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Synthetic Photochemistry. XLVII.[1] Formation and Degenerate Cope Rearrangement of 9-Dicyanomethylenebarbaralane

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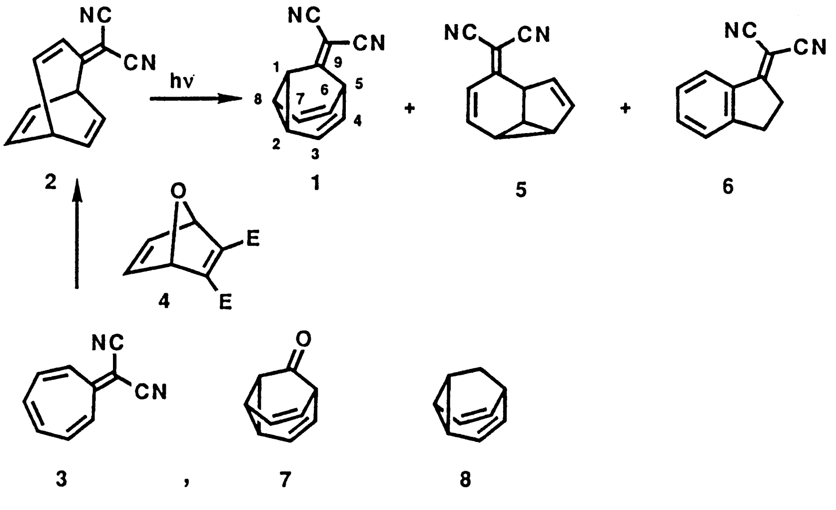
Synopsis. Photolysis of 2-dicyanomethylenehomobarrelene gave 9-dicyanomethylenebarbaralane, 5-dicyanomethylenetricyclo[4.3.0.0^{2,9}]nonadiene, and 1-dicyanomethyleneindan. Dicyanomethylenebarbaralane showed time-averaged NMR signals.

Recently, we synthesized several barbaralane derivatives[2] by a photolysis of 2-methylenehomobarrelenes[3] prepared from 1*H*-cyclohepta[*b*]furan-2-one derivatives and 2,3-bis(methoxycarbonyl)-7-oxanorbornadiene. In this paper we describe the synthesis of 9-dicyanomethylenebarbaralane (**1**)[4] from 2-dicyanomethylenehomobarrelene (**2**) and the time-averaged NMR spectrum of this internal Cope-rearrangement system.

Results and Discussion

When a chloroform solution of **2**, prepared by high-pressure cycloaddition-thermal cycloreversion procedure from 8,8-dicyanoheptafulvene (**3**) and 2,3-bis(methoxycarbonyl)-7-oxanorbornadiene (**4**),[3] was irradiated, three products (**1**,[4] **5**, and **6**[5]) were obtained in 18, 29, and 24% yields, respectively. These structures were determined by comparisons with the spectral data of the related compounds prepared previously.[3] The barbaralane derivative, **1**, revealed a time-averaged NMR spectra, as expected. A kinetic analysis of this intramolecular Cope rearrangement was carried out by measuring the half-height widths of NMR signals.[6] The kinetic parameters obtained are summarized in Table 1 together with those of related compounds, barbaralone (**7**)[4,7] and barbaralane (**8**).[4] In both toluene-d_8 and acetone-d_6, the rates of exchange were nearly equal and insensitive to the polarity of the solvent. This is consistent, together with other thermodynamic parameters, as the concerted rearrangement.[7–11]

The activation energy (E_a) of **1** was similar to that reported by Nakanishi for **7**.[7] A retardation of the



Scheme 1.

Table 1. Activation Parameters of Cope Rearrangement[a]

	E_a/kJ mol^{-1}	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J mol^{-1}K^{-1}	$\Delta G^{\neq}_{298}$/kJ mol^{-1}
7	33.9	31.4	−38.8	43.1[b]
	48.1±0.4	45.6±0.4	11.3±2.9	42.3±0.4[c]
1	45.0±1.5	42.6±1.5	−6.3±6.3	44.3±0.7[d]
	44.6±1.2	42.0±1.2	−6.5±4.9	44.0±0.5[e]
8	36.0	33.5	5.6	31.8[f]

a) Variable temperature ^{13}C NMR spectra were measured at 67.5 MHz in acetone-d_6 between −80 and 50 °C and in toluene-d_8 between −80 and 60 °C. See Experimental for the determination of activation parameters for **1**. b) In acetone-d_6.[4] c) In CS_2-CD_2Cl_2-acetone-d_6.[7] d) In acetone-d_6. e) In toluene-d_8. f) In CS_2.[4]

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rates of the degenerate Cope rearrangement for **1** and **7** may be another example of such that the electron-withdrawing carbonyl and dicyanomethylene groups strengthened the C_2-C_8 bond to raise the activation energy of the Cope rearrangement as has been already pointed out by Hoffmann and Stohrer.[12]

