Hz, 1 H, $C_2$ H), 6.92 (t, $J = 10$ Hz, $C_4$ H), 8.25 and 8.38 [each s, each 3 H, $C{=}C(CH_3)_2$], and 8.74 (s, 6 H, $C_3$ *gem*-dimethyl) (the triplet signal at $\tau$ 6.92 changed to a doublet on irradiation at the $\tau$ 4.66 signal); mass spectrum *m/e* (rel intensity) 226 (18, $M^+$), 126 (100), 111 (88), and 110 (56).

*Anal.* Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.84; H, 8.33.

A mixture of **18** (200 mg, 0.884 mmol) and lead tetraacetate (500 mg, 1.12 mmol) in dry pyridine (4 ml) was warmed at 80° for 1 min.[33] After evolution of carbon dioxide ceased, the mixture was quickly poured onto ice–water (50 ml) and extracted with petroleum ether (bp 39–44°, 30 ml). The extract was washed five times with 30-ml portions of water and dried ($Na_2SO_4$). After removal of solvent, the residual oil was purified by flask to flask distillation (bath temperature 40°, 2 mm, Dry Ice trap) to give the olefin **9** (20 mg, 16%) as an oil: ir ($CCl_4$) 1660, 1645, and 870 cm$^{-1}$ ($C{=}C$); nmr ($CCl_4$) $\tau$ 4.02 and 4.16 (each d, $J = 3.0$ Hz, each 1 H, $C_1$ H and $C_2$ H), 4.99 [broad d, $J = 9.5$ Hz, 1 H, $\mathbf{CH}{=}C(CH_3)_2$], 6.92 (d, $J = 9.5$ Hz, 1 H, $C_4$ H), 8.28 and 8.38 [each s, each 3 H, $CH{=}C(\mathbf{CH_3})_2$], 8.81 and 9.04 (each s, each 3 H, $C_3$ *gem*-dimethyl); mass spectrum *m/e* (rel intensity) 136 (100, $M^+$), 105 (45), 91 (50), and 79 (35).

*Anal.* Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.30; H, 11.69.

**1,3,3-Trimethyl-4-isobutenylcyclobutene (12) from Methylmaleic Anhydride (15) and 8.**—A solution of **8** (11.0 g, 99.8 mmol), **15** (2.20 g, 19.6 mmol), and benzophenone (650 mg) in ether (100 ml) was irradiated as above for 7 hr. Purification of the crude product on a silica gel column eluting with benzene afforded 1:1 adduct **17** as an oil (2.30 g) and unidentified solids (980 mg). The adduct **17** had ir (neat) absorptions at 1850, 1780 (anhydride), and 1660 ($C{=}C$) cm$^{-1}$, and nmr signals ($CCl_4$) at $\tau$ 4.81 and 5.13 [d, $J = 9.5$ Hz, $\mathbf{CH}{=}(CH_3)_2$], 6.89 and 7.23 (d, $J = 9.5$ Hz, $C_4$ H), and 7.33 and 7.23 (s, $C_2$ H). The appearance of the signals in pairs (each *ca.* 2:1 ratio) indicated that the adduct **17** is a mixture of two stereoisomers (syn and anti).

A mixture of **17** (550 mg, 2.47 mmol) and 3% aqueous KOH (15 ml) was stirred overnight at room temperature. The aqueous layer was washed with ether (20 ml), neutralized with 10% hydrochloric acid, and extracted twice with 20-ml portions of ether. The combined extracts were dried ($Na_2SO_4$) and evaporated to afford colorless solids (420 mg, 71%) which were recrystallized from *n*-hexane–ether to give the diacid **19** as crystals: mp 164–165°; ir (KBr) 1720 and 1670 cm$^{-1}$ (COOH); nmr ($CDCl_3$) $\tau$ −0.94 (broad s, 2 H, COOH), 4.80 (broad d, $J = 10$ Hz, 1 H, $CH{=}C$), 6.42 (d, $J = 10$ Hz, 1 H, $C_4$ H), 7.27 (s, 1 H, $C_2$ H), 8.28 [s, 6 H, $C{=}C(CH_3)_2$], 8.53 (s, 3 H, $C_1$ $CH_3$), 8.78 and 8.87 (each s, each 3H, $C_3$ *gem*-dimethyl); mass spectrum *m/e* (rel intensity) 240 (18, $M^+$), 140 (60), 125 (72), and 110 (100).

*Anal.* $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.84; H, 8.33.

A mixture of **19** (90 mg, 0.38 mmol) and lead tetraacetate (250 mg, 0.57 mmol) in dry pyridine (3 ml) was warmed at 80° for 15 min. The mixture was poured onto 10% hydrochloric acid (20 ml) and extracted two times with 25-ml portions of ether. The combined extracts were washed with water and dried ($Na_2SO_4$). Removal of the solvent gave an oil which was purified by flask to flask distillation (bath temperature 80–100°, 25 mm) to afford the olefin **12** (10 mg, 18%).

**Registry No.**—*cis*-**1**, 15259-78-6; *trans*-**1**, 827-90-7; *cis*-**2**, 18383-59-0; *trans*-**2**, 18383-58-9; *cis*-**3**, 20104-06-7; *trans*-**3**, 20104-05-6; *cis*-**4**, 20104-10-3; *trans*-**4**, 20104-09-0; *cis*-**5**, 42077-36-1; *trans*-**5**, 42077-37-2; *cis*-**6**, 42077-38-3; *trans*-**6**, 42077-39-4; **8**, 764-13-6; **9**, 42077-40-7; **12**, 42077-41-8; **15**, 616-02-4; **16**, 42077-42-9; **17**, 42077-43-0; **18**, 42077-44-1; **19**, 42077-45-2; *p*-toluenesulfonylhydrazide, 1576-35-8; maleic anhydride, 108-31-6.

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[33] *Cf.* R. Criegee, "Newer Methods of Preparative Organic Chemistry," Vol. 2, Academic Press, New York, N. Y., 1963, p 368.

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# Molecular Design by Cycloaddition Reactions. VI.[1] Observation of the Enone-π-methane Moiety in Photochemical [1,3] and [3,3] Sigmatropic Rearrangements

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Photolyses (Pyrex, >290 nm) of several substituted tropone adducts are investigated. Mechanisms for [1,3] and [3,3] sigmatropic rearrangements of thus-produced bicyclo[3.2.2]nonadienone systems (enone-π-methane moiety) are discussed.

Recently much interest has arisen in the photochemical rearrangement of the enone-π-methane moiety.[2–7]

We have found that the incorporation of heteroatoms into the bicyclo[3.2.2]nonadienone system causes some changes in its photochemical behavior;[8] irradiation of tropone–4-phenyl-1,2,4-triazoline-3,5-dione adduct in methanol afforded two products by different [3,3] sigmatropic rearrangement followed by addition of methanol. Previously, we have also reported that irradiation of Diels–Alder adducts of tropolone and epoxy-bridged cyclic olefins in methanol led to diketones by successive [1,3] sigmatropic rearrangement[9] in contrast to previous reports[3,5,8] of the light-induced rearrangement of tropone adducts in nucleophilic solvents. Thus, the hydroxyl group at the bridgehead position (α to carbonyl group) has been shown to cause a marked variation in the photochemical behavior of this system, but the mechanism was not elucidated. From these facts it seems that substituents play an important role in the photochemistry of the bicyclo[3.2.*x*]dienone system.

