H each, s); mass spectrum (no parent), *m/e* (rel intensity) 136 (base peak, 3.6), 67 (100). (b) Adduct **21**: ir (film) 1707 cm^{-1}; nmr ($CDCl_3$) τ 3.63 (1 H, 2 d, J = 2.8, J' = 1.6 Hz), 4.88 (1 H, 2 d, J = 2.8, J' = 2.0 Hz), 6.20 (1 H, s, br), 7.2 (AB, J = 12 Hz), 7.78, 8.48, and 8.83 (3 H, each, s); mass spectrum *m/e* (rel intensity) 166 (parent, 31), 110 (100). *Anal.* Calcd for $C_{10}H_{14}O_2$: C, 72.31; H, 8.43. Found: C, 72.02; H, 8.28. (c) Adduct **22**: ir (film) 1700 cm^{-1}; nmr ($CDCl_3$) τ 3.77 (1 H), 4.8 (1 H), 6.85 (1 H, m), 7.4 (2 H, m) and 7.69, 8.57, and 9.06 (3 H each, s); mass spectral parent ion at *m/e* 166.

Photochemical Reaction of 2-Benzoylfuran with 2,3-Dimethyl-2-butene. A solution of 2-benzoylfuran (**4**, 1.0 g, 6.5 mmol) and 2,3-dimethyl-2-butene (30 g) in spectrograde hexane was irradiated through a uranium glass filter for 6 hr. Evaporation of the solvent and excess olefin at reduced pressure left a viscous yellow residue which was distilled in a short-path apparatus at 0.04 mm (bath temperature 60-90°). Two fractions were collected. The first (0.32 g) was purified by gc on column B and was shown by spectral data to be olefin **25**: ir (film) 1590 cm^{-1}; nmr ($CDCl_3$) τ 2.3-2.8 (6 H, m), 3.5-3.8 (2 H, multiplets, furan H), 8.34, and 8.56 (3 H each, s); mass spectrum *m/e* (rel intensity) 198 (parent, 73), 183 (17), and 77 (100). The second, higher boiling fraction on dissolving in pentane and cooling to −20° gave oxetane **24** (0.45 g, 27%) as colorless prisms: mp 43–44°; nmr ($CDCl_3$) 2.6–2.9 (6 H, m) 3.6–3.8 (2 H, m, furan H), 8.33, 8.68, 8.88, and 9.12 (all 3 H each, s); mass spectrum (no parent ion) *m/e* (rel intensity) 198 (22), 183 (15), 174 (40), and 84 (100). *Anal.* Calcd for $C_{17}H_{20}O_2$: C, 79.70; H, 7.81. Found: C, 79.85; H, 7.68.

Irradiation of ketone **4** in the presence of excess isobutene led to dark solutions from which could be obtained by evaporation distillation only low yields of olefin **25**.

Irradiation of 1-Methyl-2-benzoylpyrrole (6) with 2,3-Dimethyl-2-butene. A solution of ketone **6** (1.0 g) and 2,3-dimethyl-2-butene made up to 120 ml in spectrograde hexane was irradiated through Pyrex for 10 hr. Work-up in the usual way gave 0.20 g of an oil, bp 76–80° (0.1 mm), which was impure **26**: ir 1616 cm^{-1}; nmr ($CDCl_3$) τ 2.6–3.0 (5 H, m), 3.6–3.9 (~3 H, m), and 8.34 (6 H, s); mass spectrum *m/e* (rel intensity) 211 (parent, 14), 184 (31), 105 (56), and 84 (100).

Quantum Yields. The quantum yields for reactions of **1** and **2** were measured in a Rayonet Chamber Reactor, using lamps whose output centered at 3000 and 3500 Å, respectively, with a rotating tube holder. For **2**, decafluorobenzophenone–decafluorobenzhydrol was used as the actinometer,[16] and for **1**, the system acetophenone–2-propanol. The measurements were made with solutions which were 0.1 *M* in ketone and 5 *M* in olefin; runs were carried to ≤5% conversion.

