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Photochemical Isomerization of 6,7-Dicyano- and 6,7-Bis(methoxycarbonyl)-3-phenylsulfonyl-(2,4-*exo*)-3-azatricyclo[3.2.1.$0^{2,4}$]oct-6-ene

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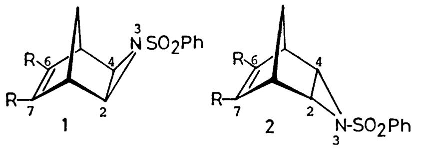
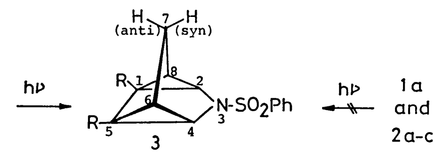
Synopsis. The photochemical reactions of 6,7-bis-(methoxycarbonyl)- and 6,7-dicyano-3-phenylsulfonyl-(2,4-exo)-3-azatricyclo[3.2.1.$0^{2,4}$]oct-6-ene afford the corresponding tetracyclic compounds (**3b** and **3c**) by the skeletal isomerization, but those of their endo isomers do not result in the formation of **3b** and **3c**.

Recently we have reported that 3-phenylsulfonyl-(2,4-*exo*)-3-azatricyclo[3.2.1.$0^{2,4}$]oct-6-enes **1a**—**c** undergo thermal rearrangement to afford the corresponding 2-phenylsulfonyl-2-azabicyclo[3.2.1]oct-3,6-dienes in high yields under moderate conditions.[1] Our interest in the reactivity of these tricyclic aziridines prompted us to examine the photochemical isomerization of compounds **1a**—**c** and their endo isomers **2a**—**c**. The photochemical isomerization of tricyclo[3.2.1.-$0^{2,4}$]oct-6-enes[2] and their 3-oxa[3] and 3-aza[4] analogs has been known to afford tetracyclo[3.3.0.$0^{2,8}$.$0^{4,6}$]-octanes by a [$2\pi+2\sigma$] cycloaddition pathway. Herein, we wish to report several results on the photochemical reaction of the tricyclic aziridines.



(a; R= H, b; R= CO_2Me , c; R = CN)

A solution of compounds **1a**—**c** and **2a**—**c** in acetonitrile was degassed in a Pyrex or quartz tube and irradiated with a high-pressure mercury lamp (300 W); the products were isolated in the usual manner. The results are summarized in Table 1. The irradiation of the unsubstituted *exo* and *endo* compounds **1a** and **2a** afforded no tetracyclic product. On the other hand, the 6,7-disubstituted *exo* compounds **1b** and **1c** were converted into the corresponding tetracyclic compounds **3b** and **3c** together with an unidentifiable polymeric material, as Table 1 shows.



(b; R = CO_2Me, c; R = CN)

The cyano and methoxycarbonyl groups made possible the intramolecular photocyclization of the *exo* tricyclic aziridines, although in the thermal rearrangements of **1a**—**c** such substituents caused a decrease in their reactivity.[1] Furthermore, the cyano group brought about a higher yield of a tetracyclic compound than that in the case of the methoxycarbonyl group. The use of a quartz tube as a reaction vessel or a low-pressure mercury lamp as a light source resulted in the increase of the amount of the polymeric material produced.

Table 1. The yields of the tetracyclic compounds in the photochemical reactions of aziridines **1a**—**c** and **2a**—**c**[a]

Compound	Tube[b]	Time/h	Yield/%	Recovery/%
1b	P	96	11	56
1b	Q	12	24	41
2b	P	96	0	96
2b	Q	12	0	53
1c	P	96	76	5
1c	Q	6	54	0
2c	P	96	0	78
2c	Q	6	0	64

a) Solvent: acetonitrile. Concentration of compound: 6.1×10^{-2} mol/l (Pyrex) and 1.3×10^{-1} mol/l (quartz). In the cases of **1a** and **2a**, the tetracyclic compounds were not obtained at all. The unreacted **1a** (*ca.* 90%) was isolated as 2-phenylsulfonyl-2-azabicyclo[3.2.1]oct-3,6-diene, which was produced by the thermal rearrangement on silica gel chromatography. The compound **2a** was recovered in *ca.* 90% yield. b) P= Pyrex and Q=quartz.

Contrary to the results in the cases of the *exo* compounds **1b** and **1c**, it was found that the 6,7-disubstituted *endo* compounds **2b** and **2c** undergo no isomerization under the similar conditions, as Table 1 shows. Thus, this result demonstrates that the bent C_2–C_4 bond directed toward the *endo* side is necessary for the photochemical isomerization of the tricyclic aziridines. A similar phenomenon has been observed in the thermal reactions of **1a**—**c** and **2a**—**c** described previously.[1]

Experimental

Melting points were uncorrected. Acetonitrile was distilled under nitrogen from CaH_2. IR, ^1H- and ^{13}C-NMR, and mass spectra were obtained on a Hitachi 216 grating infrared spectrometer, a Hitachi R-24A spectrometer, a JEOL FX 90Q Fourier transform NMR spectrometer, and a Hitachi RMU-6E mass spectrometer, respectively.

