Photochemical Reactions of 3-Alkyl-4-phenylsydnones[1]

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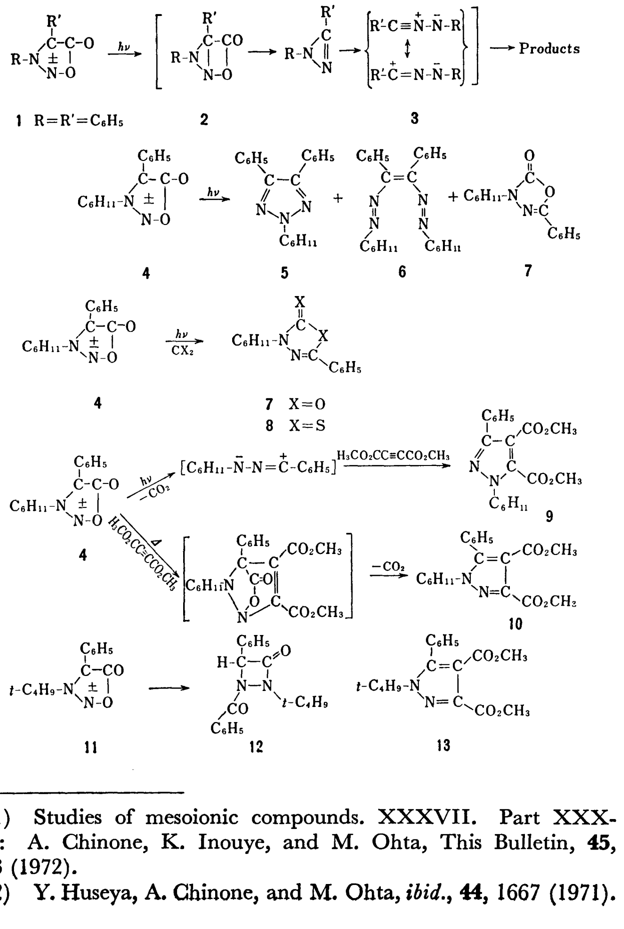
Photochemical reaction of 3-cyclohexyl-4-phenylsydnone (**4**) in nitrogen atmosphere afforded 2-cyclohexyl-4,5-diphenyl-1,2,3-triazole (**5**), 1,2-biscyclohexylazo-1,2-diphenylethylene (**6**) and 4-cyclohexyl-2-phenyl-Δ^2-1,3,4-oxadiazoline-5-one (**7**). The results showed that the reaction of **4** in the presence of carbon dioxide, carbon disulfide and dimethyl acetylenedicarboxylate proceeded *via* nitrile imine intermediate. Irradiation of 3-*t*-butyl-4-phenylsydnone (**11**) afforded 1-benzoyl-2-*t*-butyl-4-phenyl-1,2-diazetidine-3-one (**12**). Variation of the absorbance of **4** at the longest wavelength with irradiation was affected by 1,3-pentadiene, but not that of **11**. This shows that the excited triplet state is responsible for the photochemical reaction of **4**.

We reported[2] that photolysis of 3,4-diarylsydnones afforded 2,4,5-triaryltriazoles *via* bicyclic intermediate (**2**) and nitrile imine (**3**). In this report, we give details on the photolysis of 3,4-diphenylsydnone (**1**) and 3-alkyl-4-phenylsydnones.