Acknowledgments. The author wishes to express his sincere gratitude to the following individuals who greatly aided this work: Mr. Edward Sokolowski of the National Heart and Lung Institute for performing the decoupling experiments and for the ^{13}C nmr data; Dr. Henry Fales of NHLI for helpful discussions; Mr. William Landis of the National Institute of Arthritis, Metabolism, and Digestive Diseases for the mass spectra of the compounds reported; and Professor R. L. Cargill of the University of South Carolina for the emission spectra of 1–4.

Registry No.—**1**, 88-15-3; **2**, 135-00-2; **3**, 1192-62-7; **4**, 2689-59-0; **6**, 37496-06-3; **7**, 51248-17-0; **8**, 35461-78-0; **9**, 51248-18-1; **11**, 51248-19-2; **12**, 51540-14-8; **13**, 51248-20-5; **14**, 51271-74-0; **15**, 51248-21-6; **16**, 704-38-1; **17**, 51248-22-7; **18**, 51248-23-8; **19**, 51248-24-9; **20**, 51248-25-0; **21**, 35461-80-4; **22**, 35551-52-1; **23**, 51248-26-1; **24**, 35461-83-7; **25**, 51248-27-2; **26**, 51248-28-3; 2,3-dimethyl-2-butene, 563-79-1; isobutene, 115-11-7.

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Molecular Design by Cycloaddition Reactions. XV.[1] Transannular Cross Cyclization of Cyclooctatetraene–Maleic Anhydride Adduct by Electrophiles

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Reaction of tricyclo[4.2.2.0^{2,5}]deca-3,7-diene derivatives with electrophiles (bromine, *tert*-butyl hypochlorite, iodine chloride, and iodine azide) has been studied, some of which proceed by transannular cross bonding of the proximal π bonds to give novel caged compounds. The structures of these products were determined by spectral means and chemical transformations. Some mechanisms for the formation of the products are discussed.

Facile addition reactions involving transannular π participation between two double bonds are well documented in such systems as norbornadiene,[2] 1,5-cyclooctadiene,[3] and some caged compounds[4,5] containing two isolated double bonds in spatial proximity.

With a hope of providing the synthetic entry of new carbon-skeleton construction and of understanding the capability of the participation between two isolated double bonds in ionic reaction, we have investigated the electrophilic addition reaction of tricyclo[4.2.2.0^{2,5}]deca-3,7-diene-9,10-dicarboxylic anhydride (a 1:1 adduct of cyclooctatetraene and maleic anhydride).

Table I

Compd	Electrophile	Solvent	Products	Yield, %
1	*t*-BuOCl	Acetone	**3a**	Quantitative[c]
2	*t*-BuOCl	Ether	**4a**	Quantitative[c]
1	Br_2	Acetic acid	**3b**	Quantitative[c]
2	Br_2	Chloroform	**4b**	Quantitative[c]
1	Br_2	Methanol	**5**	38
1	Br_2	Acetonitrile	**6**[a]	Quantitative[c]
1	Br_2	Acetonitrile–water (1:1)	**3b** + **6**[a]	59 + 11
1	NBS	DMSO–water	**3b**	16
1	Br_2	Benzonitrile	**6**[b]	80
1	ICl	Methanol	**8** + **9**	20 + 39

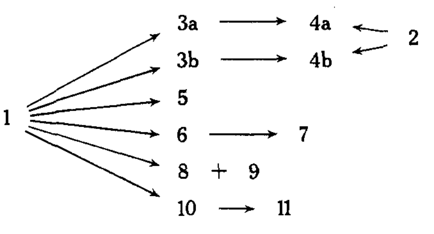
[a] Acetic acid was also detected by glpc. [b] Benzoic acid was also detected. [c] Calculation by glpc.

