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Homoconjugated Diene as a Dienophile to Troponoid Compounds: The Stereoselective Addition Reactions of Tropone and 8,8-Dicyanoheptafulvene with Tricyclo[3.2.2.$0^{2,4}$]nona-6,8-diene Derivative and Thermal and Photochemical Isomerizations of the Adducts

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Thermal addition reactions of tropone and 8,8-dicyanoheptafulvene with a homoconjugated diene, dimethyl 3-cyanotricyclo[3.2.2.$0^{2,4}$]nona-6,8-diene-6,7-dicarboxylate derivative, proceeded stereoselectively to give endo-[4+2]-type cycloadducts, where the troponoids acted as 4 π components. Upon photo-irradiation the adducts afforded intramolecular [2+2]-type addition products to verify the endo-form of the adducts. Molecular orbital caluculations suggested that the stereoselectivity could be explained by secondary orbital interactions between the HOMO of the troponoid compounds and the LUMO of the tricyclic compound. A thermal reaction of the adducts gave three-membered ring opened products, which further proceeded through an intramolecular [2+2]-type reaction upon photo-irradiation.

Much attention has been focussed on the cycloaddition reactions of tropone and fulvene derivatives from the viewpoints of synthetic utility, elucidation of the electronic behavior of the troponoid compounds, and mechanistic studies of the reactions. Many studies have been proposed to clarify whether [4+2]-type and/or [8+2]-type additions proceed with olefins or acetylene derivatives.[1] Recent reports have documented that some troponoid compounds react with several kinds of allenes to give [4+2]- and/or [8+2]-types cycloadducts.[2]

It seems that the cycloadditions of troponoid compounds have already been studied completely and that no outstanding questions remain. However, only a little has been studied concerning the reactions of troponoid compounds with homoconjugated dienes, except for recent work by Takeshita et al.,[3] which showed that the reactions of some troponoid compounds with a bicyclo[2.2.1]hepta-2,3-diene derivative proceeded with a considerable amount of stereoselectivity, which was reasonably explained by molecular orbital calculations.

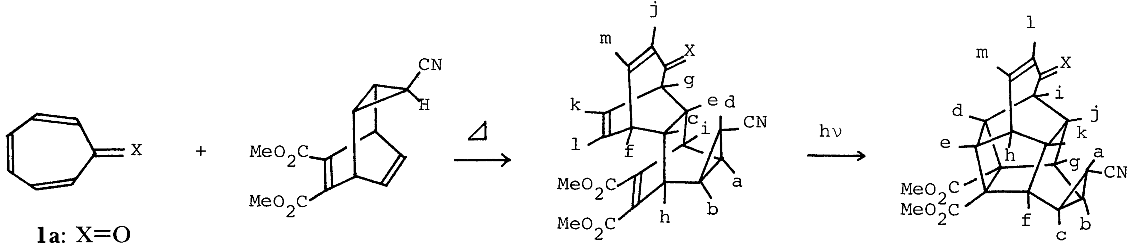
As a part of series of studies concerning the addition reactions of tropone and fulvene derivatives,[2a,4] we studied reactions of tropone (**1a**) and 8,8-dicyanoheptafulvene (**1b**) with a homoconjugated diene, dimethyl 3-cyano-tricyclo[3.2.2.$0^{2,4}$]nona-6,8-diene-6,7-dicarboxylate (**2**),[5] and conducted a molecular orbital calculations on **1a**, **1b**, and **2**, the interesting results of which are reported here.

Results and Discussion

A mixture of **2** and five equimolar amounts of **1a** was heated at 200 °C for 2 h under a nitrogen stream. Chromatographic separation and purification of the reaction mixture afforded an endo-[4+2]-type addition product **3a** in 77% yield. An analogous reaction of **1b** with three molar equivalents of **2** at 200 °C for 2.7 h also afforded an endo-[4+2]-type adduct **3b** in 45% yield.