With a hope of providing some additional data for understanding these substituent effects on the photochemical behavior, we have investigated the photochemistry of the cycloadducts of 1,4-epoxy-1,4-di-

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[1] Part V of this series: T. Sasaki, K. Kanematsu, and K. Hayakawa, *J. Amer. Chem. Soc.*, **95**, 5632 (1973).

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

[3] O. L. Chapman, M. Kane, J. D. Lassila, R. L. Loeschen, and H. E. Wright, *J. Amer. Chem. Soc.*, **91**, 6856 (1969).

[4] J. Ciabattoni, J. E. Crowley, and A. S. Kende, *J. Amer. Chem. Soc.*, **89**, 2778 (1967).

[5] (a) A. S. Kende, Z. Goldschmidt, and P. T. Izzo, *J. Amer. Chem. Soc.*, **91**, 6858 (1969); (b) A. S. Kende and Z. Goldschmidt, *Tetrahedron Lett.*, 783 (1970).

[6] T. Tezuka, R. Miyamoto, T. Mukai, C. Kabuto, and Y. Kitahara, *J. Amer. Chem. Soc.*, **94**, 9280 (1972).

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

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

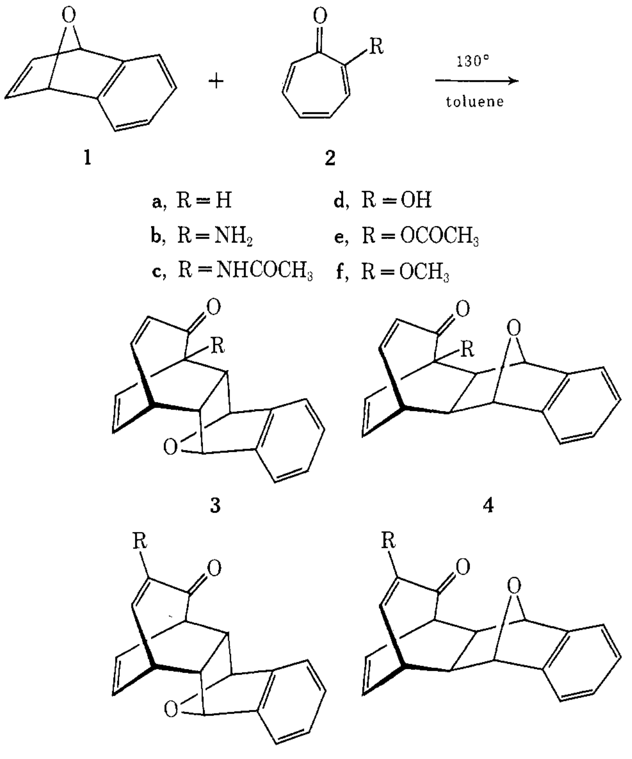
[9] T. Sasaki, K. Kanematsu, and K. Hayakawa, *J. Chem. Soc., Perkin Trans. 1*, 1951 (1972).

hydronaphthalene **1**[10] with a series of 2-substituted tropones. In this connection, we have described the cycloaddition reactions of **1** with tropone as electron-poor components and explained them in terms of a Diels–Alder mechanism with inverse electron demands.[10]

## Results and Discussion

**Cycloaddition Reactions.**—The reactions were generally carried out in toluene at 130° in a sealed tube for 40 hr (Scheme I). The results are summarized in Table I.

SCHEME I



1 2

a, R = H d, R = OH
b, R = NH$_2$ e, R = OCOCH$_3$
c, R = NHCOCH$_3$ f, R = OCH$_3$

3 4

5 6

TABLE I

| Starting material | Product (yields, %)[a] Endo–exo (**5**) | Exo–exo (**4**) | Endo–exo (**5**) | Exo–exo (**6**) |
|---|---|---|---|---|
| **2a** | **3a** (100)[b] | | | |
| **2b** | **3b** (50.2) | | | |
| **2c** | **3c** (9.3) | **4c** (5.5) | **5c** (6.5) | |
| **2d** | **3d** (49) | | | |
| **2e** | **3e** (27.1) | | **5e** (17.4) | |
| **2f** | **3f** (6.3) | | **5f** (16.5) | **6f** (6.8) |

[a] Isolated yields. [b] Reference 9.

Structural assignments were made on the basis of elemental analyses and spectroscopic data. The mass spectrum of each adduct showed a molecular ion peak and common characteristic fragment peak (m/e 118, $C_8H_6O$, isobenzofuran) of the retrocycloaddition reaction. The ir spectra showed a characteristic band of the α,β-unsaturated carbonyl group at 1650–1690 cm$^{-1}$. Unequivocal structural determinations were made on the basis of the nmr data as shown in Table II; while the absence of appreciable couplings between $H_{1,2}$, $H_{2,3}$, and $H_{10,11}$ in the nmr indicated **3b** to be an endo–exo adduct, the presence of the coupling between $H_1$ and $H_2$ ($J$ = 6.0 Hz) and the absence of appreciable couplings between $H_{2,3}$ and $H_{10,11}$ indicated **4c** to be an exo–exo adduct. Likewise, the configurations of other adducts were determined by complete analyses of the nmr spectra. The formation of the endo–exo tropolone adduct (**3d**) is in contrast to the exclusive formation of the exo–exo adduct (**4d**) in chlorobenzene.[9] The yields of the cycloadducts and the regioselectivity of the cycloaddition reactions decrease with increase in bulkiness of the substituents.

**Irradiation of the Adducts.**—These adducts were irradiated with a high-pressure 100-W mercury lamp through a Pyrex filter under nitrogen at room temperature in methanol (Scheme II). The reaction mixtures were analyzed by vapor phase chromatography and the products were separated by column chromatography. The results are summarized in Table III.

Structural proofs were based on elemental analyses and spectroscopic data. Irradiation of the aminotropone adduct **3b** led to a complicated mixture consisting of more than nine components by tlc. Since the mixtures were very air sensitive, all attempts to isolate the products were unsuccessful. Such observation might be attributable to the intramolecular charge transfer[11,12] between amino and carbonyl groups.

Irradiation of **3a**,[9] **3c**, **3e**, and **4c** gave exclusively cyclopropane esters in good yields (Table III). In all cases the possible intermediates were cyclopropylketene derivatives (**7**) which were obviously formed by [3,3] sigmatropic rearrangement. Irradiation of **5c** gave a similar product **9** in a low yield. This low yield might be explained by sterically unfavored addition of methanol to the initially formed ketene **7** ($R_2$ = $NHCOCH_3$).

On irradiation of **3f**, the dihydro derivative **8g** was obtained in addition to the normal [3,3] product **8f**. The dihydro compound **8g** might be produced by a path independent of the general [3,3] sigmatropic rearrangement path because no transformation of **8f** to **8g** was observed under the same photochemical conditions (see Discussion).