Results and Discussion

Halogenation of the Adduct. Reaction of the adduct **1** with *tert*-butyl hypochlorite resulted in the formation of compound **3a** in almost quantitative yield. Treatment of **3a** with diazomethane gave compound **4a**, which was also obtained by treatment of **2** with *tert*-butyl hypochlorite. Similar reaction of **1** with bromine in acetic acid gave compound **3b**. Esterification of **3b** gave **4b**, which was afforded also by treatment of **2** with bromine in chloroform. On the other hand, similar bromination of **1** in methanol and in acetonitrile gave compound **5** (38%) and **6** (almost quantitative), respectively. Further esterification of **6** by diazomethane or methanol in sulfuric acid gave compound **7**. In the case of **1** with bromine in acetonitrile and water (1:1), a mixture of **3b** and **6** was obtained in 59 and 11% yields. Interestingly, when **1** was treated with bromine in benzonitrile, compound **6** was also obtained together with benzoic acid. In contrast, iodination of **1** was very difficult by the standard method from iodine and potassium iodide.[6] However, when iodine chloride and/or iodine azide were employed, a mixture of **8** and **9**, and/or **10**, were obtained, respectively. Compound **10** showed a strong azide absorption at 2100 cm^{-1} in the ir spectrum, but because of its explosivity, the structural determination was based on that of the 1,3-dipolar cycloadduct **11**.

The results of the halogenations of **1** and **2** under various conditions are summarized in Table I and Scheme I.

Scheme I



Structural Elucidation of the Halogenated Compounds by Spectral Inspection and Chemical Transformation. Structural elucidation of the halogenated compounds was accomplished by their spectral analyses. These nmr data are summarized in Table II.

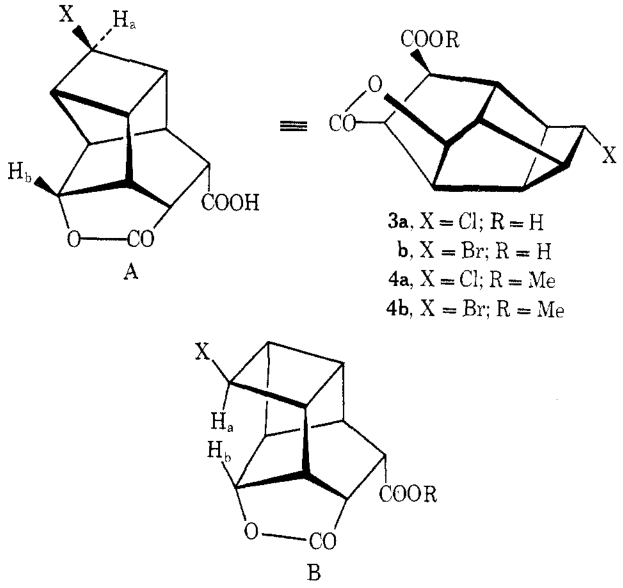
The ir spectra of both **4a** and **4b** show carbonyl absorptions at 1770 and 1735 cm^{-1}. The absorption at 1770 cm^{-1} suggests the presence of a five-membered-ring lactone moiety. The nmr spectra of **4a** and **4b** exhibited no olefinic proton signals. Elemental analyses show the products **4a** (X = Cl) and **4b** (X = Br) to be both $[C_{13}H_{13}O_4X]_n$. Thus, both compounds have two possible structures, A and B, as depicted in Chart I.

Table II
Nmr Spectral Data of Halogenated Compounds

Compd	Nmr signals ($CDCl_3$), δ (*J*, Hz)
4a	2.30–2.90 (6 H, m), 3.20 (1 H, dt, *J* = 6.75, 5.25, 1.00), 3.58 (1 H, m), 3.66 (3 H, s, $COOCH_3$), 3.90 (1 H, s, ClCH<), 4.77 (1 H, dd, *J* = 7.50, 2.25, >CHOCO)
4b	2.30–2.80 (6 H, m), 3.2 (1 H, m), 3.58 (1 H, m), 3.68 (3 H, s, $COOCH_3$), 3.88 (1 H, s, BrCH<), 4.80 (1 H, dd, *J* = 7.50, 3.00, >CHOCO)
5	2.40–2.60 (2 H, m), 2.60–2.80 (4 H, m), 3.20 (3 H, s, OCH_3), 3.25–3.60 (3 H, m), 3.89 (1 H, s, BrCH<)
7	2.30–2.50 (2 H, m), 2.50–2.70 (4 H, m), 3.05 (1 H, t, *J* = 4.50), 3.43 (1 H, m), 3.63 (4 H, s, $COOCH_3$ and 1 H), 3.83 (1 H, s, BrCH<), 6.40 (1 H, broad s, NH)[a]
9	2.43–2.83 (6 H, m), 3.23 (1 H, m), 3.43 (1 H, m), 3.70 (4 H, s, $COOCH_3$ and 1 H), 4.83 (1 H, dd, *J* = 3.75, 9.75)
11	3.15 (2 H, m), 3.40–3.88 (4 H, m), 3.90 (3 H, s, $COOCH_3$), 3.93 (3 H, s, $COOCH_3$), 4.40–4.70 (2 H, m), 6.57 (2 H, dd, *J* = 5.50, 7.50)

