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LOW TEMPERATURE PHOTOLYSIS OF 5-METHOXYCARBONYL-5H-BENZOCYCLOHEPTENE: EXCLUSIVE FORMATION OF 1-endo-METHOXYCARBONYL-1a,7b-DIHYDRO-1H-CYCLOPROPA[a]NAPHTHALENE

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Irradiation of 7-methoxycarbonyl-7H-benzocycloheptene (1) has been reported to give 1-exo-methoxycarbonyl-1a,7b-dihydro-1H-cyclopropa[a]naphthalene (exo-2) along with hydrogen-migrated products.1) We found that photochemical isomerization (HPL, Pyrex) of 5-methoxycarbonyl-5H-benzocycloheptene (3) took place readily to give exclusively exo-2 at room temperature.

The exclusive and fast migration of the methoxycarbonyl group in the formation of 2 from 3 was confirmed using a mixture of 3-5-d_1 and 2-1-d_1 (3 : 4) (D content 95%) obtained by a sensitized irradiation of 2-1-d_1 (D content 95%).2) On irradiation in methanol, the mixture afforded exo-2 as a sole product with deuterium distribution, 60% on C-1 and 40% on C-7b. The values are very close to 57% on C-1 and 43% on C-7b, the values calculated on the assumption of exclusive migration of the group in 3-5-d_1. The ester 3 was prepared by the reaction of benzotropylium cation with sodium cyanide in acetonitrile, followed by methanolysis of the corresponding cyanide. [3 ^{1}HNMR δ ppm (CCl_4) 7.0-7.5 (5H, m), 6.57 (1H,m), 6.14 (2H,m), 3.81 (3H,s), 3.64 (1H,d,J=4.5Hz); IR $\nu_{max}^{liq.\ film}$ 1734 cm^{-1}; UV λ_{max}^{EtOH} (log ε) 273 nm (3.90)]. It is supposed that 1 might exsist mostly in a conformation with the quasi-equatorial methoxycarbonyl group rather than the quasi-axial,3) but 3 would exsist rich in a conformation with the quasi-axial group, owing to the repulsive interaction between the methoxycarbonyl group and the hydrogen on C-4.4) This was confirmed by the NMR measurement at low temperature [$\Delta G^{\ddagger}$ 9.6 Kcal/mole; quasi-axial : quasi-equatorial = 48 52 at -90°C].5) Thus the facile migration of methoxycarbonyl group in 3 may be attributable to its quasi-axial conformation.

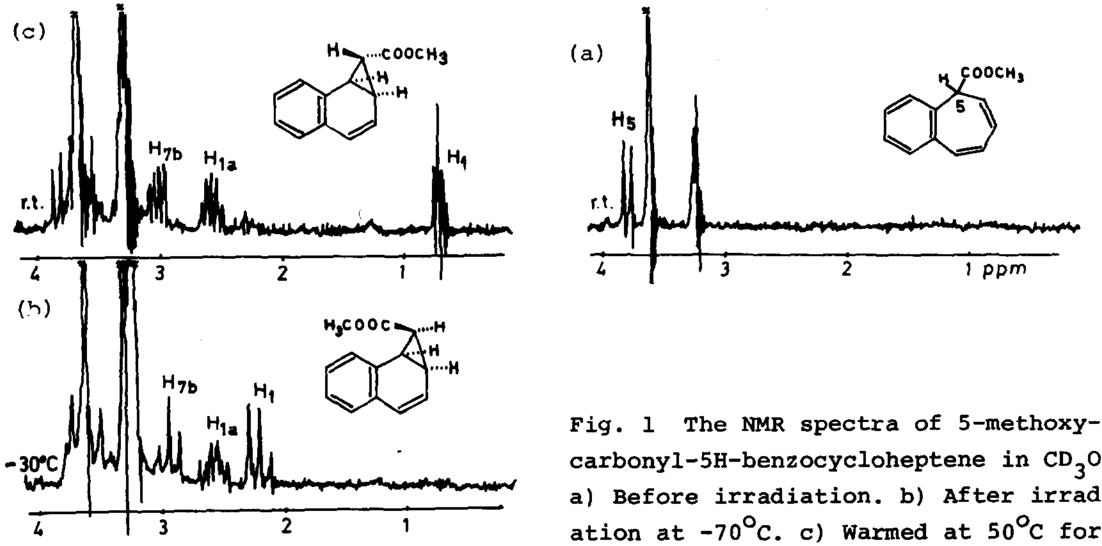
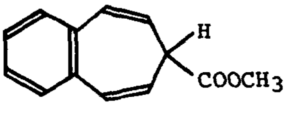
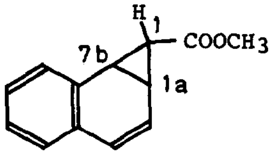


Fig. 1 The NMR spectra of 5-methoxycarbonyl-5H-benzocycloheptene in CD_3OD. a) Before irradiation. b) After irradiation at -70°C. c) Warmed at 50°C for 30 min after irradiation.