The ir spectra of these products showed a characteristic absorption of ester carbonyl group at 1720–1750 cm$^{-1}$ instead of the original carbonyl one at 1650–1690 cm$^{-1}$. Unequivocal structural determinations were made on the basis of the nmr data as shown in Table IV. From these results, it has been concluded that the configurations of these adducts could not affect the photochemistry.

On irradiation of **3d**, a quite different type of reaction occurred. In this case, the diketone **13** was obtained in a nearly quantitative yield and no other ester products could be observed. The nature of **13** as an isomer of **3d** was apparent from its mass spectrum ($M^+$ 266). The ir spectrum showed two carbonyl bands at 1740 and 1700 cm$^{-1}$. The nmr spectrum exhibited signals at δ 1.3–2.5 (m, 6 H), 2.65 (d, 1 H, $J$ = 4.5 Hz), 3.50

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(10) (a) G. R. Ziegler, *J. Amer. Chem. Soc.*, **91**, 446 (1969); (b) R. N. Warrener, *ibid.*, **93**, 2346 (1971); (c) T. Sasaki, K. Kanematsu, K. Hayakawa, and M. Uchide, *J. Chem. Soc., Perkin Trans. 1*, 2750 (1972).

(11) Although acetylaminotropone is photoisomerized to the valence isomer, aminotropone is photochemically inactive because of the intramolecular charge transfer: T. Mukai and M. Kimura, *Tetrahedron Lett.*, 717 (1970).

(12) (a) S. G. Cohen and M. N. Saddiqui, *J. Amer. Chem. Soc.*, **86**, 5047 (1964); (b) S. G. Cohen and J. I. Cohen, *J. Phys. Chem.*, **72**, 3782 (1968).

TABLE II

NMR SPECTRA OF DIELS–ALDER ADDUCTS

| Compd | C-1 | C-2 | C-3 | C-10 | C-11 | C-12 | C-14 | C-15 | C-16 | C-17 | ArH |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | δ, ppm ($J$, Hz) | | | | | | | | | | |
| **3b** | 3.48 (t, $J_{1,16}$ = 7.5, $J_{1,15}$ = 9.8) | 2.03 (d, $J_{2,11}$ = 8.0) | 5.00 (s) | 5.80 (s) | 2.50 (d) | 2.16 (s, $NH_2$) | 5.67 (d, $J_{14,15}$ = 8.25) | 7.0–7.3[a] | 6.40 (t, $J_{16,17}$ = 9.0) | 5.70 (d) | 7.0–7.3 (m) |
| **3c** | 3.45 (t, $J_{1,16}$ = 7.5, $J_{1,15}$ = 7.5) | 2.40 (d, $J_{2,11}$ = 7.5) | 5.10 (s) | 5.65 (s) | 2.62 (d) | 6.90 (s, NH)<br>2.13 (s, $CH_3$) | 5.80 (d, $J_{14,15}$ = 11.3) | 7.0–7.3[a] | 6.50 (t, $J_{16,17}$ = 9.0) | 6.20 (d) | 7.0–7.3 (m) |
| **3e** | 3.50 (t, $J_{1,15}$ = 7.5, $J_{1,16}$ = 9.0) | 2.44 (d, $J_{2,11}$ = 7.5) | 5.02 (s) | 5.49 (s) | 2.65 (d) | 2.30 (s) | 5.74 (d, $J_{14,15}$ = 11.3) | 6.9–7.3[a] | 6.40 (t, $J_{16,17}$ = 9.25) | 6.20 (d) | 6.9–7.3 (m) |
| **3f** | 3.50 (t, $J_{1,16}$ = 7.5) | 2.32 (d, $J_{2,11}$ = 7.5) | 4.98 (s) | 5.53 (s) | 2.45 (d) | 3.58 (s, $CH_3$) | 5.65 (d, $J_{14,15}$ = 9.75) | 6.9–7.3[a] | 6.40 (t, $J_{16,17}$ = 9.0) | 6.12 (d) | 6.9–7.3 (m) |
| **3d** | 3.49 (t, $J_{1,15}$ = 9.25, $J_{1,16}$ = 9.25) | 2.10 (d, $J_{2,11}$ = 7.5) | 5.04 (s) | 5.70 (s) | 2.48 (d) | 4.70 (br s, OH) | 5.75 (d, $J_{14,15}$ = 10.5) | 7.0–7.4[a] | 6.40 (t, $J_{16,17}$ = 9.25) | 6.00 (d) | 7.0–7.4 (m) |
| **4c** | 3.60 (m) | 2.55 (dd, $J_{2,11}$ = 8.25, $J_{2,1}$ = 6.0) | 4.96 (s) | 5.00 (s) | 3.58 (d) | 1.90 (s, NH)<br>2.15 ($CH_3$) | 6.15 (d, $J_{14,15}$ = 10.5) | 6.9–7.3[a] | 6.50 (t, $J_{16,17}$ = 7.0) | 6.13 (d) | 6.9–7.3 (m) |
| **5c** | 3.61 (t, $J_{1,15}$ = 9.75, $J_{1,16}$ = 9.25) | 2.30 (d, $J_{2,11}$ = 9.0) | 5.06 (s) | 5.16 (s) | 2.60 (d) | 3.93 (d, $J_{12,1}$ = 7.5) | 1.91 (s, NH)<br>2.00 (s, $CH_3$) | 8.19 (d) | 6.60 (t, $J_{16,17}$ = 8.3) | 6.10 (t) | 7.0–7.3 (m) |
| **5e** | 3.55 (t, $J_{1,15}$ = 9.0, $J_{1,16}$ = 9.0) | 2.44 (d, $J_{2,11}$ = 8.25) | 5.03 (s) | 5.13 (s) | 2.67 (d) | 3.90 (d, $J_{12,17}$ = 9.0) | 2.14 (s, $CH_3$) | 6.80 (d) | 6.54 (t, $J_{16,17}$ = 7.5) | 6.20 (t) | 7.0–7.3 (m) |
| **5f** | 3.50 (m) | 2.15 (d, $J_{2,11}$ = 9.0) | 5.03 (s) | 5.12 (s) | 2.55 (d) | 3.89 (d, $J_{12,17}$ = 8.25) | 3.44 (s, $CH_3$) | 6.10 (d) | 6.60 (t, $J_{16,17}$ = 9.0) | 6.13 (t) | 7.0–7.3 (m) |
| **6f** | 3.85 (q, $J_{1,2}$ = 4.5) | 2.45 (m) | 5.00 (s) | 5.05 (s) | 2.52 (m) | 3.55 (t, $J_{12,11}$ = 4.5) | 3.60 (s, $CH_3$) | 5.90 (d, $J_{1,15}$ = 9.0) | 6.60 (t, $J_{16,17}$ = 6.75, $J_{16,1}$ = 9.0) | 6.12 (t, $J_{12,17}$ = 6.0) | 7.0–7.3 (m) |

[a] Overlapped with aromatic protons.