[a] Exchangeable by D_2O.

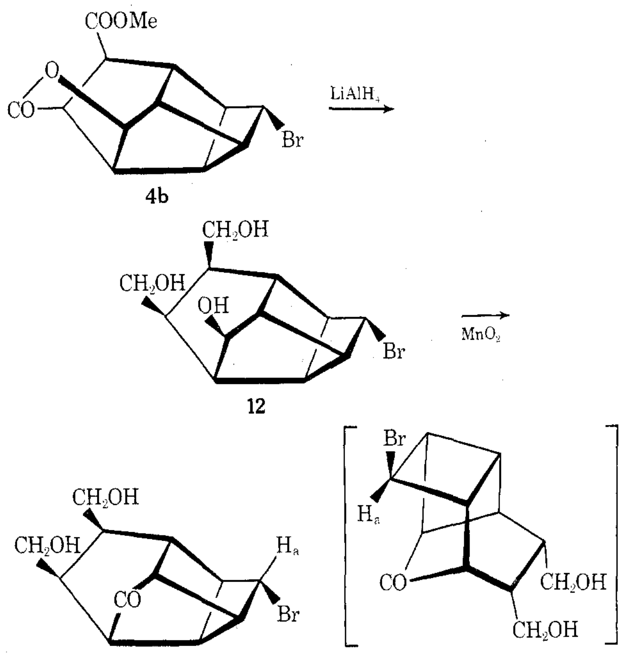
Chart I



As can be seen in Table II, the observed signal patterns were compatible with the expected one from the dihedral angles. Appearance of a sharp singlet signal of H_a at δ 3.90 in **4a** and at δ 3.88 in **4b** supports structure A, since the dihedral angle between H_a and the vicinal methine protons in structure B is not exactly 90°. Thus, the H_a signal should be split with a broad- or doublet-like pattern. Moreover, structure A for compounds **4a** and **4b** is strongly supported by the absence of NOE and spin-decoupling experiments between H_a and H_b; irradiation of the signal at δ 4.80 caused simplification of the signal at δ 3.58. The final structural determination of these compounds was accomplished by chemical transformation. Thus, reduction of **4b** with lithium aluminum hydride gave compound **12**, which was oxidized by manganese dioxide to give compound **13**. The ir spectrum of **13** shows a carbonyl absorption at 1755 cm^{-1} suggesting strongly the presence of a five-membered-ring ketone moiety.[7] Furthermore a sharp singlet signal (H_a) at δ 3.87 in the nmr could be assigned as the proton adjacent to the bromo substituent, which is considerably similar to those of **4b**, **5**, and **8**. Therefore, an alternative structure **14**, which would arise from a non-cross bond formation of **1**, could be ruled out; the carbonyl anisotropy is sufficient to account for the more upper field displacement of the proton (H_a) adjacent to the bromo substituent.

