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Photochemical Reaction of 3,4-Diphenylsydnone[1]

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In a recent communication,[2] we proposed 1*H*-1,3-diphenyldiazirine for the photolysis product of 3,4-diphenylsydnone. However, it was found later that the product was identical with the already known 2,4,5-triphenyl-1,2,3-triazole. In this paper, details of the photolysis of 3,4-diphenylsydnone and identification of the product are described. The formation of triazole derivative by the photolysis of 3,4-diphenylsydnone seems to be interesting. The reaction mechanisms are discussed.

Recently, much interest has been focussed upon the photolysis of mesoionic compounds due to their peculiar structures and 1,3-dipolar character. Krauch *et al.*[3] reported that the photolysis of 3-phenylsydone gave 4-phenyl-1,3,4-oxadiazoline-5-one, presumably *via* fused three-membered intermediate, 1*H*-diazirine derivative or nitrile imine. Kato[4] is working on photolysis of various mesoionic compounds with a view to investigating their photolysis in terms of a fused three-membered intermediate. In anticipation of the isolation of the intermediate having three-membered ring structure, we have been studying the photolysis of 3,4-disubstituted sydnone.

We reported that photolysis of 3,4-diphenylsydnone (**1**) gave a product of mp 119—120°C, which was considered, though not conclusively, to be 1,3-diphenyl-2-azirine (**3**), on the basis of elementary analysis and mass spectroscopic analysis. However, on further examination, it was found that several behaviors of the compound could not be explained satisfactorily by the proposed structure.

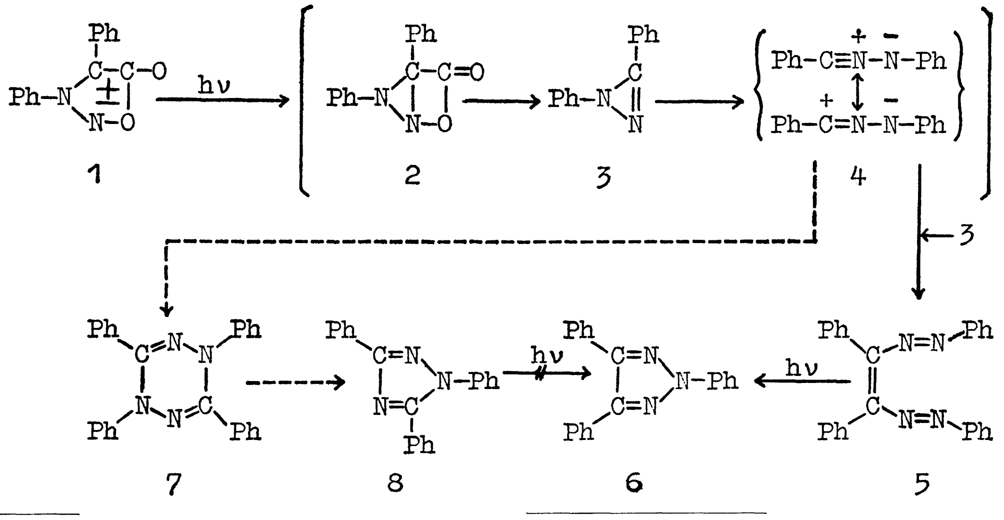
Molecular weight determination of photolysis product (A) by the Rast method or by vapor pressure osmometer gave the value 310 and as an alternative formula, $C_{20}H_{15}N_3$ is possible which is consistent with this molecular weight and elementary analysis. For this empirical formula, three isomers of triphenyltriazoles are possible. It was found that 2,4,5-triphenyl-1,2,3-triazole (**6**) synthesized by Auwers *et al.*[5] has the same melting point and chemical properties as (A). Comparison with authentic sample revealed that (A) was identical with (**6**).

The mass spectroscopic results which caused us to deduce an incorrect structure can be explained by considering that the major peak at *m/e* 194 was due to a fragment $C_6H_5CNNC_6H_5$ derived from **6**. Both **3** and **6** have no proton except that of phenyl. Thus, NMR data are not sufficiently informative for determination of the structure, and some ambiguity was encountered in analyzing the NMR absorption spectrum due to phenyl proton. However, the results can be explained by means of both **3** and **6**.

Further evidence for excluding the diazirine structure (**3**) for A is provided by the fact that product A shows no infrared absorption at about 1740 cm^{-1} due to strained C=N linkage, and that attempts to reduce A by lithium aluminum hydride or catalytic hydrogenation with palladium-charcoal were unsuccessful.

