. 117-167; d) P.B. Dervan, D.A. Dougherty, and J.A. Berson, "Biradicals," ed by W.T. Borden, Wiley, New York(1982), pp. 107-194.

2) E.M. Burgess and G. Milne, *Tetrahedron Lett.*, **1966**, 93; G. Ege, *Chem. Ber.*, **101**, 3079 (1968); G. Ege and F. Pasedach, *ibid.*, **101**, 3089 (1968); D. H. Hey, C.W. Rees, and A.R. Todd, *J. Chem. Soc., C*, **1968**,1028; N. Bashir and T.L. Gilchrist, *J. Chem. Soc., Perkin Trans.1,* **1973**, 868.

3) T.P. Ahern, T. Navratil, and K. Vaughan, *Can. J. Chem.*, **55**, 630 (1977).

4) a) R.A. Olofson, R.K. Vander Meer, and S. Stournas, *J. Am. Chem. Soc.*, **93**, 1543 (1971); b) R.A. Olofson, R.K. Vander Meer, D.H. Hoskin, M.Y. Bernheim, S. Strournas, and D.S. Morrison, *J. Org. Chem.*, **49**, 3367 (1984).

5) The following spectroscopic data have been reported4b) for a stable benzeazetinone, N-tert-butylbenzoazetinone; UV (cyclohexane) λmax(ε) 370nnm (420), 273 (2100), 222 (29400); IR (CCl_4) 3096w, 2976m, 2941-2857bw, 1812s, 1600s, 1464w, 1431m, 1391m, 1370m, 1285m, 1239m, 1225m cm^{-1}.

6) That molecular nitrogen reacts with carbenes upon excitation forming the corresponding diazo compound has been reported; C.B. Moore and G.C.Pimentel, *J. Chem. Soc.*, **41**, 3504 (1964); G. Maier and H.P. Reisenauer, *Angew. Chem., Int. Ed. Engl.*, **25**, 819 (1986).

7) By analogy with the C=N and C=C groups, the characteristic of infra-red absorption bands arising from the -N=N- linkage might be expected to appear in the 1600 cm^{-1} region, but the weak intensity of the N=N band along with aromatic absorptions appear to preclude useful correlation for this group. See for example, L.J. Bellamy, "The Infra-red Spectra of Complex Molecules," Wiley, New York(1958), p. 271.

8) Preliminary irradiation of **3** in benzene at room temperature resulted in a developement of a faint blue color in the reaction mixtures, whose characterizations are under way.

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