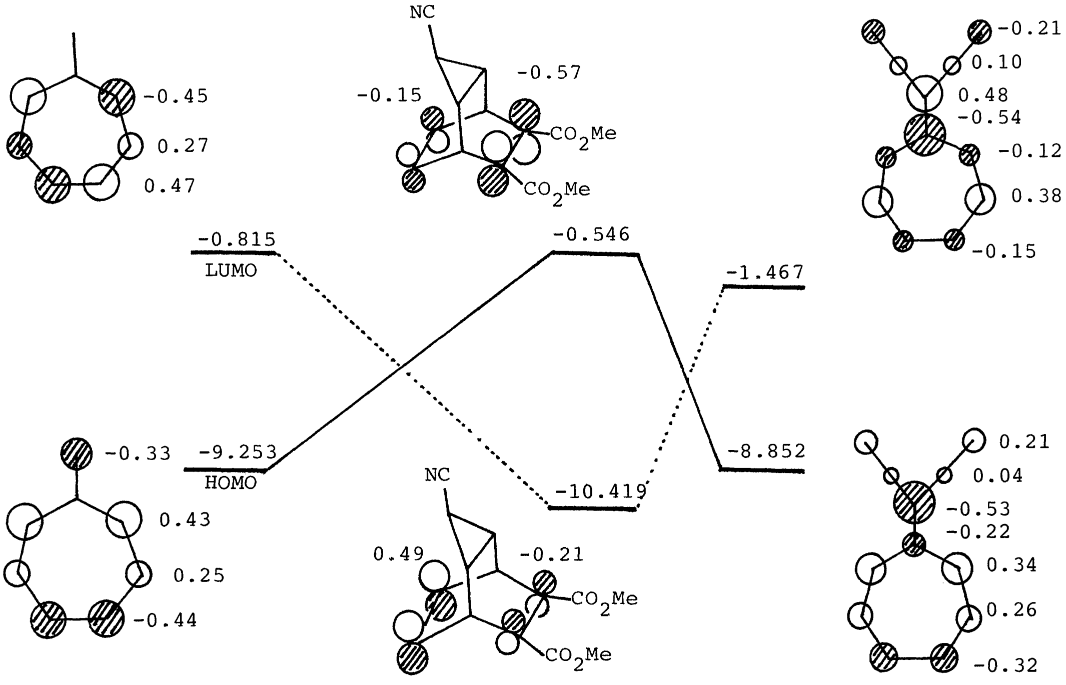
The structures of **3a** and **3b** were deduced using their spectral properties and were confirmed by their coincedences to those of analogous compounds.[6] The stereochemistries of the adducts were found to be endo-forms on the basis of the coupling-constant values between the bridgehead protons, H_c and H_f (0.0 Hz for both **3a** and **3b**), as well as H_e and H_g (0.0 Hz for both **3a** and **3b**), both of which should be expected to be ca. 6 Hz regarding their exo-forms.[3]

The stereochemistry of **3a** was further confirmed to be an endo-form by a photochemical reaction. Irradiation of a 2.5×$\cdot 10^{-3}$ M (1M=1 mol dm^{-3}) solution of **3a** in dry ether with a high-pressure mercury



1a: X=O
1b: X=C(CN)$_2$
2
3a,b
4a

Fig. 1.



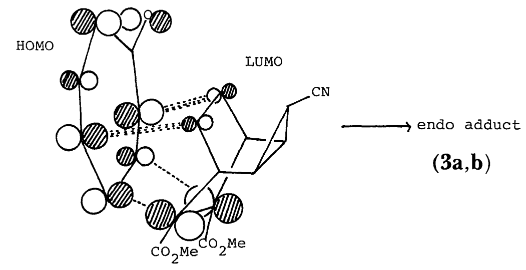
1a **2** **1b**

Fig. 2. HOMO-LUMO interaction of troponoid compounds (**1**) with tricyclo compound (**2**). Values are frontier molecular orbital energy levels [eV] and coefficients calculated by MNDO method.

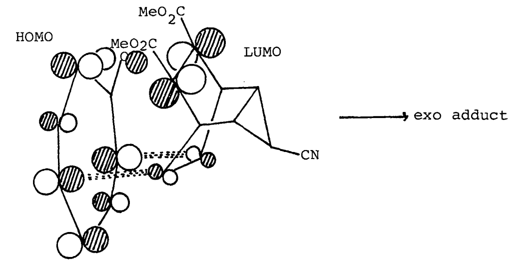
lamp afforded an intramolecular [2+2]-type addition product **4a** in 19% yield.

The structure of **4a** was deduced on the basis of its spectral properties, mainly on NMR. The signals of protons H_a (1.36 ppm), H_b, and H_c (2.15 ppm) appear at very high field in the NMR spectra, indicating the existence of a cyclopropane moiety. The dissappearance of the signals of two olefin protons and four olefin carbons in the ^{1}H NMR and ^{13}C NMR spectra, respectively, in comparison to those of the starting materials showed the appearance of [2+2]-type cycloaddition reactions. The relation of the protons, determined by using a double-resonance technique in the NMR spectra, confirmed the structure.

