Tetrahedron Vol. 36, pp. 2119 to 2123
© Pergamon Press Ltd., 1980. Printed in Great Britain

0040-4020/80/0715-2119/$02.00/0

MOLECULAR DESIGN BY CYCLOADDITION REACTIONS—36[1a]
CYCLOADDITION REACTIONS OF 7-AZABENZONORBORNADIENE WITH TROPONOID COMPOUNDS AND PHOTOCHEMISTRY OF THE ADDUCTS

TADASHI SASAKI,* TAKASHI MANABE and ETSUO WAKABAYASHI
Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan

(*Received in Japan 8 October* 1979)

Abstract—Reactions of 7-azabenzonorbornadiene 1 with tropone, tropolone and 2-aminotropone gave exclusively *endo-exo* adducts 3a–c in good yields. Similar reaction of other troponoid compounds like 2-acetylamino-, 2-acetoxy- and 2-methoxytropone afforded two isomeric cycloadducts in each case. Photolyses of tropone-adduct 3a in various solvents gave the corresponding cyclopropylcarboxylic acid derivatives 7–11 in high yields. Photochemical behaviors of these adducts 3c, e, f, 5e–f and 4d were also examined.

IT IS known that photochemical behavior of bicyclo[3.2.2]nona-3,8-dien-2-ones (enone-π-methane systems) varies depending on solvents, substituents, and multiplicity of the excited states.[2-7] We have reported the hetero-atom effects[8,9] and substituent effects[10,11] in the photochemistry of their tropone adducts. Synthetical usefulness of these photochemical reactions was exhibited by the clean formation of various complex molecules containing a cyclopropane ring in high yields.

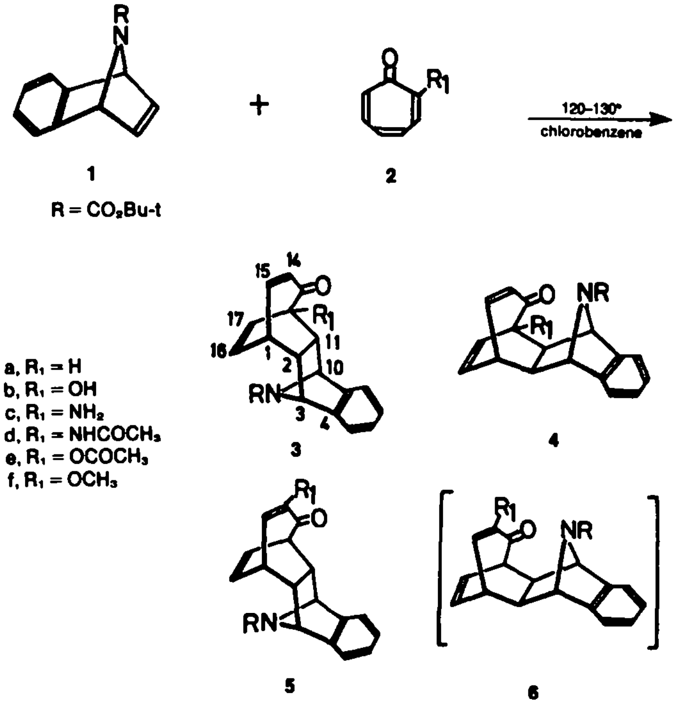
Recently, the utility of 7-azabenzonorbornadiene 1 ($R = CO_2t\text{-}Bu$) as a dienophile has been shown in the reactions with various dienes.[1b] The present paper describes the cycloaddition reactions of 1 with a series of troponoid compounds and the photochemistry of the adducts.

RESULTS AND DISCUSSION

Reactions of 7-azabenzonorbornadiene 1 with tropone derivatives. The reactions of 1 with tropone derivatives 2a–f were carried out in chlorobenzene at 120–130° in a sealed tube for 120–130 hr (Scheme 1). The results are summarized in Table 1.

The nature of products as 1:1 adducts was apparent from elemental analyses. The IR spectrum of each product showed characteristic absorptions of an α, β-unsaturated CO group and an urethane CO group at 1650–1690 cm^{-1}. Unequivocal structural determinations were made on the basis of the NMR spectra as shown in Table 2.

