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A Comparative Study of the Photo-induced Berson-Willcott Rearrangement of Methyl 3-Isopropyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene-1-*exo*- and 1-*endo*-acetate

Masahiko Kato, Masakazu Tsuji, and Toshio Miwa

Faculty of Science, Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka 558

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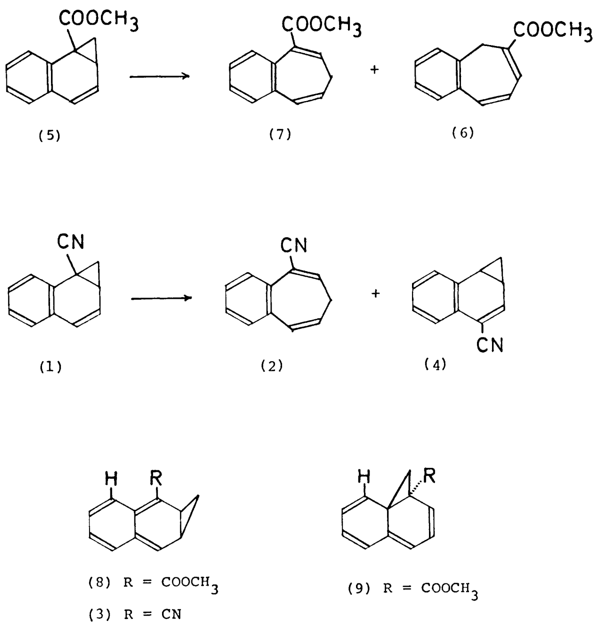
The effect of 1-*exo*- and 1-*endo*-methoxycarbonylmethyl groups on the course of the photo-induced Berson-Willcott rearrangement of methyl 1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene-1-acetate have been studied. Different reaction rates with the same final products have been observed and are discussed from the view of the stereochemical course of the reaction, which strongly supports the 60°-mechanism, *i.e.*, a slither motion of C-1 with inversion of configuration.

The photo-induced rearrangements of some benzonorcaradiene derivatives have been studied extensively.[1—5]

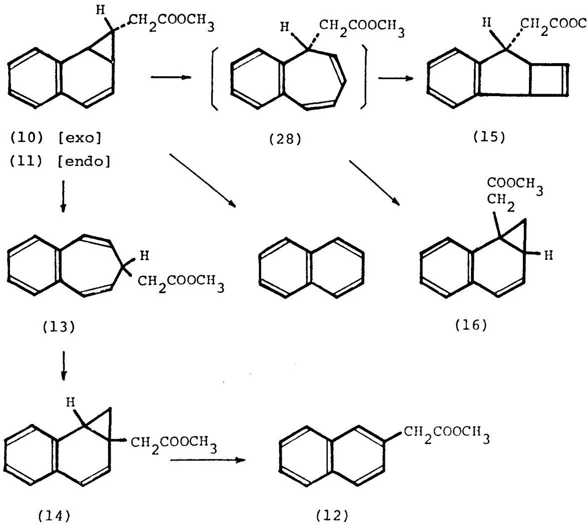
Swenton *et al.* demonstrated that the direct irradiation of 7b-cyano-1a,7b-dihydrocyclopropa[*a*]naphthalene (**1**) lead smoothly to products, **2** and **4**, through intermediate **3**. They discussed a decrease in the quantum yield of disappearance of 7b-methoxycarbonyl-1a,7b-dihydrocyclopropa[*a*]naphthalene (**5**) compared with that of **1** and the rearrangement towards **6**, in addition to **7**, on irradiation of **5** in terms of increased peri-interaction, which retarded the formation of **7**, in the intermediate **8**.

Such interaction was not observed in the intermediates, **3** and **9**, leading to **2** and **6** respectively; thus the formation of the latters becomes favorable.[3]



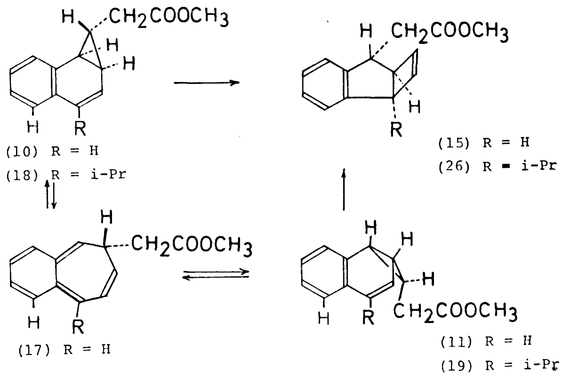
Scheme 1.