As shown above, the addition reactions were clarified to proceed stereoselectively to give endo-type products. The Dreiding models, however, showed that steric repulsions should make the exo-type products be more stable than the endo-types. In order to clarify the reaction mechanism in more detail, molecular orbital calculations by an MNDO method[7] were carried out on **1a**, **1b**, and **2** in their ground-state geometries. Regarding both pairs **1a** and **2** and **1b** and **2**, the energy gaps between the HOMO of **1** and the LUMO of **2** were smaller than the opposite combinations (see Fig. 2), suggesting that the reactions were determined by interactions between the HOMO of **1** and the LUMO of **2**. The frontier orbital interactions between the HOMO of **1** and the LUMO of **2** showed that the bonding-type secondary orbital interaction[8,9] existed in the endo-type transition state. On the other hand, no such stabilization effect could be found in the exo-type transition state.[10] Analogous effects concerning secondary orbital interactions in the reactions of homoconjugated dienes have been reported by Takeshita et al.[8]



Secondary Orbital Interaction (bonding)



Secondary Orbital Interaction (no bonding)

Fig. 3.

When **3a** was heated at 250 °C for 2 h under a

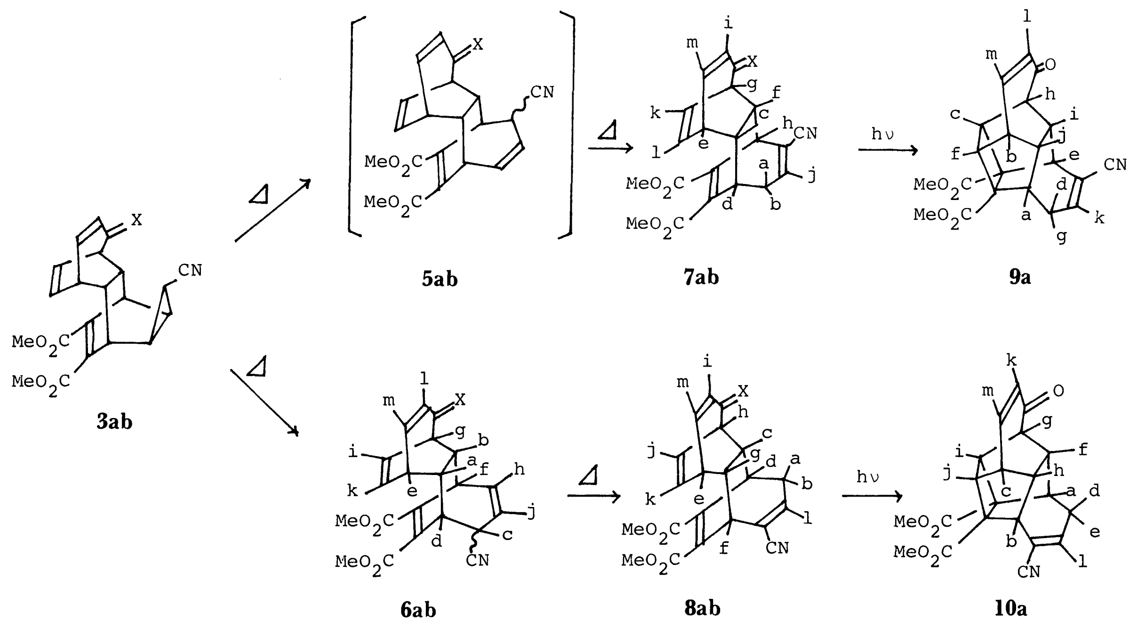


Fig. 4.

nitrogen stream, three-membered ring-opened products, **7a** and **8a**, were obtained in 18 and 23% yields, respectively. The same reaction proceeded with **3b** to form **7b** and **8b** in yields of 12 and 23%, respectively. On the other hand, in the reaction of **3b** during a short period (250 °C, 30 min), another product, **6b**, was afforded in 12% yield, as well as a 10% yield of **8b**. The intermediacy of **6b** during the formation of **8b** from **3b** was demonstrated by a quantitative isomerization of **6b** to **8b** upon heating at 250 °C for 5 min.

The structures of the products (**6**, **7**, **8**) were determined on the basis of their spectral, especially NMR, properties and were confirmed by comparisons of these data with those of analogous compounds, such as **3a** and **3b**. The increment of an olefin proton and decreasing amount of cyclopropane protons in the products (**6**, **7**, **8**), compared to the starting material (**3**) suggest the structures shown in the Figure. Conservation of the endo-configurations in the products was demonstrated by intramolecular [2+2]-type cycloaddition upon irradiation. Photoreactions of **7a** and **8a** with a low-pressure mercury lamp afforded the corresponding cage compounds, **9a** and **10a**, in 23 and 38% yields, respectively. The structures of the products were deduced on the basis of the spectral, especially NMR, properties, and were confirmed by comparisons of these data with those of analogous compounds, such as **4a**.