SCHEME II

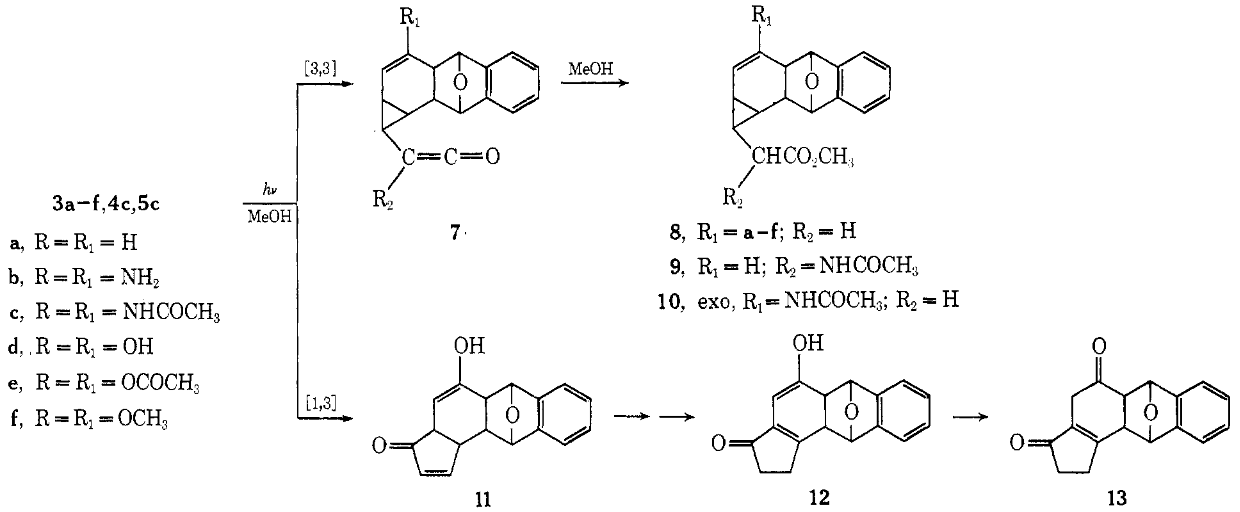

TABLE III

| Starting material | Product (yield, %) [3,3] type | [1,3] type |
|---|---|---|
| 3a | 8a (100) | |
| 3b | Decomposition | |
| 3c | 8c (100) | |
| 3d | | 13 (84) |
| 3e | 8e (100) | |
| 3f | 8f (45) + dihydro compound (8g) (19) | |
| 4c | 10 (82) | |
| 5c | 9 (28) | |

(d, 1 H, $J$ = 4.5 Hz), 5.33 (s, 1 H), 5.85 (s, 1 H), and 7.0–7.4 (m, 4 H). The formation of **13** could be explained in terms of the initial [1,3] acyl migration of **3d** to **11d** followed by successive [1,3] hydrogen shift to the conjugated diene **12d** and ultimate enol–keto tautomerization as shown in Scheme II.[9]

It is noteworthy that only the [1,3] sigmatropic rearrangement had occurred even in a nucleophilic solvent such as methanol. This is apparently due to the presence of the hydroxyl group at the bridgehead position (α to carbonyl group).

In further attempts to evaluate a role of the hydroxyl group in the photochemistry of the bicyclo[3.2.2]-nonadienone system, we have investigated the photochemical behavior of other α-hydroxy ketones such as **14**[13] and **15**.[14] These ketones were prepared from the Diels–Alder reaction of tropolone with benzyne[13] and *N*-phenylmaleimide,[14] respectively. Irradiation of **14**

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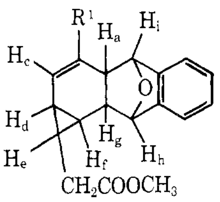
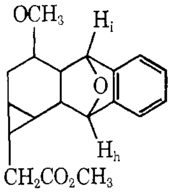
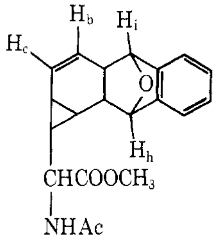
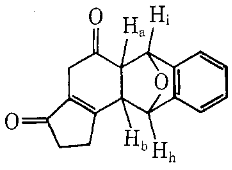
[13] M. Kato, Y. Okamoto, and T. Miwa, *Tetrahedron*, **27**, 4013 (1971).

[14] Structural determination was based on elemental analysis and spectroscopic data (see Experimental Section).

TABLE IV

NMR SPECTRA OF PHOTOREARRANGED PRODUCTS

| Structure | Compd | δ, ppm (J, Hz) | | | | | |
|---|---|---|---|---|---|---|---|
| | | $H_c$ | $H_h,H_i$ | Ar–N | $COOCH_3$ | $R_1$ | Other protons |
|  | **8c** | 5.70 (d, $J = 4.5$) | 5.15 (s) | 7.0–7.5 (m) | 3.59 (s) | $NHCOCH_3$ 2.15 (s) | 0.7–2.8 (m, 8 H, NH, $CH_2$, $H_a$, $H_d$, $H_e$, $H_f$, and $H_g$) |
| | **10** | 5.75 (d, $J = 4.5$) | 5.25 (s) | 6.9–7.4 (m) | 3.62 (s) | $NHCOCH_3$ 2.08 (s) | 2.0–3.0 (m, 5 H, NH, $CH_2$, $H_a$, and $H_g$), 1.2–1.9 (m, 3 H, $H_d$, $H_e$, and $H_f$) |
| | **8e** | 5.55 (d, $J = 6.0$) | 5.22 (s) | 6.9–7.4 (m) | 3.58 (s) | $OCOCH_3$ 2.18 (s) | 1.2–2.5 (m, 7 H, $CH_2$, $H_a$, $H_d$, $H_e$, $H_f$, and $H_g$) |
| | **8f** | 4.85 (d, $J = 4.5$) | 5.20 (s)<br>5.30 (s) | 7.0–7.4 (m) | 3.60 (s) | $OCH_3$ 3.60 (s) | 1.0–2.3 (m, 7 H, $CH_2$, $H_a$, $H_d$, $H_e$, $H_f$, and $H_g$) |
| | | $H_h,H_i$ | $COOCH_3$ | $OCH_3$ | Other protons | | |
|  | **8g** | 5.25 (s)<br>5.60 (s) | 3.40 (s) | 3.33 (s) | 1.0–3.3 (m, 10 H)<br>7.0–7.3 (m, 4 H) | | |
| | | $H_b,H_c$ | $H_h,H_i$ | $COOCH_3$ | $COCH_3$ | Other protons | |
|  | **9** | 5.95 (m) | 4.98 (s), 5.19 (s) | 3.70 (s) | 1.90 (s) | 1.1–2.0 (m, 4 H), 2.15 (d, 2 H), 4.05 (t, CH, $J = 7.5, 9.0$) 6.9–7.3 (m, 4 H) | |
| | | $H_a$ | $H_b$ | $H_h,H_i$ | Other protons | | |
|  | **13** | 3.50 (d, $J = 4.5$) | 2.65 (d) | 5.33 (s), 5.85 (s) | 1.3–2.5 (m, 6 H), 7.0–7.4 (m, 4 H) | | |

in methanol was found to give a photoisomer **16** as only one isolable main product (17%) together with several minor products (see Scheme III). No ester products could be detected by nmr spectroscopy. The isomeric nature of **16** was confirmed by mass spectrum which displayed a molecular ion peak at $m/e$ 198. The uv spectrum showed maxima at 215 nm ($\epsilon$ 68,000), 260 (157,000), 280 (80,000), 370 (7050), and 430 (382, sh), suggesting the presence of a naphthalene ring. The ir spectrum exhibited a band at 1670 $cm^{-1}$. Unequivocal structural assignments were made on the basis of its nmr spectrum: $\delta$ 2.75 (t, 2 H, $J = 7.5$ Hz), 3.25 (t, 2 H, $J = 7.5$ Hz), 2.5–3.0 (1 H, exchangeable by $D_2O$, OH), and 7.0–8.0 (m, 5 H, aromatic H).