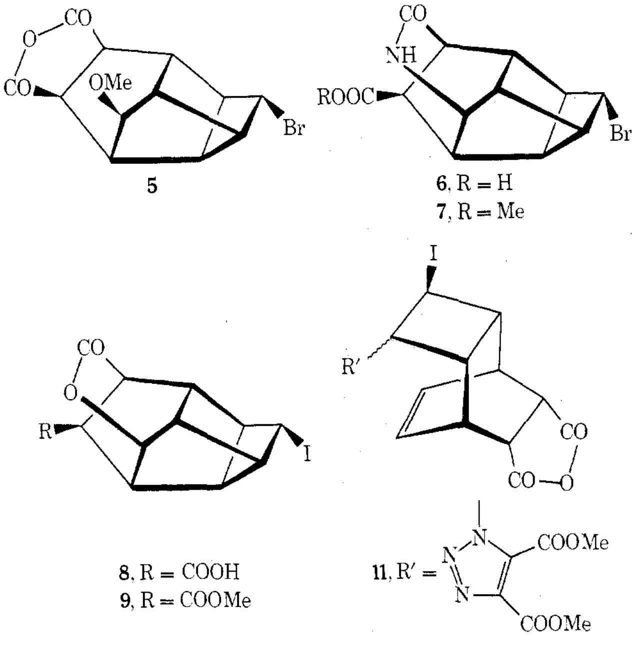
On the basis of the above facts, structures of both **3a** (**4a**) and **3b** (**4b**) were established as a cross-type compound (A) rather than a non-cross type compound (B). These results are summarized in Scheme II.

Scheme II



Compound **5** (Chart II) was easily assigned as a nonlactonization structure, since it shows anhydride absorptions at 1840 and 1770 cm^{-1} in the ir and two sharp singlet signals at δ 3.20 (3 H, OCH_3) and 3.89 (1 H, CHBr) in the nmr. Compound **7** was determined to be a bromolactamization product, which shows two carbonyl absorptions at 1730 (ester C=O) and 1675 cm^{-1} in the ir. The absorption at 1675 cm^{-1} suggests the presence of a six-membered-ring lactam moiety. The nmr spectrum of **7** is similar to those of **4a** and **4b** except for the signal for the proton adjacent to the lactone moiety.

Chart II



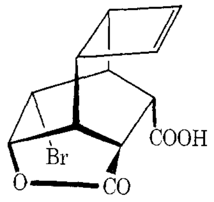
Structures **8** and **9** are supported by spectral evidence and elemental analyses. Compound **9** shows carbonyl absorptions at 1740 (a six-membered-ring lactone moiety) and 1735 cm^{-1} (ester C=O) in the ir. The nmr spectrum of **9** is grossly similar to those of **4a** and **4b** (see Table II), indicating the skeletal resemblance to each other.

The 1,3-dipolar cycloadduct might be represented by structure **11**. The nmr spectrum in the vinyl proton regions for **11** shows only two olefinic protons at δ 6.57 as a doublet and a lack of cyclobutene protons.

Mechanism for the Formation of the Halogenated Compounds. From the above results, the reaction pathway in the halogenation of **1** and **2** might involve the initial electrophilic attack of the reagent at the cyclobutene double bond to give the bridged halonium ion C as an intermediate followed by the transannular cross-bond formation, and finally lactonization affording the novel caged compounds **3** and **4** as shown in Scheme III.

In this connection, Reppe, *et al.*, reported similar halogenation of the adducts **1** and **2**, and the resulting monohalolactone compounds have been proposed to be a structure D (Chart III) according to the confirmation of the results of the Diels–Alder rule.[8]

Chart III



D

However, as described above, it is obvious that the proposed structure D could be ruled out from our present study.