The thermal reactions of **3** are considered to proceed through a reaction path analogous to that of reactions reported by Prinzbach,[11] as follows. A three-membered ring opening with a shift of the cyano group of **3** gave **5** and **6**. A migration of the double bond to conjugate with the nitrile group in **5** and **6** can form **7** and **8**, respectively.[12]

Experimental

Melting points were recorded on a Yanagimoto Micro Melting Point Apparatus and are uncorrected. The NMR spectra were measured with Hitachi R 20B or Varian XL-200 spectrometers. IR, UV, and mass spectra were measured with JASCO IRA-1, Hitachi 220A, and Hitachi M-2000S spectrometers, respectively. Photoreactions were carried out with Riko UVL-30LQ and Riko UVL 400P photoreaction apparatus. Wakogel C-200 and Wakogel B-5 F were used for column and thin-layer chromatography, respectively.

Addition Reaction of 1a with 2. A mixture of **1a** (4.86 g, 46 mmol) and **2** (2.60 g, 10 mmol) was heated at 200 °C for 2 h. The reaction mixture was chromatographed on silica gel to give the recovered **1a** (2.22 g, hexane–ethyl acetate 7:3), the recovered **2** (0.52 g, hexane–ethyl acetate 7:3) and an oil **3a** (2.82 g, 77%, hexane–ethyl acetate 65:35).

3a: HRMS: 365.1296. Calcd for $C_{21}H_{19}NO_5$: 365.1330. MS *m/z* (rel intensity): 365 (M^+, 57), 334 (92), 333 (100). IR (oil): 2250, 1730, 1710, 1665 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.94 (m, 2H, H_a and H_b), 2.24 (d, H_c), 2.27 (t, H_d), 2.40 (d, H_e), 3.13 (dd, H_f), 3.31 (d, H_g), 3.38 (bs, H_h), 3.48 (bs, H_i), 3.81 (s, 3H, Me), 3.83 (s, 3H, Me), 5.56 (d, H_j), 5.81 (dd, H_k), 6.12 (dd, H_l), 7.16 (dd, H_m). Coupling constants in Hz: J_{ad}=3.5, J_{bd}=3.5, J_{ce}=9.0, J_{fl}=7.9, J_{fm}=8.6, J_{gk}=7.6, J_{jm}=10.9, J_{kl}=7.9. ^{13}C NMR (C_6D_6) δ=11.8, 29.7, 30.1, 34.6, 38.7, 39.0, 39.7, 40.8, 51.9, 58.0, 119.3, 125.7, 129.1, 134.9, 141.5, 141.9, 153.6, 165.7, 165.8, 194.5.

Addition Reaction of 1b with 2. A mixture of **1b** (1.66 g, 9 mmol) and **2** (0.79 g, 3 mmol) was heated at 200 °C for 2.7 h. The reaction mixture was chromatographed on silica gel to give the recovered **1b** (350 mg, benzene–ether 8:2) and a mixture of the recovered **2** and **3b** (875 mg, benzene–ether 7:3), which was further separated with thin-layer chromatography on silica gel using ether–chloroform 1:1 as a developing solvent to give the recovered **2** (52 mg, R_f=0.75) and crystals **3b** (420 mg, 45%, R_f=0.52). Recrystallization from ethyl acetate gave pure **3b**.

3b: mp 206—207 °C. HRMS: 413.1351. Calcd for $C_{24}H_{19}N_3O_4$: 413.1328. MS *m/z* (rel intensity): 413 (M$^+$, 33), 381 (90), 353 (67), 321 (100). IR (KBr): 2225, 1720, 1710 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.96 (m, 2H, H_a and H_b), 2.12 (d, H_c), 2.14 (t, H_d), 2.34 (d, H_e), 3.16 (dd, H_f), 3.38 (bs, H_h), 3.53 (bs, H_i), 3.78 (d, H_g), 3.82 (s, 3H, Me), 3.85 (s, 3H, Me), 5.99 (dd, H_k), 6.17 (dd, H_l), 6.45 (d, H_j), 7.00 (dd, H_m). Coupling constants in Hz: J_{ad}=3.0, J_{bd}=3.0, J_{ce}=8.6, J_{fl}=7.6, J_{fm}=8.0, J_{gk}=7.6, J_{kl}=7.6, J_{jm}=9.6. ^{13}C NMR ($CDCl_3$) δ=11.9, 29.9, 30.0, 37.8, 38.6, 39.1, 40.7, 41.1, 46.8, 52.5, 52.6, 111.7, 112.6, 112.7, 118.8, 124.9, 125.2, 135.8, 141.1, 141.4, 152.8, 165.5, 165.7, 169.5.