From the consideration that the stability of the nitrile imine (**3**) controls the reaction, we investigated the photolysis of 3-alkyl-4-phenylsydnone. 3-Cyclohexyl-4-phenylsydnone (**4**) was prepared by treating α-(*N*-cyclohexyl-*N*-nitrosamino)phenylacetic acid with acetic anhydride. Irradiation of **4** in a dilute benzene solution was carried out with high pressure mercury lamp through a Pyrex filter under nitrogen atmosphere. The reaction was followed by withdrawal of a small aliquot at various time intervals and examination by means of UV spectroscopy. The products were separated by column chromatography and identified as 2-cyclohexyl-4,5-diphenyl-1,2,3-triazole (**5**), 1,2-biscyclohexylazo-1,2-diphenylethylene (**6**) and 4-cyclohexyl-2-phenyl-Δ^2-1,3,4-oxadiazoline-5-one (**7**). The structure of **5** was confirmed on its elementary analysis and spectral data, which were closely similar to those of 2,4,5-triphenyl-1,2,3-triazole. The structure of **6** was deduced from elementary analysis, spectral data and its characteristic red color, but the configuration was not defined unambiguously. The structure of **7** was deduced from its elementary analysis and spectral data. The IR spectrum of **7** exhibited a peak at 1780 cm^{-1} which was attributed to the CO group of 1,3,4-oxadiazoline-5-one. It is noteworthy that the yields of **5** and **6** showed correlation with the period of irradiation. The yield of **5** increased with the increase of the period of irradiation, and that of **6** decreased with the increase of the yield of **5**. The results are in line with the reaction mechanism postulated,[2-5] in which triazole was originated from bisazoethylene formed by "head to head" interaction of nitrile imine. Additional support for this mechanism was obtained by following examination. In contrast to the photochemical reaction of **1** which did not afford the corresponding oxadiazoline, **7** was obtained predominantly by irradiation of a benzene solution of **4** under carbon dioxide atmosphere. Similarly, when a benzene solution of **4** was irradiated in the presence of carbon disulfide, 4-cyclohexyl-2-phenyl-Δ^2-1,3,4-thiadiazoline-5-thione (**8**) was obtained. Formation of **7** and **8** is explained by the reaction of *N*-cyclohexyl-*C*-phenylnitrile imine with carbon dioxide and carbon disulfide, respectively. It is evident that *N*-cyclohexyl-*C*-phenylnitrile imine is more reactive than *N*,*C*-diphenylnitrile imine toward dipolarophiles such as carbon dioxide and carbon disulfide. It seems that *N*-phenylnitrile imine, which is an intermediate of the photolysis of 3-phenylsydnone,[6] reacted preferentially with carbon dioxide, giving no corresponding triazole. 1,3-Dipolar cycloaddition of **4** under irradiation was carried out in the presence of dimethyl acetylenedicarboxylate to give dimethyl 1-cyclohexyl-3-phenylpyrazole-4,5-dicarboxylate (**9**), whose structure was deduced from its composition ($C_{19}H_{22}O_4N_2$) and IR spectrum. Treatment of **4**



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with dimethyl acetylenedicarboxylate at 120—140°C afforded a product **A** whose elementary analysis gave the same formula $C_{19}H_{22}O_4N_2$ as that of **9**. A mixed melting point measurement of **A** with **9** showed a depression, and the structure of **A** was assigned to dimethyl 1-cyclohexyl-5-phenylpyrazole-3,4-dicarboxylate (**10**).

The different course of the over-all photoreaction was observed in 3-*t*-butyl-4-phenylsydnone (**11**), prepared by treating α-(*N*-*t*-butyl-*N*-nitrosamino)phenylacetic acid with acetic anhydride. Exposure of a dilute solution of **11** in benzene to a high pressure mercury lamp gave 1-benzoyl-2-*t*-butyl-4-phenyl-1,2-diazetidine-3-one (**12**). Satisfactory analytical data were obtained for **12** whose mass spectral fragmentation pattern was consistent with that of the assigned structure. Compound **12** was obtained even in toluene under the same conditions. It is known that diazetidinones are prepared photochemically by the reaction of azo compounds with ketones.[7] Formation of **12** by the irradiation of **11** may be explained by the intermolecular addition of an excited >N–N– grouping to C=C=O grouping of sydnone, followed by an introduction of benzoyl group through ambiguous mechanism. Dipolar addition of **11** to carbon dioxide, carbon disulfide and dimethyl acetylenedicarboxylate was not successful under irradiation. However, **11** reacted with dimethyl acetylenedicarboxylate in refluxing toluene to give addition product **13**.