The photo-induced rearrangement of an *exo-endo* mixture of methyl 1a,7b-dihydro-1*H*-cyclopropa[*a*]-naphthalene-1-acetates, (**10**) and (**11**), has been investigated and gives, in addition to naphthalene, **12**, **13**—**16**.[4] The stereochemical course of the rearrangement of **10** and/or **11** to methyl 2a,7a-dihydro-7*H*-cyclobut[*a*]indene-7-*anti*-acetate (**15**) has been reported.[5] However, since compounds **10** and **11** interconvert with each other under thermal (90 °C, 5 min) and photolytic conditions,[4] it was uncertain as to whether either one or both of the isomeric esters had actually rearranged to **15**.



Scheme 2.

The *exo-endo* interconversion between **10** and **11** occurs apparently through **17** by the fission of the C$_{1a}$–C$_{7b}$ bond.[4] Since substitution on the C$_3$ with a bulky group (R) would retard the interconversion by way of peri-interaction, this would be expected to effect the photochemical reaction pathways as reported by Swenton *et al.* Therefore isopropyl derivatives, **18** and **19**, were selected as candidates for the present study.

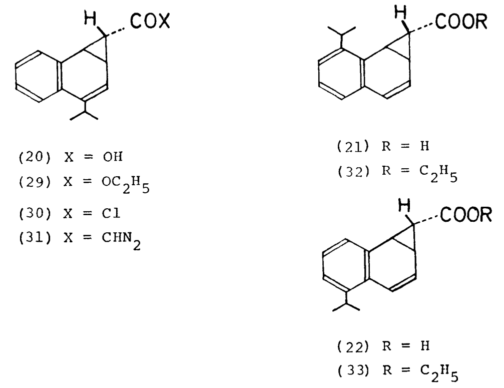


Scheme 3.

These compounds were thought to be suitable in order to gain more profound insight into the stereochemical course of the benzonorcaradiene system. Up to date, there have been no reports about the comparative study on the photochemical behavior of *exo* and *endo* isomers of 1-substituted 1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene derivatives. The *endo* isomer was of special interest since it should exibit a repulsive interaction between the pi-electron(s) on the six-membered ring and the substituent on C-1. The presence of such an interaction may possibly cause an alteration of the reaction rates or pathway.

Results and Discussion

3-Isopropyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene-1-*exo*-carboxylic acid (**20**) was formed as the main product, along with **21** and **22**, from the reaction of 1-isopropylnaphthalene (**23**) with ethyl diazoacetate and subsequent hydrolysis. Arndt-Eistert reaction of **20** gave the desired compound **18**, the 3-isopropyl derivative of **10**, as a crystalline product, mp 84.5—85.5 °C. Compound **18** exhibited a well defined NMR spectrum (100 MHz); an olefinic proton doublet at $\delta=6.01$ and isopropyl signals at 1.12(d) and 1.13(d) (6H) and 2.90 (1H, septet). Signals attributable to three protons on the cyclopropane ring were similar in their chemical shifts and coupling constants to those of **10**,[4] which indicated that the configuration of the methoxycarbonylmethyl group was *exo*. The UV spectrum was also similar in shape to that of **10**[4] but the maximum (278 nm) showed a small bathochromic shift effected by the substitution with the isopropyl group.



Scheme 4.

Heating **18** to 130 °C for 30 min, gave an equilibrium mixture composed of **18** and **19** in the ratio of 3 : 2. Isolation of **19** from the mixture was achieved using column chromatography on Silicic Acid with hexane–ether (95:5 v/v) eluant. The structure of **19** was assigned on the basis of the spectral data. The UV spectrum was superimposable with that of **18**. The NMR spectrum of **19** showed signals attributable to the three protons on the cyclopropane ring at $\delta=1.6$—1.9 (H_1), 2.24 (H_{1a}), and 2.57 (H_{7b}, t). Double resonance spectrum obtained by irradiation at H_2 gave the coupling constants ($J_{H_1-H_{1a}}=J_{H_1-H_{7b}}=7.5$; $J_{H_{7b}-H_{1a}}=9$), which defined a *cis* relation to each other. The *endo* configuration of the methoxycarbonylmethyl group was further supported by the higher field resonance of the methylene proton signals compared with those of the *exo*-isomer **18**. When heated above 130 °C, **19** gave the same mixture of **18** and **19** as that obtained from **18** by the same treatment.

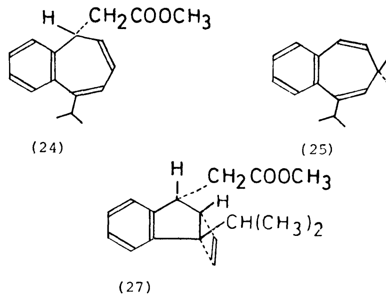
Both **18** and **19** were found to be thermally stable below 100 °C, and did not interconvert under the influence of UV irradiation, as expected from the above data.