Photoreaction of 3a. A solution of **3a** (183 mg, 0.5 mmol) in dry ether (200 ml) was irradiated using a high-pressure mercury lamp (Riko UVL 400P) for 1.5 h at room-temperature. After evaporation of the solvent on a rotary evaporator the residual oil was subjected to thin-layer chromatography on silica gel using ether as a developing solvent to give crystals **4a** (36 mg, 19%, R_f=0.34). Recrystallization from benzene gave pure **4a**.

4a: mp 182—183 °C. HRMS: 365.1259. Calcd for $C_{21}H_{19}NO_5$: 365.1262. MS *m/z* (rel intensity): 365 (M$^+$, 31), 333 (100), 350 (28), 246 (19). IR (KBr): 2950, 2230, 1730, 1720, 1655 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.36 (m, H_a), 2.15 (m, 2H, H_b and H_c), 2.27 (dd, H_d), 2.38 (dd, H_e), 2.55 (bs, 2H, H_f and H_g), 2.70 (ddd, H_h), 2.80 (ddd, H_i), 3.19 (ddd, H_j), 3.31 (ddd, H_k), 3.74 (s, 6H, 2Me), 6.33 (dd, H_l), 7.01 (dd, H_m). Coupling constants in Hz: J_{ab}=3.6, J_{ac}=3.6, J_{de}=8.3, J_{di}=2.0, J_{eh}=2.0, J_{fk}=1.3, J_{gj}=1.3, J_{hk}=3.5, J_{hm}=9.0, J_{ij}=3.5, J_{il}=2.0, J_{jk}=9.0, J_{lm}=11.0. ^{13}C NMR ($CDCl_3$) δ=3.9, 17.3, 17.4, 38.6, 39.1, 39.8, 40.9, 41.8, 42.8, 45.2, 52.4, 54.3, 54.6, 57.9, 120.3, 135.8, 149.8, 171.8, 172.0.

Thermal Reaction of 3a. Crystals of **3a** (1.34 g) was heated at 250 °C for 2 h under a nitrogen stream. The resulting oily material was subjected to thin-layer chromatography on silica gel using ether as a developing solvent to give crystals **7a** (240 mg, 18%, R_f=0.44) and **8a** (310 mg, 23%, R_f=0.26). Recrystallization from ethyl acetate gave pure **7a** and **8a**.

7a: mp 226—228 °C. HRMS: 365.1261. Calcd for $C_{21}H_{19}NO_5$: 365.1262. MS *m/z* (rel intensity): 365 (M$^+$, 50), 334 (33), 298 (73), 202 (100). IR (KBr): 3010, 2950, 2200, 1720, 1660 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.81 (ddd, H_a), 2.02 (ddd, H_b), 2.17 (d, H_c), 2.25 (dd, H_d), 2.58 (dd, H_e), 2.89 (d, H_f), 3.35 (m, 2H, H_g, H_h), 3.43 (s, 3H, Me), 3.50 (s, 3H, Me), 5.72 (dd, H_i), 5.76 (dd, H_j), 5.91 (dd, H_k), 6.06 (dd, H_l), 6.56 (dd, H_m). Coupling constants in Hz: J_{ab}=20.0, J_{ad}=4.0, J_{aj}=4.4, J_{bd}=3.0, J_{bj}=3.3, J_{cf}=8.5, J_{el}=6.8, J_{em}=8.6, J_{gi}=2.0, J_{gk}=7.9, J_{im}=11.4, J_{kl}=8.1. ^{13}C NMR ($CDCl_3$) δ=35.3, 39.3, 42.0, 42.6, 43.0, 43.8, 52.5, 52.6, 59.2, 117.6, 118.8, 127.2, 129.3, 134.3, 136.5, 140.4, 145.8, 152.4, 165.7, 166.5, 195.3

8a: mp 222—223 °C. HRMS: 365.1254. Calcd for $C_{21}H_{19}NO_5$: 365.1262. MS *m/z* (rel intensity): 365 (M$^+$, 23), 334 (29), 233 (35), 201 (100). IR (KBr): 2950, 2220, 1710, 1660 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.61 (m, 2H, H_a, H_b), 2.86 (d, H_c), 2.89 (bs, H_d), 3.25 (dd, H_e), 3.25 (s, H_f), 3.34 (d, H_g), 3.46 (dd, H_h), 3.82 (s, 6H, 2Me), 5.78 (dd, H_i), 6.06 (dd, H_j), 6.29 (dd, H_k), 6.38 (dd, H_l), 7.25 (dd, H_m). Coupling constants in Hz: J_{ad}=2.5, J_{al}=3.1, J_{bd}=2.5, J_{bl}=3.1, J_{cg}=9.7, J_{ek}=6.2, J_{em}=7.5, J_{hi}=2.0, J_{hj}=7.0, J_{im}=11.4, J_{jk}=8.1. ^{13}C NMR ($CDCl_3$) δ=34.2, 39.1, 40.8, 42.6, 43.7, 47.5, 52.6, 52.7, 61.0, 117.5, 118.7, 126.5, 129.2, 134.7, 138.2, 138.6, 145.0, 153.8, 165.2, 167.0, 195.7.