The NMR spectra of adducts 3c, 3e, and 3f were very similar to that of adduct 3b, reported earlier,[1a] except for



Scheme 1.

Table 1. Results of cycloaddition reactions of 1 with tropone derivatives

Starting Material	Product (Yields)[a] endo-exo (3)	exo-exo (4)	endo-exo (5)
2a	3a (100%)[b]		
2b	3b (60%)[b]		
2c	3c (65%)		
2d		4d (19%)	5d (40%)
2e	3e (25%)		5e (45%)
2f	3f (48%)		5f (16%)

a Isolated yields. b See reference 1.

Table 2. ^{1}H NMR spectral data of cycloadducts

Compd	C-1	C-2	C-3	C-10	C-11	C-12	C-14	C-15	C-16	C-17	ArH	t-Bu
3c	3.50 (t)	2.04 (d)	4.86 (s)	5.52 (s)	2.42 (d)	2.11 (s,NH_2)	5.72 (d)	6.9-7.4[a]	6.34 (t)	5.66 (d)	6.9-7.4 (m)	1.41 (s)
			$J_{1,15}$=$J_{1,16}$= 8.10, $J_{2,11}$= 7.5, $J_{14,15}$= 11.6, $J_{16,17}$= 9.0 Hz									
3e	3.54 (t)	2.35 (d)	4.91 (s)	5.30 (s)	2.57 (d)	2.32 (s,CH_3)	5.77 (d)	6.9-7.4[a]	6.38 (t)	6.12 (d)	6.9-7.4 (m)	1.38 (s)
			$J_{1,15}$=$J_{1,16}$=$J_{2,11}$= 7.5, $J_{14,15}$=11.6, $J_{16,17}$= 9.0 Hz									
3f	3.47 (t)	2.25 (d)	4.94 (s)	5.43 (s)	2.43 (d)	3.64 (s,CH_3)	5.68 (d)	6.9-7.4[a]	6.43 (t)	6.15 (d)	6.9-7.4 (m)	1.41 (s)
			$J_{1.15}$=$J_{1,16}$=$J_{2,11}$= 7.5, $J_{14,15}$= 11.3, $J_{16,17}$= 8.5 Hz									
5d	3.56 (t)	2.18 (d)	4.90 (br s)		2.44 (d)	3.88 (d)	2.01[b] (s,CH_3)	8.14 (d)	6.48 (t)	6.01 (t)	6.9-7.4 (m)	1.37 (s)
			$J_{1,15}$= 9.0, $J_{1,16}$=$J_{2,11}$=$J_{12,17}$=7.5, $J_{16,17}$= 7.8 Hz									
5e	3.57 (t)	2.35 (d)	4.91 (br s)		2.55 (d)	3.92 (d)	2.12 (s,CH_3)	6.82 (d)	6.50 (t)	6.12 (t)	7.0-7.4 (m)	1.38 (s)
			$J_{1,15}$=$J_{1,16}$= 9.0,$J_{2,11}$= 8.25, $J_{12,17}$=$J_{16,17}$= 7.5 Hz									
5f	3.57 (t)	2.26 (d)	4.92 (br s)		2.46 (d)	3.94 (d)	3.47 (s,CH_3)	6.15 (d)	6.53 (t)	5.96 (t)	7.0-7.4 (m)	1.39 (s)
			$J_{1,15}$=$J_{1,16}$= 9.0, $J_{2,11}$=$J_{12,17}$= 7.5, $J_{16,17}$= 8.25 Hz									
4d	3.65 (m)	2.44 (dd)	4.76 (br s)		3.47 (d)	2.15[c] (s,CH_3)	6.14 (d)	6.9-7.4[a]	6.53 (t)	6.12 (d)	6.9-7.4 (m)	1.32 (s)
			$J_{1.2}$= 6.5, $J_{2,11}$= 9.0, $J_{14,15}$= 11.4, $J_{16,17}$= 8.7 Hz									

a, Overlapped with aromatic protons.b, Plus δ 7.72(s,NH,exchangeable).
c, Plus δ 2.04 (s,NH,exchangeable).