Dirrect irradiation of **18** in methanol through a Pyrex filter with use of a HPL for 20 min gave **23**, methyl 9-isopropyl-5*H*-benzocycloheptene-5-acetate (**24**), methyl 5-isopropyl-7*H*-benzocycloheptene-7-acetate (**25**), *exo*-and *endo*-isomers of methyl 2a-isopropyl-2a,7a-dihydro-7*H*-cyclobut[*a*]indene-7-acetate (**26, 27**), in 10, 35, 15, 12, and 6% yields, respectively, estimated by GLC (15% polydiethylene glycol adipate

TABLE 1. ESTIMATED YIELDS OF PRODUCTS IN THE COURSE OF IRRADIATION OF **18** AND **19** (8×10^{-4} mol/l MeOH)

Irradiation time (h)	Starting material	Eicosane (%)	% Yields of products[a)					
			18 or **19**	**23**	**25**	**24**	**26**	**27**
0	**18**	15.4	100					
	19	12.7	100					
1	**18**	15.4	42.8	5.1	11.1	24.6	1.0	0.8
	19	12.7	24.0	6.2	7.2	42.3	3.5	1.9
2	**18**	15.4	14.1	8.4	14.8	35.2	5.8	3.2
	19	12.7	3.6	9.3	9.8	47.0	13.9	6.9
3	**18**	15.4	4.5	10.2	14.8	35.4	11.8	6.0
	19	12.7	—	9.6	8.1	37.2	19.8	9.6
4	**18**	15.3	—	11.2	15.3	29.9	17.0	8.7
	19	12.7	—	9.4	6.4	17.1	32.4	16.1
5	**18**	15.3	—	11.0	11.7	26.0	22.1	10.4
	19	12.7	—	10.6	6.0	21.0	31.3	15.1
6	**18**	15.4	—	14.1	3.3	17.4	26.6	13.0
	19	12.7	—	11.0	5.2	15.5	34.5	17.9

a) The amount of each compound was estimated by their peak areas relative to that of eicosane.



Scheme 5.

on Chromosorb WAW). Photolysis of the *endo* isomer (**19**) gave essentially the same products, except in their yields (Table 1).

The structures of these compounds were determined on the basis of their spectral data. The UV spectrum of **24** showed a maximum at 271 nm which suggested the presence of 5*H*-benzocycloheptene moiety (λ_{max} 275 nm).[7] Although the NMR spectrum taken at room temperature was too broad to investigate spin-spin coupling, those obtained at $+2$—-45 °C clearly demonstrated fine splitting. The presence of three vicinal olefinic protons was observed from the NMR spectra (δ=5.45, 5.91, 6.45; $J_{H_4-H_5}=5.5$; $J_{H_5-H_6}=9.5$; $J_{H_6-H_7}=5$ Hz). The coupling pattenrs of the benzylic methine proton and the acetate-methylene protons defined the position of the substituents.

The UV spectrum of **25** was similar to that of 7*H*-benzocycloheptene (λ_{max} 228 (ε 44000); 256 ^{sh} nm (ε 5200).[7] The presence of 1H signal (δ=6.47), corresponding to the proton alpha to phenyl group, determined the position of the isopropyl group to be C-2. The proton-proton coupling pattern of $>$CH–CH$_2$–COO [ABX type: $J_{AB}=15.5$; $J_{AX}=10$; $J_{BX}=5.5$ Hz] supported that of methyl 7*H*-benzocycloheptene-7-acetate. Direct irradiation of **24** gave mainly a mixture of **26** and **27** in a ratio of 2 : 1. The UV spectra, together with the coupling pattern of the olefinic proton signals in the NMR spectra suggested the presence of the 2a,7a-dihydro-7*H*-cyclobut[*a*]-indene structure. The absence of a lower field signal characteristic of the benzylic methine proton on the cyclobutene ring for both compounds, **26** and **27**, assigned the position of the isopropyl group on C-1. The *endo* structure for **27** was assigned from a larger separation of the two olefinic proton signals, caused by the proximity effect of the methoxycarbonyl group, and the larger splitting signal of the proton on C-5, coupled with the proton on C-4, compared with those of **26**.

It was observed in the photochemical reactions of **18** and **19** that the primary rearrangement products, **24** and **25**, were formed as the major products. Benzonorcaradiene derivatives were not detected in the products. In the photolysis of **10**, **28** was not detected and **13** was obtained in a small amount in the photolysate; further rearranged products were formed, even if the reaction was interupted at the initial stage.[4,7] Cycloheptatrienes are not planar molecules but have the boat conformations,[8] therefore the isopropyl group in **24** and **25** appears to be fixed in a non-coplanar position with respect to the peri C–H bond thereby minimising the mutual steric interaction. The isopropyl group on C-3 in **14** or **16** appears to be fixed near the coplanar position to the peri C–H bond, causing a large repulsive interaction. These steric repulsions give rise to interupt further rearrangement of the primary photo-products, **24** and **25**, to benzonorcaradienes.