Thermal Reaction of 3b. Crystals of **3b** (210 mg) was heated at 250 °C for 2 h under a nitrogen stream. The resulting oily material was subjected to thin-layer chromatography on silica gel using chloroform–ethyl acetate 4:1 as a developing solvent to give crystals **7b** (25 mg, 12%, R_f=0.75), recovered **3b** (55 mg, 26%, R_f=0.68), and **8b** (48 mg, 23%, R_f=0.55). The crystals **7b** and **8b** were purified by recrystallization from ethyl acetate.

7b: mp 173—175 °C. HRMS: 413.1373. Calcd for $C_{24}H_{19}N_3O_4$: 413.1375. MS *m/z* (rel intensity): 413 (M$^+$, 20), 382 (46), 381 (100), 294 (29). IR (KBr): 2950, 2225, 1720 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.57 (m, 2H, H_a, H_b), 2.72 (dd, H_d), 2.92 (d, H_c), 3.14 (d, H_f), 3.32 (dd, H_e), 3.40 (bs, H_h), 3.77 (dd, H_g), 3.81 (s, 3H, Me), 3.86 (s, 3H, Me), 6.04 (dd, H_k), 6.34 (dd, H_l), 6.41 (dd, H_j), 6.55 (dd, H_i), 6.98 (dd, H_m). Coupling constants in Hz: J_{ad}=3.0, J_{aj}=3.6, J_{bd}=3.0, J_{bj}=3.6, J_{cf}=8.0, J_{el}=6.8, J_{em}=8.0, J_{gi}=1.4, J_{gk}=8.0, J_{kl}=7.6, J_{im}=10.0. ^{13}C NMR δ=35.1, 39.2, 43.1, 43.5, 44.1, 45.0, 48.3, 52.7, 52.9, 111.6, 112.6, 115.6, 118.5, 125.3, 127.2, 135.1, 136.6, 139.7, 145.7, 150.6, 165.4, 166.4, 169.6.

8b: mp 165—166 °C. HRMS: 413.1374. Calcd for $C_{24}H_{19}N_3O_4$: 413.1375. MS *m/z* (rel intensity): 413 (M$^+$, 42), 381 (100), 353 (47), 294 (49). IR (KBr): 2225, 1720, 1710 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.63 (m, 2H, H_a, H_b), 2.74 (d, H_c), 2.94 (dd, H_d), 3.15—3.36 (m, 4H, H_e, H_f, H_g, H_h), 3.83 (s, 3H, Me), 3.84 (s, 3H, Me), 6.02 (dd, H_j), 6.35 (dd, H_k), 6.37 (dd, H_l), 6.56 (dd, H_i), 7.09 (dd, H_m). Coupling constants in Hz: J_{ad}=3.2, J_{al}=3.6, J_{bd}=3.2, J_{bl}=3.6, J_{ek}=6.8, J_{em}=8.8, J_{hi}=1.4, J_{hj}=7.8, J_{im}=9.8, J_{jk}=8.4. ^{13}C NMR ($CDCl_3$) δ=34.4, 40.8, 41.9, 42.5, 43.8, 48.2, 50.0, 52.7, 52.8, 111.7, 112.8, 116.8, 118.5, 125.0, 125.9, 136.3, 137.6, 138.5, 145.0, 152.8, 165.3, 166.6, 169.6.

Short Period Thermal Reaction of 3b. Crystals of **3b** (370 mg) were heated at 250 °C for 30 min under a nitrogen stream. The same treatment as mentioned gave an oil **6b** (47 mg, 12%, R_f=0.66) and crystals **8b** (37 mg, 10%, R_f=0.81).