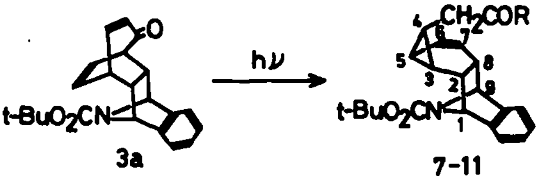
signals of the functional groups at C-12. Thus, these adducts were concluded to be the *endo,exo*-cycloadducts. In the case of **4d**, the presence of a coupling between H-1 and H-2 (J = 6.5 Hz) and the absence of appreciable couplings between H-2, H-3 and H-10, H-11 indicated the *exo,exo* configuration.

Likewise, configurations of adducts **5d**, **5e**, and **5f** were determined by complete analyses of the NMR spectra. In these cases, the substituents (R_1) located on C-14.

The yields of adducts of type **5** increased with increasing a bulkiness of R_1. Adduct of type **6** was not obtained by these cycloaddition reactions.

Photochemistry of the cycloadducts. An adduct **3a** was irradiated with a high-pressure 100-W mercury lamp through a Pyrex filter under N_2 at room temperature in the presence of several nucleophiles. Depending on the solvents used for photolysis, methyl ester **7**, carboxylic acid **8**, and amides **9–11** were obtained in high yields (Table 3).

Table 3. Photolyses of tropone-adduct 3a



Solvents	Products	Yield (%)
MeOH	7,R=OMe	95
MeCN-H_2O (1:1)	8,R=OH	95
sat.NH_3-$CHCl_3$,NH_3gas	9,R=NH_2	90
sat.$MeNH_2$-C_6H_6	10,R=NHMe	92
sat.Me_2NH-C_6H_6	11,R=NMe_2	86

Structural proofs were based on elemental analyses and spectroscopic data.

Apparently, these products were formed by nucleophilic addition of the solvents to the ketene intermediates which were formed by photochemical [3.3] sigmatropic rearrangement.

Other adducts were similarly irradiated in methanol. The results are summarized in Scheme 2 and Table 4.

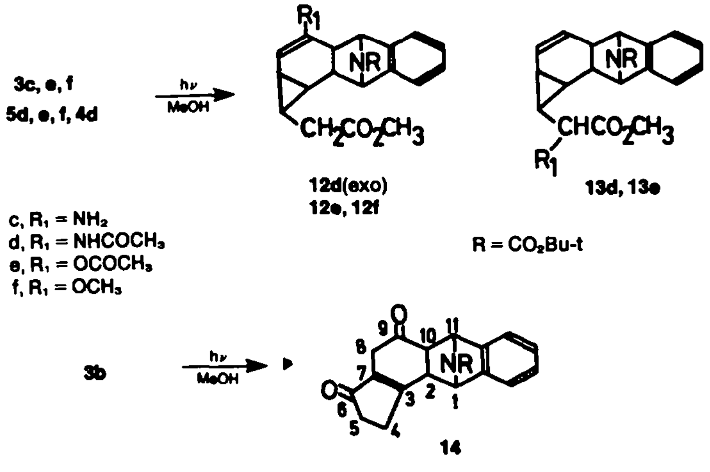
Structures of the photoproducts were proved by the NMR spectra (Table 5 and 6, Experimental).

Irradiation of compounds **3e**, **f**, **4d** and **5d**, **e** afforded the corresponding methyl esters in good yields. Similar photolyses of **3c** and **5f**, however, resulted in the formation of complex mixtures. It should be noted that photochemical behavior of tropolone adduct **3b** was quite different from other adducts. On irradiation under the same conditions, compound **3b** gave exclusively diketone **14** in almost quantitative yields. This observation is in accord with the results we have reported before.[11]

Table 4. Photolyses of tropone-adducts in methanol

Starting Materials	Product (Yields)[a]
3c	complex mixture
3e	12e (95%)
3f	12f (92%)
5d	13d (65%)
5e	13e (60%)
5f	complex mixture
4d	12d (80%)
3b	14 (90%)

a Yields are for isolated pure products.



Scheme 2.