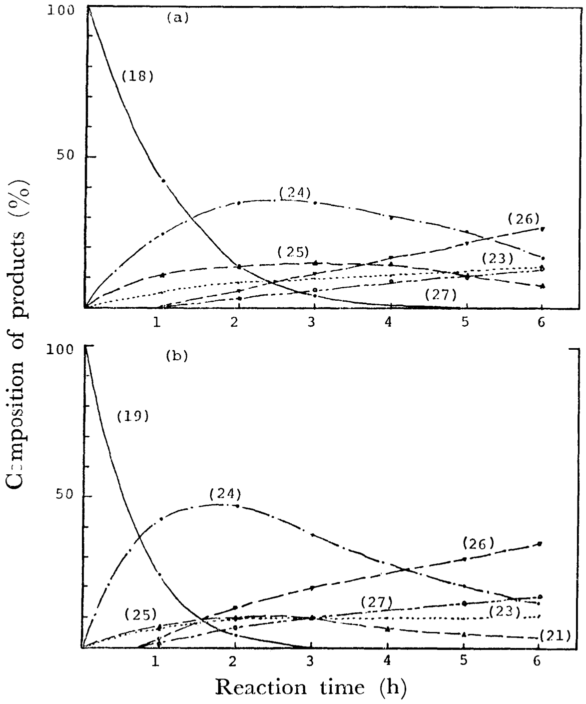


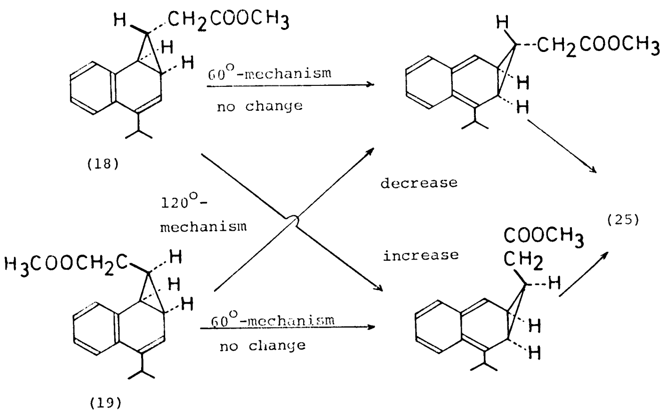
Fig. 1. Plots of the products composition *versus* irradiation time. Starting materials; (a) **18** and (b) **19**.
……: (**23**), —·—·—: (**24**), ———: (**25**), ———: (**26**), ————: (**27**).

To determine the relative reactivities of the isomeric esters, **18** and **19**, they were photolyzed independently in methanol at the same concentrations (8×10^{-4} mol/l). Eicosane was added as an internal standard and the merry-go-round apparatus was used. The products were analysed for by GLC at regular time intervals and the results are given in Fig. 1.

At the initial stage of the reaction, it may be seen that the rate of formation of **24** from **19** was twice as effective as that of **24** from **18**, in conjugation with the disappearance of **19** which disappeared twice as fast as that of **18**. Initially the rate of formation of **25** from **19** looks slower than that from **18**. However, as the decrease in concentration of **19** is much faster than that of **18**, the ratio of concentrations of **25**/**19** and that of **25**/**18** at low conversion (after one hour irradiation) are important and are almost similar (0.30 and 0.26, respectively).

Since the UV spectra of the isomeric esters, **18** and **19**, are superimposable, the methoxycarbonylmethyl group on C-1 appears to have little influence on the electronic state of the cyclopropane ring. Assuming that the electronic structures of the esters are quite similar to each other except for steric requirements, the differences in reactivities between **18** and **19** will be determined by the degree of steric freedom in the intermediates from **18** and **19**. Berson,[9] Woodward and Hoffman[10] have suggested that the Berson-Willcott rearrangement of simple norcaradienes must follow after either one of the two possible modes of mechanisms, *i.e.*, the 60°- and the 120°-mechanism. When these mechanisms are applied to the present photo-induced rearrangement of **18** and **19**, the change in steric interference will govern the reaction pathway as shown in Schemes 6 and 7.