6b: IR (oil): 2950, 2210, 1720, 1710 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.88 (dd, H_a), 2.98 (d, H_b), 3.14 (dd, H_c), 3.32 (dd, H_d), 3.40 (dd, H_e), 3.49 (d, H_f), 3.75 (dd, H_g), 3.83 (s, 3H, Me), 3.86 (s, 3H, Me), 5.44 (dd, H_h), 6.08 (dd, H_i), 6.24 (dd, H_j), 6.32 (dd, H_k), 6.54 (dd, H_l), 7.00 (dd, H_m). Coupling constants in Hz: J_{ab}=8.8, J_{ad}=3.4, J_{cd}=1.4, J_{cj}=9.0, J_{ek}=6.2, J_{em}=8.2, J_{fh}=3.6, J_{gi}=6.6, J_{gl}=1.8, J_{hj}=11.8, J_{ik}=8.2, J_{lm}=11.0. ^{13}C NMR ($CDCl_3$) δ=34.4, 41.5, 41.8, 43.2, 44.0, 44.9, 48.6, 52.7, 52.8, 111.6, 112.7, 116.7, 122.6, 125.4, 127.4, 131.7, 133.7, 134.5, 144.7, 150.9, 165.1, 167.1, 169.9.

Thermal Reaction of 6b. Crystals of **6b** (40 mg) were heated at 250 °C for 5 min under a nitrogen stream. The ^{1}H NMR spectrum showed that **6b** changed to **8b** quantitatively.

Photoreaction of 7a. A solution of **7a** (200 mg, 0.5 mmol) in dry ether (200 ml) was irradiated using a low-pressure mercury lamp (Riko UVL 30 LQ) for 5 h at room temperature under a nitrogen stream. The same treatment as above using ether–ethyl acetate 5 : 1 as a developing solvent gave crystals **9a** (44 mg, 23%, R_f=0.36), which were purified by recrystallization from benzene.

9a: mp 253—254 °C. HRMS: 365.1267. Calcd for $C_{21}H_{19}NO_5$: 365.1262. MS *m/z* (rel intensity): 365 (M$^+$, 47), 333 (100), 245 (27). IR (KBr): 2950, 2220, 1720, 1660 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.33 (m, H_a), 2.75 (ddd, H_b), 2.88 (dd, H_c), 2.89 (ddd, H_d), 3.23 (d, H_e), 3.32 (dd, H_f), 3.35 (ddd, H_g), 3.61 (ddd, H_h), 3.73 (ddd, H_i), 3.76 (s, 3H, Me), 3.79 (s, 3H, Me), 4.00 (ddd, H_j), 6.77 (dd, H_k), 7.12 (dd, H_l), 7.26 (dd, H_m). Coupling constants in Hz: $J_{ad}=3.9$, $J_{ag}=3.9$, $J_{aj}=2.0$, $J_{bf}=2.2$, $J_{bj}=3.9$, $J_{bm}=8.4$, $J_{cf}=9.0$, $J_{ch}=2.2$, $J_{dg}=20.7$, $J_{dk}=3.9$, $J_{ei}=2.0$, $J_{gk}=3.9$, $J_{hi}=4.0$, $J_{hl}=1.4$, $J_{ij}=8.4$, $J_{lm}=9.8$. ^{13}C NMR ($CDCl_3$) δ=31.7, 40.7, 43.9, 44.9, 45.4, 45.6, 45.8, 45.9, 51.6, 51.9, 55.6, 59.5, 60.8, 112.9, 135.3, 145.4, 149.3, 171.4, 171.8, 199.2.

Photoreaction of 8a. A solution of **8a** (200 mg, 0.5 mmol) in dry ether (200 ml) was irradiated using a low-pressure mercury lamp (Riko UVL30 LQ) for 1 h at room temperature. After evaporation of the solvent the residual oil was subjected to thin-layer chromatography on silica gel using ether–ethyl acetate 5:1 as a developing solvent to give crystals **10a** (74 mg, 38%, R_f=0.49), which were purified by recrystallization from benzene.

10a: mp 259—260 °C. HRMS: 365.1247. Calcd for $C_{21}H_{19}NO_5$: 365.1262. MS *m/z* (rel intensity): 365 (M^+, 54), 333 (100), 245 (25). IR (KBr): 2950, 2220, 1720, 1650 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.05 (dd, H_a), 2.47 (d, H_b), 2.69 (dd, H_c), 2.87 (m, 4H, H_d, H_e, H_f, H_g), 3.19 (ddd, H_h), 3.27 (bs, 2H, H_i, H_j), 3.76 (s, 3H, Me), 3.79 (s, 3H, Me), 6.37 (dd, H_k), 6.47 (dd, H_l), 7.05 (dd, H_m). Coupling constants in Hz: $J_{ad}=4.3$, $J_{ae}=2.9$, $J_{bh}=2.1$, $J_{ch}=1.2$, $J_{cm}=9.0$, $J_{dl}=3.1$, $J_{el}=3.1$, $J_{fh}=8.4$, $J_{gk}=1.2$, $J_{km}=10.0$. ^{13}C NMR ($CDCl_3$) δ=31.9, 41.3, 42.0, 44.2, 44.6, 44.7, 46.4, 48.8, 52.1, 52.4, 55.1, 59.6, 60.7, 112.2, 119.8, 135.5, 146.0, 150.1, 171.6, 171.7, 201.1.