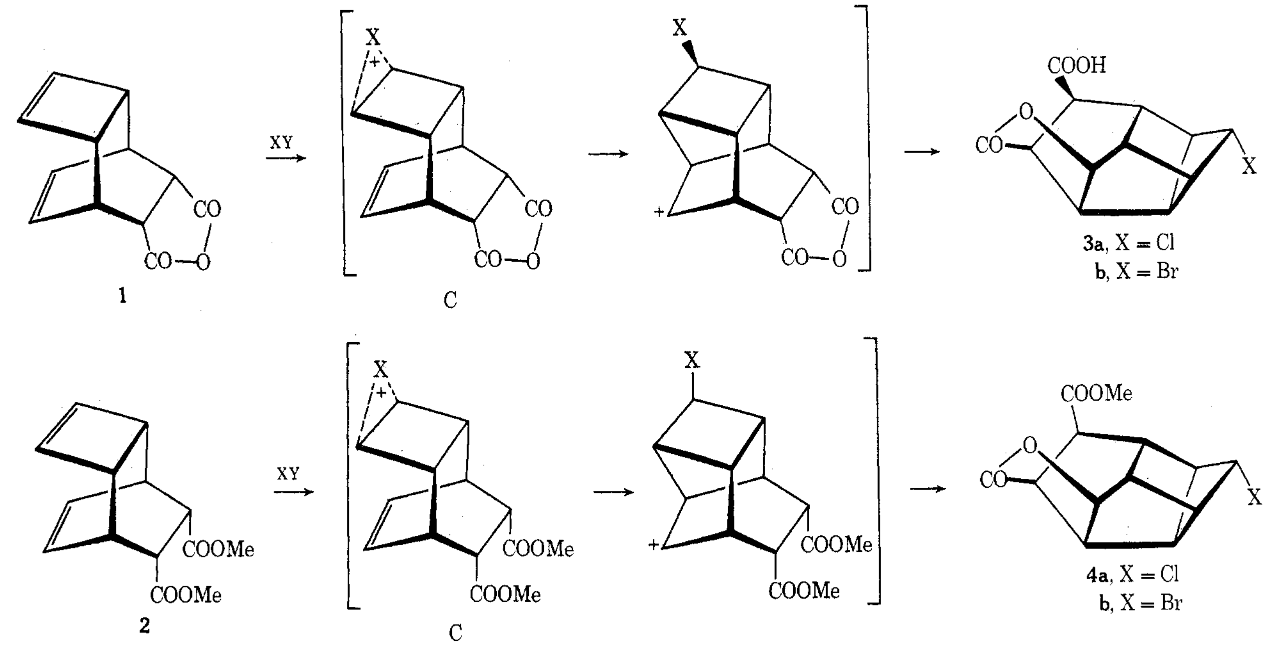
As can be seen in Table I, bromination of the adducts **1** and **2** was found to be remarkably dependent on the solvents, for which the bridged ion intermediate C should be responsible; the formation of **5** might proceed by attack of nucleophilic solvent (methanol) on the intermediate C prior to lactonization. However, the reactions in acetonitrile or benzonitrile proceed with more complexity than the one in methanol. Thus, mechanistic speculation leads to the postulation of a plausible pathway, in which initial attack of the nitrile on the intermediate C gives an intermediate E *via* Ritter-like reaction, followed by hydrolysis affording the amino compound F, and then cyclization. These reaction pathways are summarized in Scheme IV.

Finally, the formation of **11** from the 1,3-dipolar cycloaddition of the initially produced 1:1 adduct (**10**) could be explained by assuming a reaction path involving the intermediacy of iodonium ion G[4] followed by displacement of azide ion prior to the cross-bond formation as shown in Scheme V. In this case, no iodolactonization products were detected. In contrast, iodination of **1** with iodine chloride in methanol gave only iodolactonization products **8** and **9**, which underwent a smooth cyclization to the six-membered ring in comparison to the case of the five-membered-ring compounds **3** and **4**.[9]

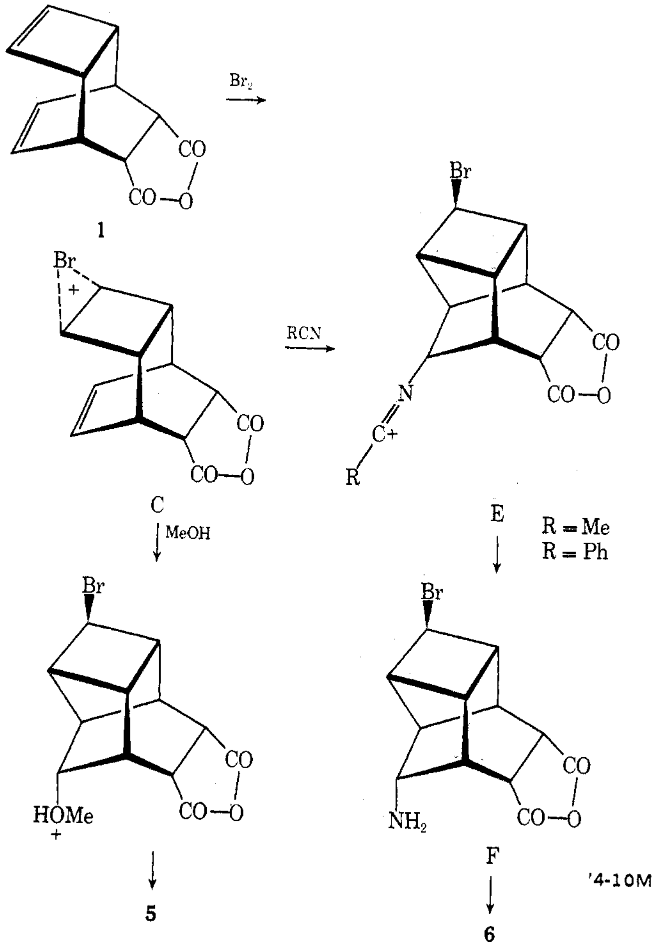
It should be noted that the reactions of the adducts **1** and **2** were dependent on electrophiles and solvents, but in each case, only regiospecific reaction products were obtained in good yields.