Material. The compounds, **1a**—**c** and **2b,c**, were prepared by the reactions of the corresponding norbornadienes with benzenesulfonyl azide. The ^1H-NMR, IR, and mass spectral data of their compounds are summarized in Table 2. The **2a** was prepared according to the methods described in the literature.[5]

General Procedure for Photochemical Reaction. All reactions were performed similarly in a pyrex or quartz tube (72 cm^3 total capacity). A reaction tube was charged with 0.61—0.65 mmol of **1a**—**c** and **2a**—**c** and 5—10 ml of dry

TABLE 2. SPECTRAL DATA OF COMPOUNDS **1a**—**c** AND **2b**,**c**

Compound	IR (KBr) ν/cm^{-1}	^{1}H-NMR (δ, CDCl$_3$)	MS m/e(M$^+$)
1a	1345(ν_{SO_2})	7.38—8.11(m, 5H, aromatic), 6.35(t, 2H, J=1.6 Hz, 6-H, 7-H), 3.17(s, 2H, 2-H, 4-H), 3.00(m, 2H, 1-H, 5-H), 1.16(d, 1H, J=8.3 Hz, 8-Hs), 1.72(d, 1H, J=8.3 Hz, 8-Ha)	247
1b	1740(ν_{CO}) 1345(ν_{SO_2})	7.30—8.00(m, 5H, aromatic), 3.80(s, 6H, OCH$_3$), 3.45(brs, 4H, 1-H, 2-H, 4-H, 5-H), 1.83(d, 1H, J=8.7 Hz, 8-Hs), 1.41(d, 1H, J=8.7 Hz, 8-Ha)	363
2b	1730(ν_{CO}) 1325(ν_{SO_2})	7.40—8.00(m, 5H, aromatic), 3.72(brs, 2H, 2-H, 4-H), 3.66(s, 6H, OCH$_3$), 3.38(m, 2H, 1-H, 5-H), 1.98(brs, 2H, 8-CH$_2$)	363
1c	2240(ν_{CN}) 1335(ν_{SO_2})	7.46—8.16(m, 5H, aromatic), 3.50(brs, 2H, 1-H, 5-H), 3.43(s, 2H, 2-H, 4-H), 2.03(d, 1H, J=10.7 Hz, 8-Hs), 1.55(d, 1H, J=10.7 Hz, 8-Ha)	297
2c	2230(ν_{CN}) 1325(ν_{SO_2})	7.50—8.30(m, 5H, aromatic), 3.81(m, 2H, 2-H, 4-H), 3.45(m, 2H, 1-H, 5-H), 2.15(s, 2H, 8-CH$_2$)	297

a) The spectra were measured at 60 MHz.

TABLE 3. SPECTRAL DATA OF COMPOUNDS **3b**,**c**

Compound	IR (KBr) ν/cm^{-1}	^{1}H-NMR (δ)$^{a)}$	^{13}C-NMR (δ)$^{b),c)}$
3b	1725(ν_{CO}) 1320(ν_{SO_2})	CDCl$_3$: 7.30—8.00(m, 5H, aromatic), 4.12(d, 2H, J=9.0 Hz, 2-H, 4-H), 3.53(s, 6H, OCH$_3$), 2.22(m, 2H, 6-H, 8-H), 1.98(m, 1H, 7-H$_{anti}$), 1.70(d, 1H, J=13 Hz, 7-H$_{syn}$)	CDCl$_3$: 167(s, C=O), 54(d, 2-C, 4-C), 52(q, OCH$_3$), 36(s, 1-C, 5-C), 32(d, 6-C, 8-C), 23(t, 7-C)
3c	2230(ν_{CN}) 1320(ν_{SO_2})	DMSO-d_6: 7.40—8.05(m, 5H, aromatic), 4.56(d, 2H, J=9.0 Hz, 2-H, 4-H), 2.36(m, 2H, 6-H, 8-H), 1.94(m, 1H, 7-H$_{anti}$), 1.52(d, 1H, J=13.0 Hz, 7-H$_{syn}$)	DMSO-d_6: 115(s, CN), 54 (d, 2-C, 4-C), 31(d, 6-C, 8-C), 23(t, 7-C), 21(s, 1-C, 5-C)

a) The spectra were measured at 90 MHz. b) Splitting patterns were obtained by off-resonance decoupling. c) Signals of aromatic protons are omitted.

acetonitrile. After the air in the tube was replaced by argon by a freezing method, the tube was sealed and irradiated for a definite time at an equidistant (5 cm) location from a 300 W mercury lamp. After the removal of acetonitrile *in vacuo*, the residue was chromatographed on silica gel. The **3b** and **3c** were eluted with (12:1) benzene–acetone, **3b** was recrystallized from ethanol to give colorless prisms, and **3c** from chloroform to give needles. **3b**: 120—122 °C; MS *m/e* 363 (M$^+$). Found: C, 55.90; H, 4.74; N, 4.01%. Calcd for $C_{17}H_{17}NO_6S$: C, 56.19; H, 4.68; N, 3.86%. **3c**: 197—199 °C; MS *m/e* 297 (M$^+$). Found: C, 60.55; H, 3.67; N, 14.40%. Calcd for $C_{15}H_{11}N_3O_2S$: C, 60.61; H, 3.70; N, 14.14%. The ^{1}H- and ^{13}C-NMR and IR spectral data of their compounds are summarized in Table 3.

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