Table 5. ¹H NMR spectral data of photoproducts

Compd	H-6,H-7	H-1,H-9	H-2,H-8,CH_2Y	H-3,H-4,H-5	ArH	t-Bu	Other protons
7	5.84 (m)	4.82(s) 5.06(s)	1.9-2.16 (m)	1.35-1.67 (m)	7.0-7.4 (m)	1.37 (s)	3.59 (s,Me)
8	5.78 (m)	4.78(s) 5.01(s)	1.85-2.23 (m)	1.28-1.67 (m)	7.0-7.4 (m)	1.37 (s)	7.0-7.4[a] (COOH)
9	5.88 (m)	4.84(s) 5.07(s)	1.75-2.17 (m)	1.25-1.71 (m)	7.0-7.4 (m)	1.37 (s)	5.68[b] (br s,NH_2)
10	5.84 (m)	4.80(s) 5.02(s)	1.72-2.14 (m)	1.32-1.70 (m)	6.9-7.3 (m)	1.36 (s)	2.72(d,NMe) 1.85[b](br s,NH)
11	5.84 (m)	4.81(s) 5.04(s)	1.70-2.15 (m)	1.30-1.66 (m)	6.8-7.4 (m)	1.35 (s)	2.85 (s,NMe_2)

a Overlapped with aromatic protons. b Exchangeable by D_2O.

Table 6. ^{1}H NMR spectral data of photoproducts

Compd	H-6	H-1,H-9	ArH	CO_2CH_3	R_1	t-Bu	Other protons
12d	5.81 (d,J=4.5)	4.94(s) 5.07(s)	6.9-7.4 (m)	3.65 (s)	$NHCOCH_3$ 2.11(s)	1.31 (s)	1.2-1.9(m,3H;H-3,H-4 and H-5) 2.0-3.0(m,5H;NH,CH_2,H-2 and H-8)
12e	5.57 (d,J=4.5)	5.10(s)	7.0-7.4 (m)	3.58 (s)	$OCOCH_3$ 2.19(s)	1.39 (s)	1.2-2.5(m,7H;H-3,H-4,H-5, CH_2,H-2 and H-8)
12f	4.81 (d,J=4.5)	5.12(s) 5.23(s)	7.0-7.4 (m)	3.61 (s)	OCH_3 3.61(s)	1.39 (s)	1.1-2.3(m,7H;H-3,H-4,H-5, CH_2,H-2 and H-8)
13d	5.90 (m,2H)[b]	4.81(s) 5.05(s)	7.0-7.5 (m)	3.62 (s)	$NHCOCH_3$[a] 1.91(s)	1.36 (s)	1.1-2.6(m,5H;H-3,H-4,H-5, H-2 and H-8) 4.01(t,J=9.0;CH)
13e	5.89 (m,2H)[b]	4.84(s) 5.07(s)	6.8-7.4 (m)	3.64 (s)	$OCOCH_3$ 2.06(s)	1.38 (s)	1.3-2.6(m,5H,H-3,H-4,H-5, H-2 and H-8) 4.38(d,J=9.0;CH)

a Plus δ3.42 (s; NH,exchangeable), b Overlapped with the signal for H-7.

EXPERIMENTAL

M.ps were measured with a Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were performed on a Perkin–Elmer 240 elemental analyser. UV spectra were determined with a Hitachi spectrophotometer (Model 200-10). NMR spectra were taken with a JEOL C-60-HL spectrometer and with a JEOL FX 60 FT NMR spectrometer, with TMS as an internal standard. IR spectra were taken with a JASCO-IRA-1 spectrometer.

General procedure for cycloaddition reactions

A soln of 1:1 mixture of **1**[12] and derivative **2c–f** in chlorobenzene was heated at 120–130° in a sealed tube for 120–130 hr. After removal of the solvent, the mixture was purified by chromatography on a silica gel column.

(a) *With 2-aminotropone* (**2c**). A soln of **1** (0.49 g, 2.02 mmol) and **2c** (0.25 g, 2.07 mmol) in chlorobenzene (8 ml) was heated. Chromatography on silica gel using chloroform, followed by recrystallization from benzene gave adduct **3c** (0.48 g, 65%) as colorless crystals: mp 165–167°; IR(KBr) 3400, 1680, 1660 cm^{-1}; UV (ethanol) λ_{max} 240 nm (ϵ 5201), 271 (1412), 326 (82). (Found: C, 76.01; H, 6.90; N, 6.25. Calc. for $C_{22}H_{24}N_2O_3.C_6H_6$: C, 75.99; H, 6.83; N, 6.33).