Irradiation of **15** in methanol gave a diketone **17** in a quantitative yield (see Scheme III). The structural assignment was based on the spectral data: ir (KBr) 1790, 1740, 1710, and 1659 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 1.34–2.85 (m, 6 H, methylene), 3.68 (d, 1 H, $J = 10.5$ Hz), 3.75 (d, 1 H, $J = 10.5$ Hz), and 7.0–7.5 (m, 5 H, aromatic).

These results indicate that [1,3] sigmatropic rearrangement is more significant than [3,3] rearrangement on irradiation of the tropolone adduct even in a nucleophilic solvent. This is in a sharp contrast to Kende's conclusion for the tropone adduct.[5] Attempts to sensitize photolysis of **15** in methanol using benzophenone (absorbing over 90% of incident light) sharply retarded the appearance of **17** and led to a complex mixture (no ester products by nmr inspection).[15]

This strongly suggested that the [1,3] rearrangement of a tropolone adduct may arise from a singlet excited state similar to [1,3] and [3,3] rearrangements of tropone adducts.[5,6] Thus, the presence of a hydroxyl group at the bridgehead position ($\alpha$ to carbonyl carbon) is a major factor governing the photoisomerization of this system. This can be explained in terms of intramolecular hydrogen bonding between carbonyl oxygen and hydroxyl group.[16] Evidence for such hydrogen bonding in the excited state was obtained by the uv spectral comparison of **3a**[9] with **3d** in various solvents (Table V).

For a tropone adduct **3a**, the typical solvent dependence on n–$\pi^*$ transition (*i.e.*, hypsochromic shift with increasing solvent polarity)[17] was observed. In

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(15) Use of benzophenone as a sensitizer in a solvent with readily abstractable hydrogen atoms can lead to photoreduction of the substrate due to hydrogen abstraction by excited benzophenone followed by hydrogen atom transfer to the substrate. Unless the concentration of substrate is high enough to quench the benzophenone triplet efficiently, this can be the predominant reaction. This may be the reason for the complex mixture which was observed.

(16) The reaction course of tropolone adduct could not be changed by replacement of the H bond with a weaker D bond, since irradiation of **15** in $CH_3CN$–$D_2O$ (1:1), in which over 90% of the hydroxyl proton was exchanged by $D_2O$, gave exclusively the [1,3] product.

(17) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965.

SCHEME III

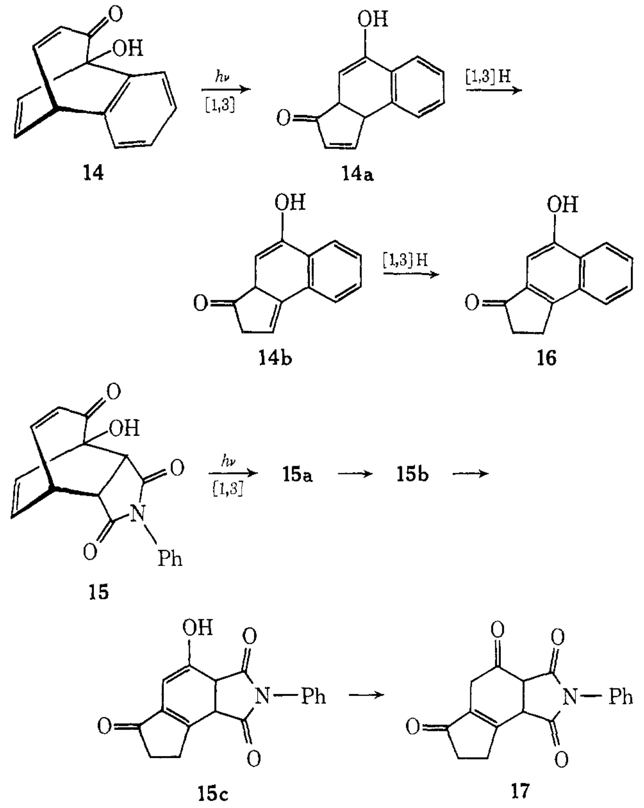


TABLE V

| Solvent | Dielectric constant[a] | λ$_{max}$, nm (ε) 3a | 3d |
|---|---|---|---|
| *n*-Hexane | 1.87 | 355 (52) | 335 (102) |
| Chloroform | 4.9 | 350 (121) | 335 (143) |
| Ethanol | 25.7 | 350 (100) | 335 (100) |
| Methanol | 33.7 | 345 (108) | 335 (114) |
| Acetonitrile | 38.8 | 345 (106) | 332 (124) |

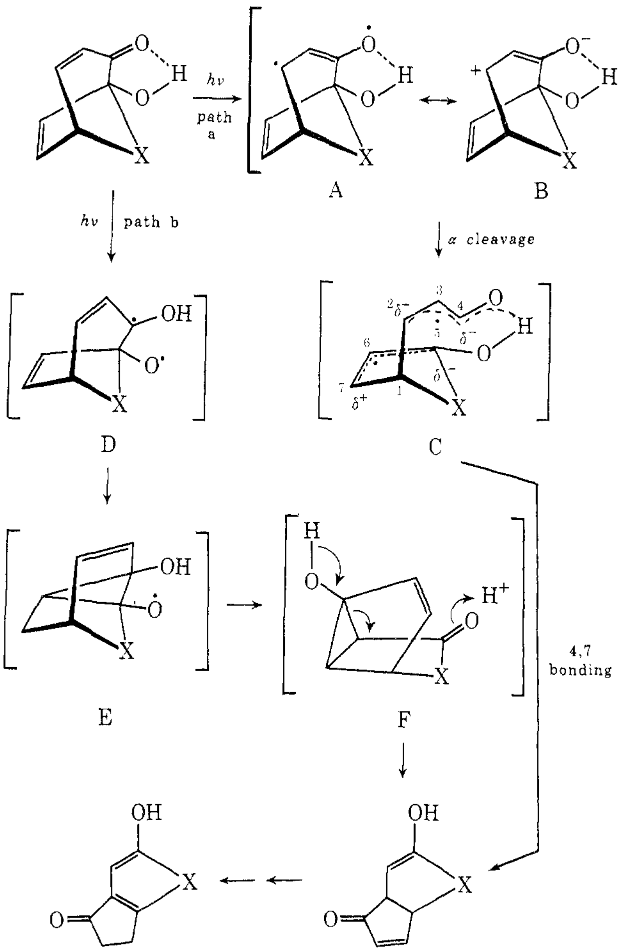
[a] International Critical Tables (at 20°).

contrast, the uv spectrum of the tropolone adduct **3d** was not affected by changing the solvents. These differences are probably attributed to the intramolecular hydrogen bonding of the ketone **3d**.