The photolyses of 3-*p*-chlorophenyl-4-phenylsydnone and 4-phenyl-3-*p*-tolylsydnone were carried out under the same conditions to give corresponding 1,2,3-triazole derivatives.

The unexpected formation of **6** is unusual and some considerations are given on the mechanism of this



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[1] Studies of mesoionic compounds, XXXV. Part XXXIV: A. Chinone, S. Sato, and M. Ohta, This Bulletin, **44**, 826 (1971).

[2] A. Chinone, Y. Huseya, and M. Ohta, *ibid.*, **43**, 2650 (1970).

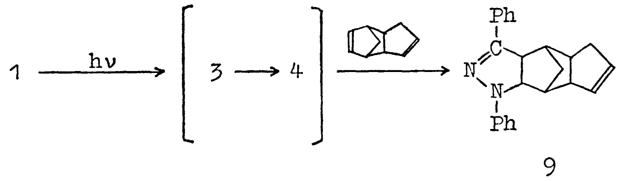
[3] C. H. Krauch, J. Kuhls, and H. J. Piek, *Tetrahedron Lett.*, **1966**, 4043.

[4] Hiroshi Kato, Private communication.

[5] a) K. Auwers and V. Meyer, *Ber.*, **22**, 540 (1889). b) K. Auwers and M. Siegfeld, *ibid.*, **26**, 792 (1893).

reaction. Similar to the photolysis of 3-phenylsydnone, the intermediacy of 1*H*-1,3-diphenyldiazirine (**3**) or diphenylnitrile imine (**4**) is probable in the photolysis of **1**. It was reported that diphenylnitrile imine produced from 2,5-diphenyltetrazole by thermolysis gave 1,3,4,6-tetraphenyl-1,2,4,5-tetrazine (**7**) by head-to-tail dimerization.[6] On the contrary, Scheiner and Dinda[7] stated that the formation of **6** from 2,5-diphenyltetrazole by photolysis proceeds *via* 1,2-bisphenylazo-1,2-diphenylethylene (**5**), and suggested that **5** is formed by photodimerization involving tetrazole-tetrazole association and not by head-to-head dimerization of 1,3-dipolar nitrile imine (**4**). The head-to-tail thermal dimerization of **4** should afford 1,2,4,5-tetrazine (**7**). As it is known that irradiation of some heterocyclic five membered rings yields rearranged products,[8] the formation of **6** from **7** *via* 1,3,5-triphenyl-1,2,4-triazole (**8**) seems to be probable. However, photolysis of authentic sample of **8**[9] resulted in the recovery of starting material. Thus, if the formation of **6** by photolysis of **1** proceeds *via* **5**, it would be unreasonable to consider that **6** is derived exclusively from nitrile imine.

Krauch *et al.*[3] reported that 1,3-dipolar cycloaddition of 3-phenylsydnone did not take place by photolysis. Our attempt on this reaction using dicyclopentadiene as a dienophile was also unsuccessful. While thermal 1,3-dipolar cycloaddition to 3-phenylsydnone is well known,[10] the same reaction by photolysis has not been realized. For the purpose of intercepting the intermediate nitrile imine, we have attempted the photolysis of 3,4-diphenylsydnone in the presence of dicyclopentadiene as a dipolarophile. The irradiation of a suspension of 3,4-diphenylsydnone in dicyclopentadiene gave a product to which tetracyclic structure (**9**) may be assigned, on the basis of elementary analysis, the same melting point as reported by Huisgen *et al.*[11] and spectroscopic data, indicating that the cycloaddition of dicyclopentadiene to **4** (or 1,3-position of **3**) occurred and addition of dicyclopentadiene to 2,3-position of **3** did not occur. These results show that the photolysis of 3,4-diphenylsydnone is not similar to thermal 1,3-dipolar cycloaddition observed in sydnone, which occurs at 2,4-position of sydnone. The thermal 1,3-dipolar cycloaddition of **1** was tried in dicyclopentadiene at 165°C to give intractable oil.