(b) *With 2-acetylaminotropone* (**2d**). A soln of **1** (2.0 g, 8.23 mmol) and **2d** (1.3 g, 7.96 mmol) in chlorobenzene (40 ml) was heated and then subjected to silica gel chromatography using chloroform-n-hexane. The first fraction gave adduct **5d** (1.29 g, 40%) as colorless crystals: m.p. 205–207° (EtOH); IR(K Br) 3330, 1683, 1665, 1652, 1628, 1508 cm^{-1}; UV (EtOH) λ_{max} 259 nm (ϵ 4469), 265(4895), 272(5107), 285(4682), 326(936). (Found: C, 70.75; H, 6.50; N, 7.13. Calc. for $C_{24}H_{26}N_2O_4$. C, 70.91; H, 6.45; N, 6.89%).

The second fraction gave **4d** (0.61 g, 19%) as colorless crystals: mp 229–231° (chloroform-n-hexane); IR(KBr) 3390, 1687, 1673, 1640, 1492 cm^{-1}; UV (EtOH) λ_{max} 259 nm (ϵ 2979), 264(2554), 271(2128), 326(85). (Found: C, 70.61; H, 6.73; N, 6.90. Calc. for $C_{24}H_{26}N_2O_4$. C, 70.91; H, 6.45; N, 6.89%).

(c) *With 2-acetoxytropone* **2e**. A soln of **1** (0.49 g, 2.02 mmol) and **2e** (0.33 g, 2.01 mmol) in chlorobenzene (10 ml) was heated. The mixture was subjected to silica gel chromatography and fractional crystallization from EtOH to give **3e** (0.21 g, 25%) and **5e** (0.37 g, 45%). Adduct **3e**: mp 187–188°; IR(KBr) 1745, 1692, 1667, 1242, 1070 cm^{-1}; UV (EtOH) λ_{max} 240 nm (ϵ 5710), 264(2039), 271(1305), 326(98). (Found: C, 70.51; H, 6.21; N, 3.48. Calc. for $C_{24}H_{25}NO_5$. C, 70.74; H, 6.18; N, 3.44%). Adduct **5e**: m.p. 222–224°; IR(KBr) 1767, 1668, 1427, 1206 cm^{-1}; UV (EtOH) λ_{max} 245 nm (ϵ 6379), 272(2392), 326(120). (Found: C, 70.45; H, 6.13; N, 3.45. Calc. for $C_{24}H_{25}NO_5$. C, 70.74; H, 6.18; N, 3.44%).

(d) *With 2-methoxytropone* (**2f**). A soln of **1** (0.99 g, 4.07 mmol) and **2f** (0.55 g, 4.04 mmol) in chlorobenzene (20 ml) was heated. The mixture was chromatographed on a silica gel column using benzene-acetone. The first fraction gave **3f** (0.73 g, 48%) as colorless crystals: m.p. 100–102° (dichloromethane-n-hexane); IR(KBr) 1670, 1653 cm^{-1}; UV (EtOH) λ_{max} 263 nm (ϵ 2300), 271(1533), 326(100). (Found: C, 72.91; H, 6.52; N, 3.70. Calc. for $C_{23}H_{25}NO_4$. C, 72.80; H, 6.64; N, 3.69%). The second fraction gave **5f** (0.25 g; 16%) as colorless crystals: m.p. 147–149° (dichloromethane-n-hexane); IR(KBr) 1680, 1660, 1430, 1122 cm^{-1}; UV (EtOH) λ_{max} 264 nm (ϵ 4049), 271(4124), 282(3524), 327(150). ((Found: C, 73.02; H, 6.62; N, 3.84. Calc. for $C_{23}H_{25}NO_4$. C, 72.80; H, 6.64; N, 3.69%).

General procedure for photolyses tropone adducts

A soln of tropone adduct in the appropriate solvent was irradiated with a high pressure 100 W mercury lamp through a Pyrex filter at room temp. The photolyses were monitored by tlc. The solvent was removed under reduced pressure and the residue was purified by recrystallization. The NMR data of products are summarized in Table 5 and 6.