The absorption spectra of **1**,**4** and **11** in cyclohexane showed bands at 345 mμ (ε 9750), 325 mμ (ε 10890) and 312 mμ (ε 7090), respectively. A hypsochromic shift in a more polar solvent was observed as shown in Table 1. The absorptions might be assigned to n-π^* transition, though relatively high extinction coefficient are observed. Under irradiation, the variation of absorbances of **1**, **4** and **11** at the longest wavelength corresponded to their concentrations, since their photoreaction products showed no absorptions in these regions. The variations of absorbances at the longest wavelength of **4** and **11** in the absence or presence of 1,3-pentadiene, which is known as a quencher of triplet state, are plotted against irradiation time (Fig. 1 and 2). This shows that a sydnone (**4**) excited state transferred its energy to 1,3-pentadiene. Irradiation of a benzene solution of **4** in the presence of 1,3-pentadiene gave **5** in a low yield (6%). Colorless crystals whose structure was not determined were obtained with a mp of 201—202°C. On the other hand, variation of the absorbance of **11** was not appreciably affected by 1,3-pentadiene. The yield of **12** did not decrease even in the presence of 1,3-pentadiene.

Table 1. UV spectra

Compound	**1**	**4**	**11**
λ_{max}(cyclohexene) mμ(ε)	345(9750)	325(10890)	312(7090)
λ_{max}(methanol) mμ(ε)	330(9140)	310(9490)	297(7800)

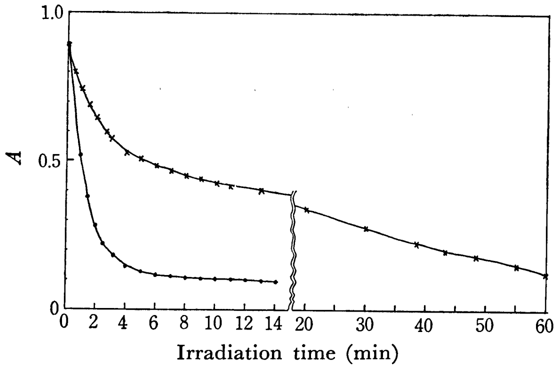

Fig. 1. Variation of absorbance of **4** at the longest wavelength, $\lambda_{max}^{benzene}$ 322 mμ.
—●— in the absence of 1,3-pentadiene
—✕— in the presence of 1,3-pentadiene

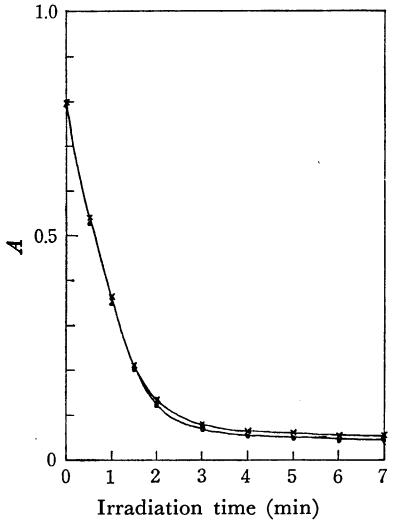

Fig. 2. Variation of absorbance of **11** at the longest wavelength, $\lambda_{max}^{benzene}$ 310 mμ.
—●— in the absence of 1,3-pentadiene
—✕— in the presence of 1,3-pentadiene

From the results a mechanism is postulated which rationalizes the experimental observations. It seems that the photochemical reaction of **4** is derived from the lowest triplet state, which has an n-π^* configuration. The reaction proceeds from the triplet state *via* bicyclic intermediate, from which diazirine is formed by the extrusion of carbon dioxide as in the case of the photochemical reactions of 3,4-diarylsydnones. It is suggested that either the excited triplet state of **11** is not responsible for the conversion into **12**, or the triplet state has too low energy to be affected by 1,3-pentadiene. It seems that the photochemical reaction of **11** proceeds through an intermediate other than nitrile imine.