Path a



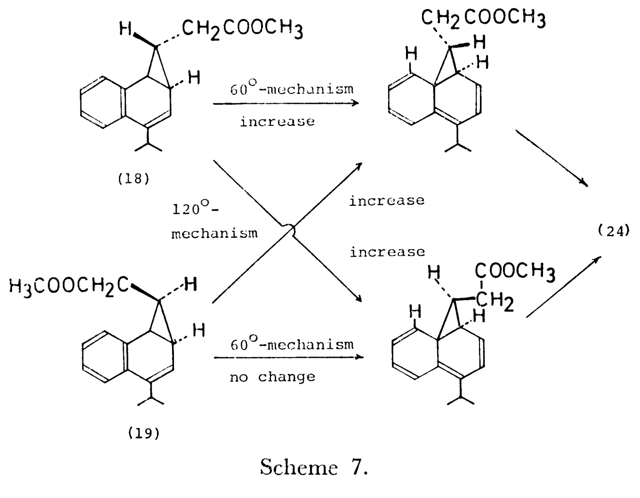
Scheme 6.

As observed from previous experiments on optically active **10**,[10] high stereospecificity of these reactions suggests that the reaction may follow either of the two mechanisms.

If the reactions toward Path a follow 60°-mechanism, formation of **25** from both **18** and **19** will proceed at similar rates. If it follows 120°-mechanism, formation of **25** from **18** will become less than that from **19**. The results on the ratios of concentrations (**25**/**19** and **25**/**18**) at low conversion discussed above support the 60°-mechanism.

Similarly, since formation of **24** from **18** is apparently retarded compared with that from **19** (Fig. 1), another Path b clearly follows the 60°-mechanism, that is, slither motion of C-1 with inversion of the configuration. This latter claim is in line with the results obtained from the study on an photo-induced rearrangement of optically active substance **10**.[5]

Path b



Scheme 7.

The data supports the 60°-mechanism for the photo-induced rearrangement of methyl 3-isopropyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene-1-acetate in both directions. The precise stereochemistry for Path a has recently been established with use of the optically active 3-*t*-butyl derivative of **10** and the results will be reported elswhere.

Experimental

The NMR spectra were obtained on a JEOL Model PS-100 spectrometer with carbon tetrachloride as the solvent and TMS as the internal standard, unless otherwise specified. The chemical shifts are expressed in ppm from TMS. The IR spectra were recorded on a JASCO spectrometer Model IRE and the UV on a Hitachi Recording Spectrometer Model 323. GLC analysis was carried out on a Varian Aerograph Model 90P gas chromatograph under quoted conditions. The light source for photolysis, used throughout this experiments, was a Ushio high pressure mercury lamp, UM-452, with Pyrex filter.

*Synthesis of 3-Isopropyl-1a,7b-dihydro-1*H*-cyclopropa*[a]*naphthalene-1-*exo*-carboxylic Acid (**20**).* *Reaction of Isopropylnaphthalene (**23**) with Ethyl Diazoacetate*: To 24.6 g (0.144 mol) of **23**, containing 195 mg of copper powder heated at 145—150 °C, was added drop by drop 2.88 g (25.2 mmol) of ethyl diazoacetate over a period of 1 h with vigorous stirring. The mixture was further stirred for 2 h at 145 °C (gas evolution; 610 ml at 25 °C, 95% of theoretical), and then 21.5 g of **23** was recovered by distillation (97—100 °C/7 mmHg). The experiment was repeated three times and the collected residue taken in CH_2Cl_2 was filtered from copper powder and subsequently distilled to give 7.34 g of yellow liquid, bp 136—140.5 °C (1 mmHg). Repeated column chromatography of the distillate on Silicic Acid[11] (hexane-ether 19 : 1 v/v) gave three fractions: Fr. 1; 2.32 g [**29**+**32**]; Fr. 2; 1.73 g [**29**+**32**+**33**]; Fr. 3; 2.08 g [**29**+**33**].

Alkaline Hydrolysis of Fraction 3. The above Fr. 3 (2.08 g), dissolved in 0.5 M 85% aq ethanolic KOH (32 ml) was refluxed for 3 h. The resulting solution was then diluted with water (32 ml) and reduced to half volume under reduced pressure. After being washed with ether, the ice-cooled aq solution was acidified carefully with cold 2 M HCl in the presence of 30 ml of ether. The separated aq solution was extracted three times with ether, and the combined ether extracts were washed with saturated aq NaCl and dried (anhyd Na_2SO_4). After subsequent evaporation of ether, the remaining crystalline acid mixture was recrystallized from aq methanol to give **20** (647 mg) and a 1 : 1 mixture of **20** and **22** (390 mg). **20** mp 200—201.5 °C. IR ν_{max}^{Nujol}: 2650, 2560, 1680, 955 cm^{-1}. NMR ($CDCl_3$) δ=0.78 (1H, t, J=3.5 Hz), 1.14 (3H, d, J=6.5 Hz), 1.17 (3H, d, J=6.5 Hz), 2.75 (1H, d,d,d, J=8, 5.5, 3.5 Hz), 3.01 (1H, septet, J=6.5 Hz), 3.16 (1H, d,d, J=8, 3.5 Hz), 6.16 (1H, d, J=5.5 Hz), 7—7.6 (4H, m), 7.9 (1H, b). Found: C, 78.66; H, 7.10%. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06%.