Further, the hydroxyl absorption of **3d** in 1 and 10% chloroform solutions by ir showed the same pattern suggesting the presence of intramolecular hydrogen bonding.

According to the Woodward–Hoffmann rule,[18] suprafacial [$_\pi 2_s + {}_\sigma 2_s$] [1,3] sigmatropic rearrangement is photochemically allowed, but a [3,3] shift is symmetry forbidden.

SCHEME IV



From these results, two mechanistic paths a and b may be postulated to account for the formation. Assuming the initial α cleavage of the tropolone adducts to give the diradical intermediate C, the above results can be depicted in Scheme IV; the α cleavage of ketones is well known to be favored by substitution α to the carbonyl.[19,20] Two allyl radical moieties (*i.e.*, C$_2$–C$_3$–C$_4$ and C$_5$–C$_6$–C$_7$) in C must be somewhat polarized by the intramolecularly hydrogen-bonded oxygens. Hence 2,5 and 4,7 bonding rather than 2,7 bonding would be electronically favored. Considering the stability of the resulting structures, it is apparent that 4,7 bonding is more favored than 2,5 bonding which would lead to a more strained structure (*i.e.*, bicyclo[2.2.1]heptene). In other cases[3,5,9] where there is no such hydrogen bonding, 2,7 bonding (*i.e.*, [3,3] rearrangement) is most favored because of the closer bond distance between C-2 and C-7. On the other hand path b might proceed by a complete hydrogen atom transfer to the carbonyl, followed by a "walk" process (*via* D → E) and then a prototropic shift.[21]

The formation of the photoreduction product **8g** from the ketone **3f** suggests the diradical mechanism depicted in Scheme V. The initially formed diradical intermediates G and H are somewhat stabilized by the methoxyl group and abstract hydrogen from the solvent leading to **8g**. Thus, path c could compete with path d *via* intramolecular ring closure by [3,3] rearrangement.

From these results, it is to be noted that intramolecular hydrogen bonding plays an important role in governing the photoisomerization of the bicyclo[3.2.2]nonadienone system, although further studies are necessary to settle the mechanism.

## Experimental Section

Melting points are uncorrected. Microanalyses were performed with a Perkin-Elmer 240 elemental analyzer. Uv spectra were determined with a JASCO ORD-UV-5 recorder. Nmr

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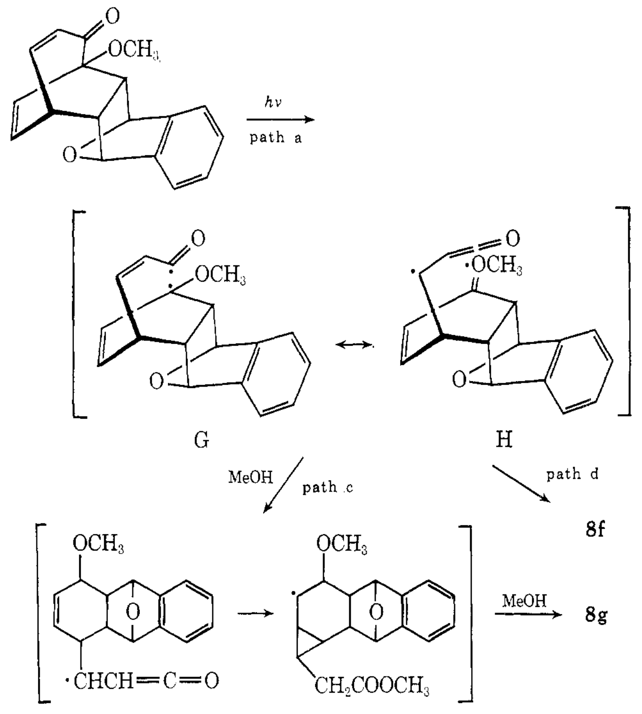
[18] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie-Academic Press, New York, N. Y., 1970.

[19] (a) P. J. Wagner and R. W. Spoerk, *J. Amer. Chem. Soc.*, **91**, 4437 (1969); (b) J. C. Dalton, D. M. Pond, D. S. Weuss, F. D. Lewis, and N. J. Turro, *ibid.*, **92**, 564 (1970).

[20] W. C. Agosta and A. B. Smith, III, *J. Amer. Chem. Soc.*, **93**, 5513 (1971).

[21] We are indebted to a referee for pointing out this possibility to us.

SCHEME V



spectra were taken with a JEOL C-60-XL spectrometer and with a Varian A-60 recording spectrometer, with tetramethylsilane as internal standard. Ir spectra were taken with a JASCO-IR-S spectrophotometer. Mass spectra were obtained with a Hitachi RMU-D double-focusing spectrometer operating at an ionization potential of 70 eV. The solid samples were ionized by electron bombardment after sublimation directly into the electron beam at 100–150°. Glpc analyses were performed with a NEVA gas chromatograph Model 1400 and preparative glpc with a Varian Aerograph Model 700 (silicon SE-30).

**General Procedure for Cycloaddition Reactions.**—A solution of 1:1 mixture of oxabenzonorbornadiene (1) and 2-substituted tropone in toluene was heated at 130° in a sealed tube for 40 hr. After removal of the solvent, the reaction mixture was analyzed by glpc and then purified by chromatography on a silica gel column.

**A. With 2-Aminotropone (2b).**—A solution of 595 mg of 1 and 500 mg of **2b** in 50 ml of toluene was heated. Work-up gave 550 mg of adduct **3b** as colorless crystals: mp 151–153° (benzene); ir (KBr) 3400, 1660 cm$^{-1}$; uv (ethanol) $\lambda_{max}$ 225 nm ($\epsilon$ 6160), 263 (1620), 271 (1040), 340 (108); *m/e* 265 (parent), 118.

*Anal.* Calcd for $C_{17}H_{15}O_2N$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.66; H, 5.70; N, 5.21.

**B. With 2-Acetylaminotropone (2c).**—A solution of 1.2 g of 1 and 1.3 g of **2c** in 50 ml of toluene was heated. The reaction mixture was subjected to silica gel chromatography using chloroform. The first fraction gave 120 mg of adduct **5c** as colorless crystals: mp 177–179 (benzene–ethanol); ir (KBr) 3350, 1685, 1650, 1620, 1510 cm$^{-1}$; uv (ethanol) $\lambda_{max}$ 264 nm ($\epsilon$ 3070), 271 (3200), 284 (3420), 345 (192); *m/e* 307 (parent), 118.

*Anal.* Calcd for $C_{19}H_{17}O_3N$: C, 74.25; H, 5.58; N, 4.56. Found: C, 74.20; H, 5.66; N, 4.80.

The second fraction gave 100 mg of adduct **4c** as colorless crystalls: mp 220° dec (benzene–ethanol); ir (KBr) 3500, 1680, 1645, 1500 cm$^{-1}$; uv (ethanol) $\lambda_{max}$ 240 nm ($\epsilon$ 4300), 265 (2580), 270 (1650), 330 (74); *m/e* 307 (parent), 118.