Experimental

3-Cyclohexyl-4-phenylsydnone (4). Mandelonitrile prepared from 30 m*l* of benzaldehyde was added dropwise to a mixture of cyclohexylamine (25 g), sodium acetate (0.5 g) and ethanol (25 m*l*) and the reaction mixture was heated at 60—70°C for a few minutes. After being stirred at room temperature for 2 hr, α-cyclohexylaminophenylacetonitrile precipitated, mp 57.5—58.5°C, 28.6 g (52%).

α-Cyclohexylaminophenylacetonitrile (5 g) was stirred in

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[7] J. H. Hall and R. Kellogg, *J. Org. Chem.*, **31**, 1079 (1966).

15 m*l* of concentrated sulfuric acid for 2 days at room temperature. The reaction mixture was added to 75 m*l* of water, and concentrated aqueous ammonia was added until the pH became about 9, and α-cyclohexylaminophenylacetamide precipitated was collected, mp 115—117°C, 5.3 g (98%).

After refluxing a 10% hydrochloric acid solution (43 m*l*) of α-cyclohexylaminophenylacetamide (5.3 g) for 6 hr, the reaction mixture was cooled to room temperature, and concentrated aqueous ammonia was added until the pH became about 4. α-Cyclohexylaminophenylacetic acid precipitated as white crystals, mp (decomp.) 280°C, 4.5 g (85%).

An aqueous solution of sodium nitrite (1.5 g/10 m*l*) was added dropwise below 0°C to a solution of α-cyclohexylaminophenylacetic acid (4.7 g) in 10% hydrochloric acid (86 m*l*). The reaction mixture was kept below 0°C for 1 hr and allowed to stand overnight at room temperature. α-(*N*-Cyclohexyl-*N*-nitrosamino)phenylacetic acid precipitated as yellow crystals, mp 133—136°C, 3.5 g (66%). After being dried the acid was dissolved in 30 m*l* of acetic anhydride and kept at 60—70°C for 20 min. After cooling, the reaction mixture was poured into 100 m*l* of water and stirred vigorously. Precipitates were collected and recrystallized from ethanol to give colorless prisms with a mp of 161—162°C, 3 g (91%).

Found: C, 68.98; H, 6.58; N, 11.76%. Calcd for $C_{14}H_{16}O_2N_2$: C, 68.83; H, 6.60; N, 11.47%. IR: $\nu_{C=O}$ 1730 cm^{-1}.

Irradiation of ***4***. *i) Under Nitrogen Atmosphere*: A solution of 1.0 g of **4** in 300 m*l* of benzene was irradiated with a 100 W high pressure mercury lamp using a Pyrex filter under nitrogen atmosphere. The reaction was followed by withdrawal of small aliquots at various time intervals and measurement of their UV spectra. After irradiation for 3 hr, the solvent was removed *in vacuo* and the resulting residue was placed on a silica gel column. A petroleum ether solution was used to elute the column. The first elute contained an oil whose structure was not determined. The next petroleum ether-benzene (2 : 1) solution contained a white solid, which was recrystallized from ethanol to give colorless needles, mp 131—132°C, 0.08 g (12%). This was identified as **5**.

Found: C, 79.46; H, 7.12; N, 14.15%. Calcd for $C_{20}H_{21}N_3$: C, 79.17; H, 6.89; N, 13.85%. IR: 3050; 2920, 1460, 1440, 1350, 1260, 1080, 990, 770, 700 cm^{-1}. UV: λ_{max}^{MeOH} 255 mμ (ε 9170).

The next petroleum ether-benzene (1 : 1) solution afforded a crude solid, which was recrystallized from methanol to give red needles, mp 100—101°C, 0.13 g (15%), and identified as **6**.

Found: C, 77.63; H, 7.77; N, 14.21%. Calcd for $C_{26}H_{32}N_4$: C, 77.96; H, 8.05; N, 13.99%. IR: 3030, 2910, 1490, 1440, 760, 710, 700 cm^{-1}. UV: λ_{max}^{MeOH} mμ(ε) 310 (6440), 253 (10900). NMR: τ_{Me_4Si} ($CDCl_3$) 2.6—2.9 (10H), 6.2—6.7 (2H), 8.1—9.1 (20H).