Experimental

Irradiation of 2. a) A $CHCl_3$ solution (2 cm^3) of **2** (320 mg) was irradiated for 4 h as previously described[3] to give **1** [colorless crystals, mp 142—143 °C, 31.3 mg, 18%. Found: C, 79.99; H, 4.24; N, 15.43%. Calcd for $C_{12}H_8N_2$: C, 79.88; H, 4.47; N, 15.54%. ^{1}H NMR δ[13]=3.68 (2H, tm, *J*=6.7 Hz), 4.46 (4H, tm, *J*=6.7 Hz), and 5.76 (2H, tt, *J*=6.7, 1.5 Hz). δ (toluene-d_8 at −90 °C)=1.58 (2H, br s), 2.30 (1H, br s), 3.36 (1H, br s), and 4.90 (4H, br s). δ (toluene-d_8 at 50 °C)=3.15 (2H, tm, *J*=5.9 Hz), 3.62 (4H, tm, *J*=5.9 Hz), and 5.11 (2H, tm, *J*=5.9 Hz). ^{13}C NMR at 60 °C δ=36.2 (2C), 76.6, 80.3 (br, 4C), 112.2 (2C), 121.2 (2C), and 178.9. IR ν: 2240 and 1585 cm^{-1}. UV (MeOH): 244.0 (ε 13400) and 300.0 nm (5600). MS *m/z* (%) 180 (M$^+$, 20), 153 (32), 115 (base), 63 (37), 51 (41), and 39 (32)], **5** [yellow crystals, mp 110—111 °C, 51 mg, 29%. Found: C, 80.13; H, 4.29; N, 15.52%. Calcd for $C_{12}H_8N_2$: C, 79.88; H, 4.47; N, 15.54%. ^{1}H NMR δ=2.14 (1H, td, *J*=7.5, 4.5 Hz), 2.52 (1H, td, *J*=7.5, 6.0 Hz), 2.96 (1H, dddd, *J*=7.5, 6.0, 2.5, 0.5 Hz), 4.12 (1H, ddm, *J*=7.5, 2.0 Hz), 5.36 (1H, dm, *J*=5.5 Hz), 5.89 (1H, ddd, *J*=5.5, 2.5, 1.5 Hz), 6.38 (1H, dd, *J*=10.0, 4.5 Hz), and 6.80 (1H, dd, *J*=10.0, 1.0 Hz). ^{13}C NMR δ=24.4, 30.9, 45.1, 48.1, 78.3, 112.0, 112.8, 125.4, 132.0, 133.8, 140.4, and 171.7. IR ν: 2210, 1595, and 1540 cm^{-1}. UV (MeOH): 242.0 (ε 5200 sh), 279.8 (7500), and 339.2 nm (10900). MS (%) 180 (M$^+$, 26), 153 (51), and 115 (base)], **6** [colorless crystals, mp 146—147 °C, 43 mg, 24%. Found: C, 79.77; H, 4.14; N, 15.37%. Calcd for $C_{12}H_8N_2$: C, 79.88; H, 4.47; N, 15.54%. ^{1}H NMR δ=3.1—3.4 (4H, m), 7.3—7.7 (3H, m), and 8.20 (1H, dm, *J*=7.5 Hz). ^{13}C NMR δ=29.6, 34.6, 78.0, 112.9, 113.5, 126.1, 126.2, 128.1, 135.1, 135.7, 154.0, and 179.2. IR ν : 2240 and 1575 cm^{-1}. UV (MeOH): 230.0 (ε 8300), 236.0 (7450), 255.4 (1850), 290.0 (11800 sh), 306.4 (15500), and 331.8 nm (17800). MS *m/z* (%) 180 (M$^+$, 63), 153 (47), 115 (base), 43 (68), and 39 (38)], and unreacted **2** (142.2 mg). **b)** An acetone-d_6 solution (1 cm^3) of **2** (143 mg) was irradiated to give **1** [16.9 mg, 15%], **5** [30.6 mg, 28%], **6** [26.7 mg, 24%], and unreacted **2** [32.8 mg].

Kinetics Measurements. A kinetic analysis was carried out by variable-temperature ^{13}C NMR measurements at 67.5 MHz (JEOL 270) in acetone-d_6 and toluene-d_8. The rate constants of the chemical exchange process were determined by broadened line widths of the exchangeable signals at the half height. Natural line widths were obtained from the signals of C-3 and C-7 around δ 121 in toluene and δ 122 in acetone. The temperature range was between −80 and 60 °C in toluene and between −80 and 50 °C in acetone.

References

1) Part. XLVI: G. R. Tian, A. Mori, N. Kato, and H. Takeshita, *Bull. Chem. Soc. Jpn.*, **62**, 506 (1989).

2) G. R. Tian, S. Sugiyama, A. Mori, H. Takeshita, M. Higashi, and H. Yamaguchi, *Chem. Lett.*, **1988**, 941.

3) G. R. Tian, S. Sugiyama, A. Mori, and H. Takeshita, *Bull. Chem. Soc. Jpn.*, **61**, 4397 (1988).

4) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967).

5) D. M. W. Anderson, F. Bell, and J. L. Duncan, *J. Chem. Soc.*, **1961**, 470.

6) H. Günther, J. Runsink, H. Schmickler, and P. Schmitt, *J. Org. Chem.*, **50**, 289 (1985).

7) H. Nakanishi and O. Yamamoto, *Chem. Lett.*, **1975**, 513.

8) H. Nakanishi and O. Yamamoto, *Chem. Lett.*, **1973**, 1273.

9) H. Nakanishi and O. Yamamoto, *Tetrahedron Lett.*, **1974**, 1803.

10) H. Günther and J. Ulmen, *Tetrahedron*, **30**, 3781 (1974).

11) A. K. Cheng, F. A. L. Anet, J. Mioduski, and J. Meinwald, *J. Am. Chem. Soc.*, **96**, 2887 (1974).

12) R. Hoffmann and W.-D. Stohrer, *J. Am. Chem. Soc.*, **93**, 6941 (1971).

13) NMR spectra were measured in $CDCl_3$ solution unless otherwise specified.