*Anal.* Calcd for $C_{19}H_{17}O_3N$: C, 74.25; H, 5.58; N, 4.56. Found: C, 74.53; H, 5.74; N, 4.52.

The third fraction gave 170 mg of adduct **3c** as pale yellow crystals: mp 229° (benzene–ethanol); ir (KBr) 3400, 1690, 1655, 1520 cm$^{-1}$; uv (ethanol) $\lambda_{max}$ 262 nm ($\epsilon$ 2080), 272 (1200), 340 (100); *m/e* 307 (parent), 118.

*Anal.* Calcd for $C_{19}H_{17}O_3N$: C, 74.25; H, 5.88; N, 4.56. Found: C, 74.48; H, 5.78; N, 4.41.

**C. With Tropolone (2d).**—A solution of 520 mg of 1 and 400 mg of **2d** in 50 ml of toluene was heated. Work-up gave 450 mg of adduct **3d** as colorless crystals: mp 166–167.5° (ethanol); ir (KBr) 3400, 1650, 1630, 1100 cm$^{-1}$; uv (ethanol) $\lambda_{max}$ 265 nm ($\epsilon$ 1690), 270 (980), 340 (84); *m/e* 266 (parent), 118.

*Anal.* Calcd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.46; H, 5.40.

**D. With 2-Acetoxytropone (2e).**—A solution of 590 mg of 1 and 620 mg of **2e** in 50 ml of toluene was heated. After evaporation of the solvent, the resulting residue was subjected to silica gel chromatography and fractional crystallization from ethanol to give 330 mg of adduct **3e** and 210 mg of adduct **5e**.

For the first, **3e**, the following was observed: mp 209–211° (ethanol); ir (KBr) 1740, 1660, 1240, 1060 cm$^{-1}$; uv (ethanol) $\lambda_{max}$ 260 nm ($\epsilon$ 1620), 269 (1020), 340 (137); *m/e* 308 (parent), 118.

*Anal.* Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 73.96; H, 5.28.

For the second, **5e**, the following was observed: mp 189–191° (ethanol); ir (KBr) 1755, 1660, 1205 cm$^{-1}$; uv (ethanol) $\lambda_{max}$ 265 nm ($\epsilon$ 2200), 270 (1440), 340 (59); *m/e* 308 (parent), 118.

*Anal.* Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 73.90; H, 5.34.

**E. With 2-Methoxytropone (2f).**—A solution of 480 mg of 1 and 550 mg of **2f** was heated. The reaction mixture was chromatographed on a silica gel column using benzene–acetone. The first fraction gave 65 mg of adduct **3f** as colorless crystals: mp 128–130° (ethanol); ir (KBr) 1655, 1105 cm$^{-1}$; *m/e* 280 (parent), 118.

*Anal.* Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.10; H, 5.79.

The second fraction gave 170 mg of adduct **5f** as colorless crystals: mp 185–188° (ethanol); ir (KBr) 1650, 1630, 1600, 1220, 1200, 1140, 1120 cm$^{-1}$; uv (ethanol) $\lambda_{max}$ 265 nm ($\epsilon$ 3090), 267 (3220), 274 (3360), 280 (3190), 330 (174); *m/e* 280 (parent), 118.

*Anal.* Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.08; H, 5.79.

The third fraction gave 70 mg of adduct **6f**: mp 175–178° (ethanol); ir (KBr) 1650, 1620, 1610, 1120 cm$^{-1}$; *m/e* 280 (parent), 118.

*Anal.* Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.00; H, 5.69.

**General Procedure for Irradiations.**—A solution of the adduct in dry methanol was irradiated by a high-pressure 100-W mercury lamp through a Pyrex filter under nitrogen at room temperature. The photolyses were monitered by tlc and glpc. The solvent was removed under reduced pressure, and the residue was analyzed by nmr and then purified by silica gel chromatography.

**Photolysis of 3b.**—A solution of 200 mg of **3b** in 50 ml of methanol was irradiated for 1 hr. Tlc analysis indicated the presence of more than nine components which decomposed to intractable materials during the purification.

**Photolysis of 3c.**—A solution of 100 mg of **3c** in 50 ml of methanol was irradiated for 75 min. Work-up gave 110 mg of ester (**8c**) as pale yellow crystals: mp 72–73° (benzene–hexane); ir (KBr) 3280, 1725, 1650, 1540 cm$^{-1}$; *m/e* 339 (parent), 118.

*Anal.* Calcd for $C_{20}H_{21}O_4N$: C, 70.78; H, 6.24; N, 4.13. Found: C, 70.91; H, 6.44; N, 3.92.

**Photolysis of 4c.**—A solution of 60 mg of **4c** in 40 ml of methanol was irradiated for 1 hr. Nmr analysis of the reaction mixture indicated the presence of unconverted **4c** (18%) and ester **10** (82%). After removal of solvent, the residue was subjected to silica gel chromatography using chloroform. The first fraction gave 50 mg of **10** as colorless crystals: mp 143–145° (benzene–hexane); ir (KBr) 3250, 1730, 1650, 1540 cm$^{-1}$; *m/e* 339 (parent), 118.

*Anal.* Calcd for $C_{20}H_{21}O_4N$: C, 70.78; H, 6.24; N, 4.13. Found: C, 70.88; H, 6.35; N, 4.01.

**Photolysis of 5c.**—A solution of 1.0 g of **5c** in 100 ml of methanol was irradiated for 11 hr. Work-up gave 310 mg of **9** as colorless crystals: mp 104–106° (benzene–hexane); ir (KBr) 3300, 1740, 1650, 1530 cm$^{-1}$: *m/e* 339 (parent), 118.

*Anal.* Calcd for $C_{20}H_{21}O_4N$: C, 70.78; H, 6.24; N, 4.13. Found: C, 70.53; H, 6.18; N, 4.00.

**Photolysis of 3d.** A solution of 250 mg of **3d** in 50 ml of methanol was irradiated for 1.5 hr. Work-up gave 210 mg of diketone **13** as colorless crystals: mp 193–195° (benzene–hexane); ir (KBr) 1740, 1700, 850, 760 cm$^{-1}$; *m/e* 266 (parent), 118.

*Anal.* Calcd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.45; H, 5.51.

**Photolysis of 3e.**—A solution of 70 mg of **3e** in 50 ml of methanol was irradiated for 0.5 hr. After evaporation of the solvent, the resulting residue was recrystallized from methanol to give 80 mg of **8e** as colorless crystals: mp 145.5–146°; ir (KBr) 1750, 1730, 1230, 1200 cm$^{-1}$; *m/e* 340 (parent), 118.

*Anal.* Calcd for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92. Found: C, 70.41; H, 5.74.

**Photolysis of 3f.**—A solution of 75 mg of **3f** in 50 ml of methanol was irradiated for 0.5 hr. After evaporation of the solvent, the resulting residue was subjected to silica gel chromatography and then fractional crystallization from ether to give 50 mg of **8f** and 25 mg of **8g**.