The next benzene solution contained a crude solid, which was recrystallized from methanol to give colorless prisms, mp 78—80°C, 0.15 g (15%), and identified as **7**.

Found: C, 68.78; H, 6.47; N, 11.64%. Calcd for $C_{14}H_{16}O_2N_2$: C, 68.83; H, 6.60; N, 11.47%. IR: 3060, 2920, 1780, 1450, 1350, 1020, 740, 700 cm^{-1}. UV: λ_{max}^{MeOH} 268 mμ (ε 7350).

ii) Under Carbon Dioxide Atmosphere: A solution of **4** (1.0 g) in benzene (300 m*l*) was irradiated under carbon dioxide atmosphere for 3 hr, and treated as mentioned above to give **7**, 0.47 g (47%).

iii) In the Presence of Carbon Disulfide: Compound **4** (1.0 g) was dissolved and irradiated in a mixture of 200 m*l* of benzene and 100 m*l* of carbon disulfide. After removal of the solvent in a vacuum, the residue was placed on a silica gel column and eluted with a petroleum ether-benzene (1 : 1) solution. The elute contained a crude solid, which was recrystallized from ethanol to give colorless silky crystals, mp 136—137°C, 0.19 g (20%), and identified as **8**.

Found: C, 60.61; H, 5.65; N, 10.03; S, 22.93%. Calcd for $C_{14}H_{16}N_2S_2$: C, 60.86; H, 5.84; N, 10.14; S, 23.16%. IR: 3050, 2910, 1490, 1450, 1350, 1280, 1210, 1060, 760, 690 cm^{-1}.

The starting material (0.15 g) was eluted with benzene-ethyl acetate (3 : 1).

iv) In the Presence of Dimethyl Acetylenedicarboxylate: A solution of **4** (1.0 g) and dimethyl acetylenedicarboxylate (1.2 g) in benzene (300 m*l*) was irradiated for 2.3 hr. The reaction mixture was treated as mentioned above and the resulting residue was eluted first with petroleum ether to give 0.7 g starting material and next with benzene to give a crude solid, which was recrystallized from methanol to give colorless needles, mp 92—93°C, 0.6 g (43%), and identified as **9**.

Found: C, 66.40; H, 6.32; N, 8.15%. Calcd for $C_{19}H_{22}O_4N_2$: C, 66.65; H, 6.48; N, 8.18%. IR: 3050, 2920, 1730, 1530, 1450, 1250, 1160, 790, 700 cm^{-1}.

Reaction of ***4*** *with Dimethyl Acetylenedicarboxylate.* A mixture of **4** (1.0 g) and dimethyl acetylenedicarbaxylate (2.0 g) was heated at 120—140°C for 4 hr, during which time evolution of carbon dioxide was observed. Excess dimethyl acetylenedicarboxylate was removed, and a small amount of methanol was added to the residue and the reaction mixture was kept in a refrigerator. Precipitates were collected and recrystallized from methanol to give colorless prisms, mp 98—99°C, 0.3 g (21%), identified as **10**.

Found: C, 66.60; H, 6.67; N, 8.32%. Calcd for $C_{19}H_{22}O_4N_2$: C, 66.65; H, 6.48; N, 8.18%. IR: 2940, 1730, 1550, 1500, 1440, 1220, 1170, 1080, 760, 700 cm^{-1}.

*3-*t*-Butyl-4-phenylsydnone (**11**).* Mandelonitrile prepared from 75 m*l* of benzaldehyde was added to a mixture of *t*-butylamine (52 g), sodium acetate (1.3 g) and ethanol (60 m*l*) under ice cooling. The reaction mixture was kept at 50—60°C for 5 min, and allowed to stand overnight with stirring at room temperature. Unreacted *t*-butylamine and ethanol were removed *in vacuo*. To the residue was added 500 m*l* of 5% hydrochloric acid and the mixture was vigorously stirred, and the precipitates were filtered off. Filtrate was neutralized with aqueous potassium hydroxide and oily layer was extracted with ether. After drying the ether layer over sodium sulfate, ether was evaporated off and crude α-*t*-butylaminophenylacetonitrile (100 g) was obtained, which was added dropwise to 300 m*l* of concentrated sulfuric acid under ice cooling. After the solution was stirred for 2 days at room temperature, the reaction mixture was diluted with sixford amount of water and treated with activated charcoal and neutralized with concentrated aqueous ammonia until the pH became 8. Precipetates were collected and refluxed in 800 m*l* of 10% hydrochloric acid for 14 hr. The solution was treated with activated charcoal and hydrochloric acid solution of α-*t*-butylaminophenylacetic acid was subjected to subsequent reaction.