(1)



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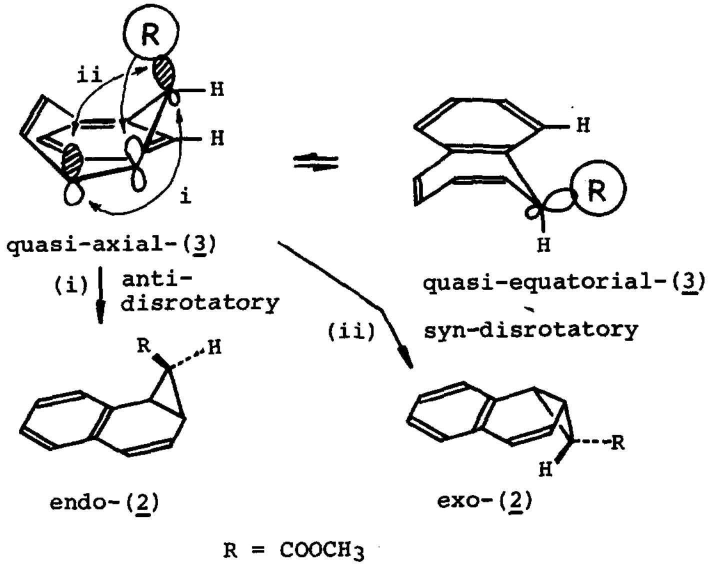

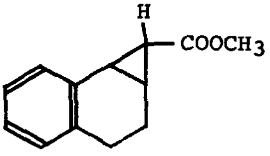

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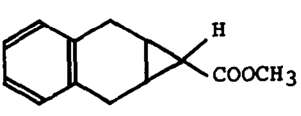

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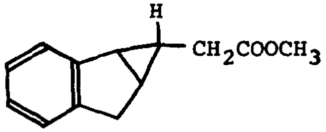

(6)

If the rearrangement of the group occurs simultaneously with the formation of three membered ring in a concerted mechanism, two possibilities arise: the anti-disrotatory mode ring formation and the syn-disrotatory mode. The former may lead to 1-endo derivative of 2 and the latter 1-exo one. To clarify this point, 3 dissolved in CD_3OD was irradiated at -70°C and the reaction was monitored by NMR spectroscopy.[6)] Fig. 1 shows the NMR spectra before and after irradiation. New signals appear at δ 2.20 (1H,d-d,J=9.5, 8.5Hz), 2.58 (1H,d-d-d,J=9.5, 8.5, 5.5Hz), 2.94 (1H,t,J=8.5Hz), 3.31 (3H,s), 5.86 (1H,d-d,J=9.8, 5.5Hz), and 6.49 ppm (1H,d,J=9.8Hz); the first three signals are attributable to the hydrogens on cyclopropane ring and the coupling constants between them correspond to the ones for cis orientation. It should be pointed out that the signals due to exo-2 are not found in the photolysate but they appear, in place of the signals due to endo-2, after warming the photolysate at 50°C for 30 min. The thermal isomerization of endo to exo isomer of 1-substituted 1a,7b-dihydro-1H-cyclopropa[a]naphthalenes is believed to occur through 6H-benzocycloheptene structure with energy barrier $\Delta H^{\ddagger}$ 19-22 Kcal/mole.[7)8)]

The endo structure was confirmed by hydrogenation in the presence of an active rhodium catalyst below -10°C to give the dihydro-endo derivative along with some of the dihydro-exo isomer (24%). The former was isolated in pure form and the degradation pattern in mass spectrum (m/e 202.0987 M^+: calcd for $C_{13}H_{14}O_2$; 202.0994) was quite similar to that of the known exo-isomer.[9)] The presence of a three membered ring with one hydrogen on each carbon and two methylene groups in the molecule is revealed by the C-13 NMR spectra.[10)] Of the three possible structures, 4-6, the unsymmetrical structure with two adjacent methylene groups, endo-4, is best fitted to every physical[10)] and chemical data.

References

1) D. M. Madigan and J. S. Swenton, J. Am. Chem. Soc., 92, 7513 (1970); Tetrahedron, 28, 2703 (1972).

2) M. Kato, S. Ito, and K. Takatoku, unpublished work.

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5) Compare with the data for 5-cyano-5H-benzocycloheptene [$\Delta G^{\ddagger}$ 9.6 Kcal/mole; quasi-axial : quasi-equatorial = 19 : 81 at -90°C].

6) We obtained endo-2, instead exo-2, along with other products by irradiation of 1 under the low temperature conditions (-35°∿ -45°C).

7) O. L. Chapman, M. Kane, J. D. Lassila, R. L. Loeschen, and H. E. Wright, J. Am. Chem. Soc., 91, 6856 (1969).

8) E. Vogel, D. Wendisch, and W. R. Roth, Angew. Chem., 76, 432 (1964).

9) R. Huisgen and G. Juppe, Chem. Ber., 94, 2332 (1961): The physical data of exo-4: UV λ_{max}^{EtOH} (log ε) 229 (4.02), 268 (2.75), 276.5 nm (2.65); ^{1}HNMR δ ppm (CCl_4) 7.2 (1H,m), 7.0 (3H,m), 3.63 (3H,s), 1.96-2.7 (7H,m); Mass m/e(%) 115 (10.9), 128(100), 129 (25.0), 141 (39.0), 142 (37.5), 143 (33.4), 169 (16.8), 170 (48.1), 171 (15.1), 187 (14.8), 202 (45.1).

10) The physical data of endo-4: IR $\nu_{max}^{liq.\ film}$ 3015, 2940, 1730, 1194, 1161 cm^{-1}. UV λ_{max}^{EtOH} (log ε) 269.5 (2.78), 277 nm (2.74); ^{1}HNMR δ ppm (CCl_4) 7.0 (4H,m), 3.41 (3H,s), 1.8-2.8 (7H,m); ^{13}CNMR δ ppm ($CDCl_3$) 18.2 (t,J=132Hz), 19.0 (d,J=162Hz), 20.9 (d,J=169Hz), 26.0 (d,J=163Hz), 28.1 (t), 51.3 (q,J=147Hz), 126.1 (d), 126.4 (d), 127.8 (d), 129.8 (d), 132.3 (s), 138.3 (s), 170.7 (s); Mass m/e(%) 115 (11.0), 128 (100), 129 (25.5), 141 (34.6), 142 (35.5), 143 (31.2), 169 (15.5), 170 (44.4), 171 (13.7), 187 (12.1), 202 (32.9).

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