*Preparation of Methyl 3-Isopropyl-1a,7b-dihydro-1*H*-cyclopropa*[a]*naphthalene-1-*exo*-acetate (**18**).* To a cold solution of **20** (3.03 g, 13.3 mmol) dissolved in benzene (66 ml), was added oxalyl chloride (10 g, 80 mmol). After stirring for 4 h at room temperature, the solution was evaporated below 20 °C and the residue was evaporated with benzene (three times, each 10 ml) under reduced pressure to give an acid chloride (**30**) as an orange liquid. **30** IR $\nu_{max}^{liq.film}$: 1758 cm^{-1}.

To the dried ether solution of diazomethane, prepared from *N*-nitroso-*N*-methylurea (24 g), 50% aq KOH (75 ml) and ether (240 ml), was added drop by drop **30**, dissolved in benzene (15 ml), over a period of 2 h with cooling (ice-water). After further stirring for 1.5 h at that temperature, the mixture was evaporated and taken in dichloromethane. After drying, the solution was evaporated below 20 °C under reduced pressure to give an orange solid (**31**) (4.06 g). IR ν_{max}^{Nujol}: 2055, 1610 cm^{-1}.

The diazomethyl ketone (**31**), dissolved in 1240 ml of methanol was divided into three portions. Each portion was independently irradiated under nitrogen with an HPL for 40 min with external cooling (ice–water) and collected. Subsequent evaporation of solvent left an orange liquid (3.74 g), which was chromatographed on Silicic Acid (120 g) using hexane–ether (9:1 v/v) as the solvent to give **18** as light yellow crystals (1.86 g; 54.4%). Recrystallization from hexane gave colorless crystals, **18**, 1.26 g; mp 84.5—85.5 °C. **18** IR ν_{max}^{Nujol}: 1730, 1460, 1380, 1207, 1192, 1168, 995, 762, 740 cm^{-1}. UV λ_{max}^{EtOH} (log ε): 224.5 (4.29), 231 (4.28), 237.5 $^{infl.}$(4.13), 278 (3.77), $307^{infl.}$nm(3.35). NMR δ=0.26 (1H, t,t, J=7, 4.3 Hz), 1.12 (3H, d, J=6.5 Hz), 1.13 (3H, d, J=6.5 Hz), 1.76 (1H, d,d,d, J=4.3, 5.5, 8.2 Hz), 2.18 (1H, d,d, J=4.3, 8.2 Hz), 2.31 and 2.34 (–CH$_2$–CH⟨, J_{AB}=15.8 Hz, J_{AX}=J_{BX}=7 Hz), 2.90 (1H, septet, J=6.5 Hz), 3.56 (3H, s), 6.01 (1H, J=5.5 Hz), 6.95—7.6 (4H, m). Found: C, 79.60; H, 7.86%. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86%.

*Methyl 3-Isopropyl-1a,7b-dihydro-1*H-*cyclopropa*[a]*naphthalene-1*-endo-*acetate (**19**).* Compound **18** (20 mg), dissolved in DMSO-*d*$_6$ (0.5 ml) in a sealed NMR tube, was kept at 130 °C to give a mixture of **18** and **19**. The product ratios were estimated every 10 min by means of the NMR spectra. Ratio (**18**:**19**): After 10 min (2:1) 20 min (3:2); 30 min (3:2).

To obtain **19** in quantity, **18** (250 mg) was heated at 140 °C for 30 min and the product was chromatographed on 60 g of Silicic Acid (hexane–ether 95 : 5 v/v). Following to **18**, a mixture of **18** and **19** (rich in **19**) was obtained. Further chromatography gave a sample of **19** (50 mg) as a colorless liquid. This was further purified by distillation at 60 °C (1 mmHg) with the aid of a sublimation apparatus. **19** NMR δ=1.20 (3H, d, J=7 Hz), 1.25 (3H, d, J=7 Hz), 1.6—1.9 (–CH$_2$–CH⟨), 2.24 (H$_{1a}$, m), 2.57 (H$_{7b}$, t, J=7.5 Hz), 3.06 (1H, septet, J=7 Hz), 3.53 (3H, s), 5.89 (1H, d, J=5.5 Hz), 7.08—7.5 (4H, m). UV λ_{max}^{EtOH} (log ε): 224.5 (4.22), 231(4.21), $237.5^{infl.}$(4.08), 278(3.70), $307^{infl.}$nm(3.21). Mass spectrum (JMS-D300); M$^+$ (*m*/*e*): 256.145; Calcd for $C_{17}H_{20}O_2$; 256.146.