For the first, **8f**, the following was observed: mp 97–98° (benzene–hexane); ir (KBr) 1730, 1660 1210, 1170 cm$^{-1}$; *m/e* 312 (parent), 118.

*Anal.* Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 73.03; H, 6.44.

For the second, **8g**, the following was observed: mp 212–214° (petroleum ether); ir (KBr) 1730, 1110 cm$^{-1}$; *m/e* 314 (parent), 118.

*Anal.* Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 72.88; H, 6.99.

**Reaction of 2d with *N*-Phenylmaleimide.**—A solution of 500 mg of **2d** and 775 mg of *N*-phenylmaleimide in 30 ml of toluene was refluxed for 9 hr. Evaporation of the solvent under the reduced pressure gave a pale yellow residue which was recrystallized from ethanol to give 560 mg of colorless solid. Glpc and nmr analyses showed it to be a mixture of endo adduct **15** and exo adduct in the ratio 2:1. Because of its low solubility, the purification was very difficult and only major product **15** was isolated as colorless crystals by fractional crystallization from ethanol: mp 213–215°; ir (KBr) 3400, 1780, 1700, 1670, 1380 cm$^{-1}$; nmr ($CDCl_3$) δ 3.46 (d, 1 H, *J* = 7.5 Hz), 3.62 (d, 1 H, *J* = 7.5 Hz), 4.10 (m, 1 H), 4.90 (s, 1 H, exchangeable by $D_2O$), 6.0–6.3 (m, 3 H), 6.55 (t, 1 H, *J* = 9.0 Hz), 7.0–7.5 (m, 5 H); *m/e* 295 (parent).

*Anal.* Calcd for $C_{17}H_{13}O_4N$: C, 69.14; H, 4.44; N, 4.74. Found: C, 69.01; H, 4.63; N, 4.75.

**Photolysis of 14.**—A solution of 106 mg of **14** in 50 ml of methanol was irradiated for 2 hr under the same conditions as above. The reaction mixture was analyzed by nmr and then chromatographed on a silica gel column using chloroform. The first fraction gave 10 mg of unconverted **14**. The second fraction gave 15 mg of photoproduct **16**: mp 134–135° (ethanol); ir (KBr) 3300, 1665, 1585 cm$^{-1}$; *m/e* 198 (parent).

*Anal.* Calcd for $C_{13}H_{10}O_2$: C, 78.77; H, 5.09. Found: C, 78.54; H, 5.13.

**Photolysis of 15.**—A suspension of 150 mg of **15** in 50 ml of methanol was irradiated for 1 hr. After removal of the solvent, the resulting residue was chromatographed using chloroform. The first fraction gave 10 mg of unconverted **15** and the second fraction gave 90 mg of diketone **17** as colorless crystals: mp 199–201° (benzene–ethanol); ir (KBr) 1780, 1740, 1710, 1695, 1500 cm$^{-1}$; *m/e* 295 (parent).

*Anal.* Calcd for $C_{17}H_{13}O_4N$: C, 69.14; H, 4.44; N, 4.74. Found: C, 69.39; H, 4.57; N, 4.62.

**Registry No.**—**1**, 573-57-9; **2a**, 539-80-0; **2b**, 6264-93-3; **2c**, 6422-12-4; **2d**, 533-75-5; **2e**, 33739-54-7; **2f**, 2161-40-2; **3a**, 38276-32-3; **3b**, 42150-82-3; **3c**, 42150-83-4; **3d**, 42150-84-5; **3e**, 42150-85-6; **3f**, 42150-86-7; **4c**, 42150-87-8; **5c**, 42150-88-9; **5e**, 42150-89-0; **5f**, 42150-90-3; **6f**, 42150-91-4; **8c**, 42150-92-5; **8e**, 42150-93-6; **8f**, 42150-94-7; **8g**, 42150-95-8; **9c**, 42150-96-9; **13**, 38276-37-8; **14**, 33655-59-3; **15**, 42150-99-2; *exo*-**15**, 42151-00-8; **16**, 5824-32-8; **17**, 42151-02-0; *N*-phenylmaleimide, 941-69-5.

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# Halogenated Ketenes. XXIV. Cycloaddition of Alkylhaloketenes and Methylenecycloalkanes. Spiro Compounds[1]

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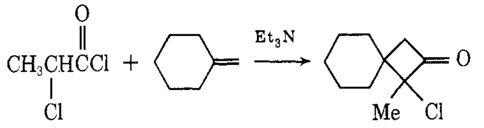
*Received July 9, 1973*

The cycloaddition of methylchloroketene with methylenecyclohexane, methylenecyclobutane, β-pinene, and 5-methylene-2-norbornene to yield the corresponding spiro[3.5] and spiro[3.3] ketones has been investigated. The cycloaddition of ethylchloroketene with methylenecyclobutane is also described. The spiro ketones are all readily reduced to the corresponding spiro alcohols. Some base-catalyzed rearrangement reactions are described including ring contractions to spiro[5.2] compounds.

A number of reports have appeared in recent years on the cycloaddition of ketenes and olefinic compounds. The majority of these reports have been concerned with the reactive cyclopentadiene and/or other activated olefins. Cycloadditions with methylenecycloalkanes has received little attention and in the scattered reports few details are given.[2-4]

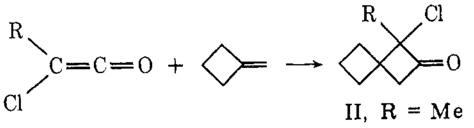
We now report the cycloaddition of the reactive alkylhaloketenes and methylenecycloalkanes to yield [3.*n*] spiro ketones depending on the particular methylenecycloalkane employed. The spiro ketones and particularly the spiro alcohols undergo a base-catalyzed ring contraction reaction to yield other spiro compounds, thus providing an excellent general method for a wide variety of spiro compounds.

The *in situ* cycloaddition of methylchloroketene and methylenecyclohexane resulted in a 60% yield of the spiro[5.3]nonanone I. The optimum conditions for effecting this cycloaddition are in refluxing hexane. A slow addition of acid halide to the amine and olefin in hexane are desirable to minimize the formation of the α-halovinyl ester.[5,6]



I

This *in situ* cycloaddition also occurs with methylenecyclobutane to yield the corresponding spiro[3.3]heptanones in 30 and 35% yields, respectively (II and III). The yield is lower with this olefin because the



II, R = Me
III, R = Et

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[1] Paper XXIII: W. T. Brady and G. A. Scherubel, *J. Amer. Chem. Soc.*, in press.

[2] P. R. Brook and J. G. Griffiths, *Chem. Commun.*, 1344 (1970).

[3] R. Maurin and M. Bertrand, *Bull. Soc. Chim. Fr.*, 998 (1970).

[4] J. R. Wiseman and H. F. Chan, *J. Amer. Chem. Soc.*, **92**, 4749 (1970).

[5] R. Giger, M. Rey, and A. S. Dreiding, *Helv. Chim. Acta*, **51**, 1466 (1968).

[6] W. T. Brady, F. H. Parry, III, R. Roe, Jr., E. F. Hoff, Jr., and L. Smith, *J. Org. Chem.*, **35**, 1515 (1970).