(a) *Photolysis of* **3a** *in methanol*. A soln of **3a** (125 mg, 0.36 mmol) in dry MeOH (70 ml) was irradiated for 3.5 hr. Evaporation and recrystallization from chloroform-n-hexane gave **7** (130 mg, 95%) as needles, m.p. 137–139°; IR(KBr) 1736, 1687 cm^{-1}. (Found: C, 72.15; H, 7.05; N, 3.83. Calc. for $C_{23}H_{27}NO_4$. C, 72.42; H, 7.13; N, 3.67%).

(b) *Photolysis of* **3a** *in acetonitrile-water*. A soln of **3a** (150 mg, 0.43 mmol) in acetonitrile-water (1:1) (100 ml) was irradiated for 3.5 hr. Recrystallization from ether-n-hexane gave **8** (150 mg, 95%) as needles, m.p. 168–170°; IR(KBr) 1735, 1645 cm^{-1}. (Found: C, 72.00; H, 6.59; N, 3.98. Calc. for $C_{22}H_{25}NO_4$. C, 71.91; H, 6.86; N, 3.81%).

(c) *Photolysis of* **3a** *in ammonia*. A soln of **3a** (150 mg, 0.43 mmol) in $CHCl_3$ (80 ml) saturated with dry ammonia was irradiated for 3 hr under bubbling dry ammonia gas. Recrystallization of the residue from ether-n-hexane gave **9** (142 mg, 90%) as needles, m.p. 175–177°; IR(KBr) 3443, 3347, 1672, 1655 cm^{-1}. (Found: C, 71.96; H, 7.36; N, 7.58. Calc for $C_{22}H_{26}N_2O_3$. C, 72.10; H, 7.15; N, 7.65%).

(d) *Photolysis of* **3a** *in methylamine*. A soln of **3a** (118 mg, 0.34 mmol) in benzene (100 ml) saturated with dry methylamine was irradiated for 1 hr. Recrystallization of the residue from chloroform-n-hexane gave **10** (119 mg, 92%) as needles, m.p. 166–168°; IR(KBr) 3290, 1681, 1637 cm^{-1}. (Found: C, 72.58; H, 7.40; N, 7.23. Calc. for $C_{23}H_{28}N_2O_3$. C, 72.60; H, 7.42; N, 7.36%).

(e) *Photolysis of* **3a** *in dimethylamine*. A soln of **3a** (138 mg, 0.40 mmol) in benzene (60 ml) saturated with dry dimethylamine was irradiated for 3 hr. Recrystallization of the residue from chloroform-n-hexane gave **11** (134 mg, 86%) as needles, m.p. 166–167°; IR(KBr) 1685, 1639 cm^{-1}. (Found: C, 73.24; H, 7.63; N, 7.25. Calc. for $C_{24}H_{30}N_2O_3$. C, 73.06; H, 7.67; N, 7.10%).

(f) *Photolysis of* ***3e*** *in methanol.* A soln of **3e** (200 mg, 0.49 mmol) in dry MeOH (100 ml) was irradiated for 1.5 hr. Recrystallization from MeOH gave **12e** (205 mg, 95%) as needles, m.p. 130–132°; IR(KBr) 1755, 1730, 1680 cm^{-1}. (Found. C, 68.42; H, 6.66; N, 3.33. Calc. for $C_{25}H_{29}NO_6$. C, 68.32; H, 6.65; N, 3.19%).

(g) *Photolysis of* ***3f*** *in MeOH.* A soln of **3f** (147 mg, 0.39 mmol) in dry MeOH (80 ml) was irradiated for 0.5 hr. Recrystallization from MeOH gave **12f** (147 mg, 92%) as needles, m.p. 145–147°; IR(KBr) 1738, 1690, 1395, 1370 cm^{-1}. (Found: C, 70.29; H, 7.16; N, 3.62. Calc. for $C_{24}H_{29}NO_5$. C, 70.05; H, 7.10; N, 3.40%).