*Irradiation of **18** in Methanol*: Identification of Products. Compound **18** (300 mg), dissolved in methanol (320 ml), was irradiated using an HPL under nitrogen for 15 min with external cooling (ice–water). After evaporation of the solvent, the residue (303 mg), taken in hexane–ether (90 : 10 v/v), was developed on 30 g of Silicic Acid and elution was continued with the same solvent (95:5 v/v). Each 15 ml-fraction was collected separately and the solvent evaporated to give fractions as follows: Fr. 1—3, 15 mg (**23**); Fr. 6—7, 5 mg (**26**, **27**, and **25**); Fr. 8—9, 76 mg (**25** (main) and **24** (minor)); Fr. 10, 31 mg (**24**); Fr. 11—15, 100 mg (**18**).

Fraction 8 and 9 were rechromatographed on 20 g of Silicic Acid (hexane–ether 95 : 5 v/v) to give a pale yellow liquid (14 mg; **25**), which was purified by means of GLC [5% Silicone OV-17 on Chromosorb WAW, 1/4″×3 m; column temperature, 173 °C; He flow rate, 40 ml/min; retention time, **25** 12.6 min]. **25** NMR δ=0.735 (3H, d, J=7 Hz), 1.20 (3H, d, J=7 Hz), 2.2—2.45 (1H) and 2.48—2.65 (2H) [AB$_2$ type], 2.93 (1H, septet, J=7 Hz), 3.60 (3H, s), 5.44 (1H, d, J=5 Hz), 5.80 (1H, d,d, J=5, 10 Hz), 6.47 (1H, d, J=10 Hz), 7.05—7.2 (3H, m), 7.24—7.65 (1H, m). UV λ_{max}^{EtOH} (log ε): 227 (4.55), $255^{infl.}$nm(3.85). Found: C, 79.66; H, 7.90%. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86%.

Fraction 10 (31 mg) was rechromatographed on 8 g of Silicic Acid (hexane–ether 95 : 5 v/v) to give a sample of **24** (10 mg). This compound could not be purified by GLC owing to a very slow isomerization to isomer(s) with the same retention time under these conditions. For CH analysis, GLC separation was carried out [5% Silicone OV-17, 170 °C; He, 40 ml/min]. **24** NMR δ=0.9—1.5 (6H, bm), 2.2—3.1 (3H, bm), 3.22 (1H, septet, J=7 Hz), 3.65 (3H, bs), 5.35—5.6 (1H, bm), 5.8—6.1 (1H, bm), 6.25—6.5 (1H, bm), 7.0—7.7 (4H, m); (CD$_3$OD) at +1 °C δ=0.96 (3H, d, J=7 Hz), 1.35 (3H, d, J=7 Hz), 2.77—2.99 (1H) and 3.07 (2H) [AB$_2$ type], 3.51 (weak s, axial-COOCH$_3$?)[12], 3.65 (3H, s, COOCH$_3$), 5.45 (1H, d,d, J=9.5, 5.5 Hz), 5.97 (1H, bd, d, J=9.5, 5 Hz), 6.45 (1H, d, J=5.5 Hz), 7.11—7.75 (4H, m). UV λ_{max}^{EtOH} (log ε): 271 (3.82); λ_{min} 246 nm (3.61). Found: C, 79.68; H, 7.91%. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86%.

To obtain **26** and **27** in quantity, photolysis of **18** was performed for 30 min. Fractions corresponding to Fr. 6—7 of the above mentioned chromatography were separated and purified by means of GLC [15% polydiethylene glycol adipate, 184 °C; He, 40 ml/min; retention times; **26**, 10 min; **27**, 12 min]. **26** (solidified) IR $\nu_{max}^{liq.film}$: 1730, 1480, 1460, 1440, 1365, 1250, 1165, 1040, 1000, 770, 759, 742 cm^{-1}. NMR δ=0.82(3H, d, J=6.5 Hz), 0.99(3H, d, J=6.5 Hz), 2.22 (1H, septet, J=6.5Hz), 2.21 and 2.51(CH$_2$, AB part of ABX type, J_{AB}=15.5 Hz, J_{AX}=10 Hz, J_{BX}=5.5 Hz), 2.84 (1H, bs, $\Delta\tau_{1/2}$=3.5 Hz), 3.31 (1H, d,d,d, J=10, 5.5, 1.5Hz), 3.62(3H,s), 6.04(1H, d, J=2.7Hz), 6.25 (1H, d, J=2.7Hz), 6.98—7.18 (4H, m). UV λ_{max}^{EtOH} (log ε): 262 (2.89), 268.5 (3.07), 275.5 nm (3.10). Found: C, 79.69; H, 7.91%. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86%. **27** IR $\nu_{max}^{liq.film}$: 1730, 1480, 1460, 1440, 1390, 1366, 1165, 995, 880 ,855, 812, 778, 760, 725 cm^{-1}. NMR δ=0.84 (3H, d, J=6.5Hz), 1.01 (3H, d, J=6.5Hz), 2.23 (1H, septet, J=6.5 Hz), 2.32—3.1(2H, m), 3.48(2H, bs, $\Delta\tau_{1/2}$=8 Hz), 3.64 (3H, s), 5.95(1H, d, J=2.7 Hz), 6.37 (1H, d, J=2.7Hz), 6.9—7.3 (4H, m). UV λ_{max}^{EtOH}: 262, 268.5, 275.5 nm.