References

1) Y. Kitahara, I. Murata, and T. Nitta, *Tetrahedron Lett.*, **1967**, 3003; J. Ciabattoni, J. E. Crowly, and A. S. Kende, *J. Am. Chem. Soc.*, **89**, 2778 (1967); M. Oda and Y. Kitahara, *J. Chem. Soc., Chem. Commun.*, **1969**, 352; M. Oda, H. Tani, and Y. Kitahara, *ibid.*, **1969**, 739; T. H. Kinstle and P. D. Carpenter, *Tetrahedron Lett.*, **1969**, 3943; M. Oda and Y. Kitahara, *Bull. Chem. Soc. Jpn.*, **43**, 1920 (1970); M. Oda, Y. Kayama, and Y. Kitahara, *J. Chem. Soc., Chem. Commun.*, **1971**, 505.

2) a) K. Saito, T. Watanabe, and K. Takahashi, *Chem. Lett.*, **1989**, 2099; b) R. P. Gandhi and M. P. S. Ishar, *ibid.*, **1989**, 101; c) K. Hayakawa, H. Nishiyama, and K. Kanematsu, *J. Org. Chem.*, **50**, 512 (1985); d) R. Gomper and U. Wolf, *Annalen*, **1979**, 1388.

3) G. R. Tian, S. Sugiyama, A. Mori, and H. Takeshita, *Bull. Chem. Soc. Jpn.*, **61**, 2393 (1988); G. R. Tian, S. Sugiyama, A. Mori, H. Takeshita, M. Higashi, and H. Yamaguchi, *Chem. Lett.*, **1988**, 941.

4) K. Saito, *Chem. Lett.*, **1983**, 463; K. Saito, H. Kojima, T. Okudaira, and K. Takahashi, *Bull. Chem. Soc. Jpn.*, **56**, 175 (1983); K. Saito, *ibid.*, **60**, 2105 (1987); K. Saito and K. Takahashi, *Chem. Lett.*, **1989**, 925.

5) K. Alder, K. Kaiser, and M. Schmacher, *Ann. Chim.*, **602**, 80 (1957); S. Kagabu, Ph. D. Thesis, University of Freiburg, Germany, 1970; H. Prinzbach, *Tetrahedron Lett.*, **1979**, 3487: K. Saito, S. Isobe, K. Ito, S. Kagabu, and K. Takahashi, *Chem. Lett.*, **1989**, 1541; K. Saito, K. Ito, and K. Takahashi, *Heterocycles*, **29**, 2135 (1989).

6) J. Meinwald, S. L. Emerman, N. C. Yang, and G. Buchi, *J. Am. Chem. Soc.*, **77**, 4400 (1955); T. Nozoe, T. Mukai, T. Nagase, and Y. Toyooka, *Bull. Chem. Soc. Jpn.*, **33**, 1247 (1960).

7) Molecular orbital calculations were carried out at the Computer Center of the Institute for Molecular Science using MOPAC program (J. J. P. Stewart, *Q. C. P. E. Bull.*, **3**, 43 (1983)).

8) H. Takeshita, T. Hatsui, I. Shimooda, and H. Mametsuka, *Bull. Chem. Soc. Jpn.*, **55**, 2291 (1982).

9) The authors are indebted to the referee for his suggestion that an another type of explanation for the favorable endo-type formation can be given according to the following report: W. C. Herndon and L. H. Hall, *Tetrahedron Lett.*, **1967**, 3095.

10) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2045 (1969); M. C. Bohm, R. V. C. Carr, R. Gleiter, and L. A. Paquette, *ibid.*, **102**, 7218 (1980).

11) H. Prinzbach, *Chem. Ber.*, **101**, 4066 (1968).

12) C. H. Depuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *J. Am. Chem. Soc.*, **87**, 4006 (1965); R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965); C. W. Jefford, S. Mahajan, J. Waslyn, and B. Waegell, *ibid.*, **87**, 2183 (1965); L. Ghosez, P. Laroche, and S. Slinckx, *Tetrahedron Lett.*, **1967**, 2767; L. Ghosez, G. Slinckz, M. Glineur, P. Hoet, and P. Laroche, *ibid.*, **1967**, 2773; C. W. Jefford and R. T. Medary, *Tetrahedron*, **23**, 4123 (1967).