(h) *Photolysis of* ***5d*** *in MeOH.* A soln of **5d** (197 mg, 0.49 mmol) in dry MeOH (85 ml) was irradiated for 1 hr. Recrystallization from dichloromethane-n-hexane gave **13d** (140 mg, 65%) as needles, m.p. 148–150°; IR(KBr) 1725, 1673, 1642, 1625, 1350 cm^{-1}. (Found: C, 68.27; H, 6.85; N, 6.64. Calc. for $C_{25}H_{30}N_2O_5$. C, 68.47; H, 6.90; N, 6.39%).

(i) *Photolysis of* ***5e*** *in MeOH.* A soln of **5e** (156 mg, 0.38 mmol) in dry MeOH (70 ml) was irradiated for 1.5 hr. Recrystallization from dichloromethane-n-hexane gave **13e** (100 mg, 60%) as needles, m.p. 129–131°; IR(KBr) 1758, 1735, 1682 cm^{-1}. (Found: C, 68.32; H, 6.70; N, 3.38. Calc. for $C_{25}H_{29}NO_6$. C, 68.32; H, 6.65; N, 3.19%).

(j) *Photolysis of* ***4d*** *in MeOH.* A soln of **4d** (21 mg, 0.05 mmol) in dry MeOH(70 ml) was irradiated for 0.5 hr. Recrystallization from chloroform-n-hexane gave **12d** (18 mg, 80%) as needles, m.p. 123–125°; IR(KBr) 1730, 1685, 1645, 1540 cm^{-1}. (Found: C, 68.35; H, 6.87; N, 6.40. Calc. for $C_{25}H_{30}N_2O_5$. C, 68.47; H, 6.90; N, 6.39%).

(k) *Photolysis of* ***3b*** *in methanol.* A soln of **3b** (217 mg, 0 59 mmol) in dry MeOH (100 ml) was irradiated for 1.5 hr. Chromatography on silica gel using $CHCl_3$, followed by recrystallization from benzene-n-hexane gave **14** (195 mg, 90%) as needles, m.p. 171–172°; IR(KBr) 1748, 1700, 1685 cm^{-1}; NMR($CDCl_3$) δ 1.33 (9H, s), 1.5–2.5 (6H, m; 2H–4, 2H–5 and 2H–8), 2.63 (1H, d, $J_{2,10} = 5.7$ Hz; H–2), 3.48 (1H, d; H–10), 5.14 (1H, s; H–1 or H–11), 5.62 (1H, s; H–1 or H–11), 7.0–7.4 (4H, m; ArH). (Found: C, 76.03; H, 6.73; N, 3.37. Calc. for $C_{22}H_{23}NO_4.C_6H_6$. C, 75.82; H, 6.59; N, 3.16%).

REFERENCES

[1a] Part 35 of this series; T. Sasaki, T. Manabe and S. Nishida, *J. Org. Chem.* submitted for publication; [b] *Idem.*, *Ibid.*

[2] O. L. Chapman and J. D. Lassila, *J. Am. Chem. Soc.* **90**, 2449 (1968).

[3] J. Ciabattoni, J. E. Crowley and A. S. Kende, *Ibid.* **89**, 2778 (1967).

[4] A. S. Kende, Z. Goldschmidt and P. T. Izzo, *Ibid*, 91, 6858 (1968).

[5] A. S. Kende and Z. Goldschmidt, *Tetrahedron Letters*, 783 (1970).

[6] H. Hart and G. M. Love, *J. Am. Chem. Soc.* 93, 6266 (1971).

[7] T. Tezuka, R. Miyamoto, T. Mukai, C. Kabuto and Y. Kitahara, *Ibid.* **94**, 9280 (1972).

[8] T. Sasaki, K. Kanematsu and K. Hayakawa, *J. Chem. Soc.* (C) 2142 (1971).

[9] T. Sasaki, K. Kanematsu and K. Hayakawa, *Ibid.* Perkin I, 783 (1972).

[10] *Idem.*, *Ibid.* 1951 (1972).

[11] T. Sasaki, K. Kanematsu, K. Hayakawa and A. Kondo. *J. Org. Chem.* **38**, 4100 (1973).

[12] L. A. Carpino and D. E. Barr, *Ibid.* 31, 764 (1966).