*Short Period Irradiation of **18** and **19** in Methanol.* Compound **19** (40 mg), dissolved in methanol (105 ml), was irradiated for 5 min using an HPL with external cooling (ice-water) under nitrogen. After the solvent had been carefully evaporated below 20 °C, the products were analyzed by NMR and GLC. The NMR spectrum revealed that the mixture did not contain any of the *exo*-isomer, **18**. The GLC analysis [15% polydiethylene glycol adipate on Chromosorb WAW, 187 °C; He, 40 ml/min] showed it contained six species, estimated as follows: Retention time (product ratio) : 4.9 min (**23**, 7.5%), 12.8 min (**26**, 5.2%), 14.4 min (**27**, 3.4%), 18.2 min (**25**, 9.0%), 21 min (**24**, 44%), 28.4 min (**19**, 30%).

An identical experiment using the same concentration of **18**, instead of **19**, in methanol was carried out. The products did not contain any of **19** and the ratio of products were obtained as follows: **23**, 9.7%; **26**, 3.2%; **27**, 1.5%, **25**, 14.5% **24**, 33%; **18**, 38.3%.

*Irradiation of **24**.* Compound **24** (60 mg), dissolved in methanol (130 ml), was irradiated with an HPL under nitrogen with external cooling. The occurrence of **26** and

27, in compensation for **24**, was observed by monitoring the reaction using GLC [10% Apiezone L on Chromosorb WAW, 190 °C; He, 40 ml/min: Compound (retention time); **26** (8.8 min), **27** (10 min), **24** (13.2 min)] and NMR [**26** δ=6.04 (d), 6.25 (d): **27** δ=5.95 (d), 6.37 (d): **24** δ=5.35—5.6 (bm)] measurements.

*Competitive Photo-induced Reaction of **18** and **19**.* Each 15 ml of a solution of **18** or **19**, (each 50 mg) dissolved in methanol (244ml) separately, was charged in Pyrex test tubes (ϕ1.5×13 cm), which were stoppered after flushing with nitrogen. Seven tubes each were arranged in a merry-go-round apparatus, cooled with ice-water, and irradiated concurrently with an HPL settled in the center of the apparatus. The reaction products from **18** and **19** were monitored every hour using GLC [15% polydiethylene glycol adipate on Chromosorb WAW, 175 °C; He, 40 ml/min]. The results are given in Table 1.

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References

1) G. W. Gruber and M. Pomerantz, *J. Am. Chem. Soc.*, **91**, 4004 (1969).

2) M. D. Madigan and J. S. Swenton, *J. Am. Chem. Soc.*, **93**, 6316 (1971).

3) J. S. Swenton, K. A. Burdett, D. M. Madigan, T. Johnson, and P. D. Rosso, *J. Am. Chem. Soc.*, **97**, 3428 (1975).

4) M. Kato, M. Kawamura, Y. Okamoto, and T. Miwa, *Tetrahedron Lett.*, **1972**, 1171.

5) M. Kato, M. Funakura, M. Tsuji, and T. Miwa, *J. Chem. Soc., Chem. Commun.*, **1976**, 63.

6) In the case of **10**, the equilibrium (**10**$\rightleftharpoons$**13**=2 : 1) is established after 5 min at 90 °C.

7) M. Pomerantz, G. W. Gruber, *J. Am. Chem. Soc.*, **93**, 6615 (1971).

8) M. Traetteberg, *J. Am. Chem. Soc.*, **86**, 4265 (1964).

9) J. A. Berson, *Acc. Chem. Res.*, **1**, 152 (1968).

10) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry" Verlag Chemie, Bergstrsse, Germany (1970), pp. 132—140.

11) Mallinckrodt Chemical Works Silicic Acid (100 mesh) analytical grade was used throughout this experiment.

12) It has been found that methyl 5*H*-benzocycloheptene-5-carboxylate exists in an equilibrated mixture of the two conformers with pseudo-equatorial and a pseudo-axial methoxycarbonyl groups, which were detected by a low temperature NMR spectroscopy (below −90 °C)[M. Kato, K. Takatoku, S. Ito, and T. Miwa, unpublished work]. Likewise, **24** seems to exist in such mixture and the presence of 9-isopropyl group in **24** would make the interconversion much more difficult.