An aqueous solution of sodium nitrite (18 g/100 m*l*) was added dropwise below 0°C with vigorous stirring to a hydrochloric acid solution of α-*t*-butylaminophenylacetic acid. The reaction mixture was kept below 0°C for one hour, and stirred at room temperature for 24 hr. α-(*N*-*t*-Butyl-*N*-nitrosamino)phenylacetic acid precipitated as pale yellow crystals, mp 179—180°C.

To this was added 250 m*l* of acetic anhydride and the mixture was stirred at room temperature for 3 days in the dark. The resulting yellow solution was concentrated in a vacuum to one-third of the total volume, and poured into 1 *l* of water with vigorous stirring to give colorless crystals. Recrystallization from ethanol afforded colorless prisms, mp 124—125.5°C, 23 g (19%).

Found: C, 65.82; H, 6.49; N, 13.10%. Calcd for $C_{12}H_{14}O_2N_2$: C, 66.03; H, 6.47; N, 12.84%. IR: $\nu_{C=O}$ 1750 cm^{-1}.

Irradiation of ***11.*** *i) Under Nitrogen Atmosphere*: After irradiation of a solution of **11** (1.0 g) in 300 m*l* of benzene for 1.5 hr, the solvent was removed *in vacuo* and the resulting residue was analyzed by column chromatography. A benzene-ethyl acetate (4 : 1) elute contained a solid, which was recrystallized from ethanol to give colorless needles, mp 114—115°C, 0.42 g (59%) and identified as **12**.

Found: C, 73.57; H, 6.52; N, 9.05%. Calcd for $C_{19}H_{20}O_2N_2$: C, 74.00; H, 6.54; N, 9.09%. IR: 2960, 1780, 1680, 1280, 750, 730, 700 cm^{-1}. NMR τ_{Me_4Si} ($CDCl_3$) 2.3—2.9 (m, 10H), 4.6 (s, 1H), 8.4 (s, 9H). Mass spectra M$^+$ *m/e* 308, C_6H_5CO *m/e* 105 (base peak), C_6H_5-$CHNCOC_6H_5$ *m/e* 209 (70% of the base peak), C_6H_5CHCO *m/e* 118 (90%), $C_6H_5CH_2$ *m/e* 91 (84%).

Compound **12** was also obtained by irradiation of a solution of **11** in toluene with a yield of 68%.

ii) Under Carbon Dioxide Atmosphere: Irradiation of a solution of **11** under carbon dioxide atmosphere for 1.5 hr afforded **12** in a yield of 62%.

iii) In the Presence of Carbon Disulfide: A solution of **11** (0.8 g) in 200 m*l* of benzene and 100 m*l* of carbon disulfide was irradiated under the same conditions for 1.5 hr to give 0.08 g (14%) of **12**.

Reaction of ***11*** *with Dimethyl Acetylenedicarboxylate.* A solution of 0.75 g of **11** and 0.9 g of dimethyl acetylenedicarboxylate in 5 m*l* of toluene was refluxed for 1.5 hr. Analysis by column chromatography afforded **13**, which was recrystallized from methanol, mp 117—119°C, 0.84 g (77%).

Found: C, 64.09; H, 6.17; N, 8.41%. Calcd for $C_{17}H_{20}O_4N_2$: C, 64.54; H, 6.37; N, 8.86%. IR: 2980, 1730, 1240, 1200, 1080, 760, 710 cm^{-1}.