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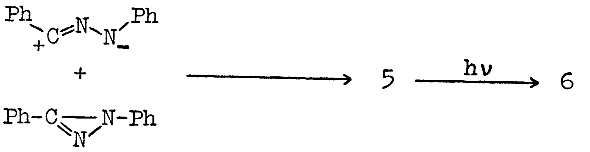
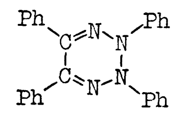
Thus, it is most likely that the reaction may proceed through the sequence indicated below.[12,13]





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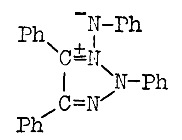

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Experimental

All melting points were determined on a hot stage, and were not corrected.

Photolysis of 3,4-diphenylsydnone. A solution of 3.0 g of 3,4-diphenylsydnone[15,16] in 300 m*l* of dioxane was placed in a Pyrex vessel, purged with nitrogen for 0.5 hr, and irradiated with a high-pressure mercury lamp (100W) under nitrogen. The reaction ended after 30 hr. The solvent was evaporated under reduced pressure, and the residue was chromatographed over alumina. Elution with benzene gave 0.45 g (24%) of **6**, mp 119—120°C, IR ν(KBr) 3050, 1595, 1493, 970, 775, 700 cm^{-1}. The identity of **6** was established by comparison (IR and mixed mp) with an authentic sample. The same procedures were employed with two other sydnones.

Irradiation of 4-phenyl-3-*p*-tolysylsydnone[16] gave 4,5-diphenyl-2-*p*-tolyl-1,2,3-triazole (23%), mp 114—116°C, IR ν(KBr) 3050, 1510, 975, 825, 770 cm^{-1}.

Found: N, 13.32%. Calcd for $C_{21}H_{17}N_3$: N, 13.50%.

Irradiation of 3-*p*-chlorophenyl-4-phenylsydnone[16] gave 2-*p*-chlorphenyl-4,5-diphenyl-1,2,3-triazole (21%), mp 99—101°C, IR ν(KBr) 3050, 1490, 975, 825, 770, 700 cm^{-1}.

Found: N, 12.64%. Calcd for $C_{21}H_{17}N_3Cl$: N, 12.86%.

Photolysis of 3,4-diphenylsydnone with dicyclopentadiene. A suspension of 2.0 g of **1** in 300 m*l* of commercial dicyclopentadiene was irradiated with a high-pressure mercury lamp for 20 hr. Removal of the solvent under reduced pressure and recrystallization of the residue from ethanol gave 0.55 g of 1,3-diphenyl-4,8-methane-3a, 4,4a, 7a, 8, 8a-hexahydroindeno[5,6-*c*]pyrazole, mp 178—179°C (lit,[11] mp 173—174°C).

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[6] R. Huisgen, J. Sauer, and M. Seidel, *Chem. Ber.*, **94**, 2503 (1961).

[7] P. Scheiner and J. F. Dinda, *Tetrahedron*, **26**, 2619 (1970).

[8] a) P. Beak and W. Messer, *ibid.*, **25**, 3287 (1969). b) H. Wynberg, R. M. Kellogg, H. Driel, and G. E. Beekhuis, *J. Amer. Chem. Soc.*, **89**, 3501 (1964).

[9] Engelhardt, *J. Prakt. Chem.*, [2] **54**, 153 (1897).

[10] a) R. Huisgen, R. Grashey, H. Gotthardt, and R. Schmidt, *Angew. Chem.*, **74**, 29 (1962). b) R. Huisgen, H. Gotthardt, and G. Grashey, *ibid.*, **74**, 30 (1962).

[11] R. Huisgen, M. Siedel, G. Wallbillich, and H. Knupfer, *Tetrahedron*, **17**, 3 (1962).

[12] Compound **5** has been prepared by the oxidation of β-benzyl phenylosazone, to which 1,2,3,4-dihydrotetrazine structure (**10**) was assigned by Spasov *et al.*[14] and the open chain structure (**5**) by Scheiner and Dinda[7].

[13] Scheiner and Dinda[7] suggested the intermediacy of azomethine imine (**11**) in the conversion of **5** to **6**.

[14] A. V. Spasov, D. Elenkov, and St. Rovev, *Bulgarska Akad. Nauk., Otdel. Geol.-Geograf Khim. Nauk., Izvest. Khim. Inst.*, **1**, 229 (1951); *Chem. Abstr.*, **47**, 2153 g (1953).

[15] E. Knoevenagel, *Ber.*, **37**, 4073 (1904).

[16] W. Baker, W. D. Ollis, and V. D. Poole, *J. Chem. Soc.*, **1949**, 307.