There is another important and interesting aspect to the mechanism of the bond formation; the close proximity of the olefinic bonds in **1** and **2** is shown by the facile cross-type ring closure affording the novel caged com-

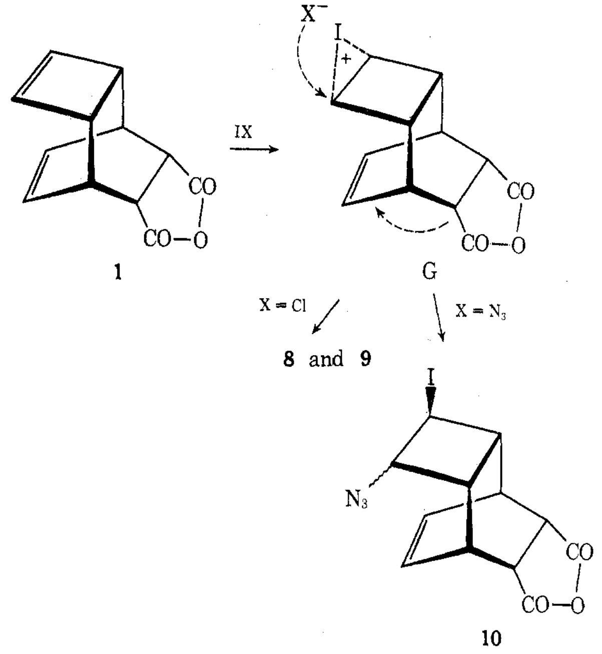
Scheme III



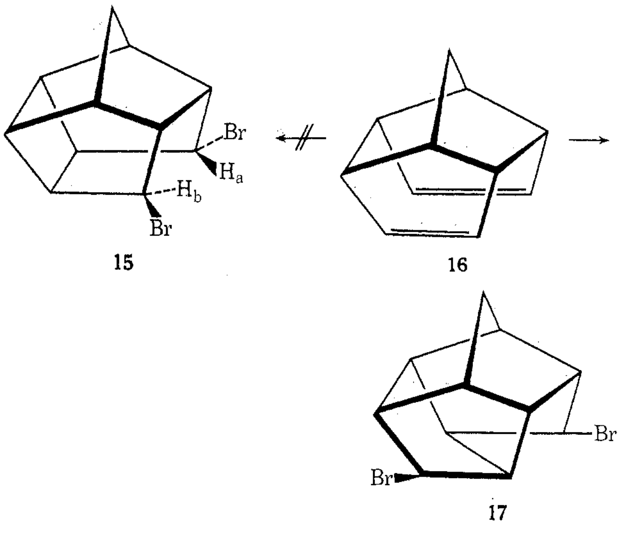
Scheme IV



Scheme V



Scheme VI



pounds **3–9**. An examination of each stereomodel shows that during bond formation leading to cross-type ring closure, van der Waals repulsion among the methine protons in the cyclobutane moiety is released more than it is during the non-cross type closure, and the product resulting from the latter might be expected to have more total strain energy. Similar arguments can be applied to the case of the polycyclic bridged olefin **16** (Scheme VI); the production of cross-type dibromide **17** might involve a transition state which is considerably less strained than the transition states leading to non-cross type dibromide **15**.[4] An examination of a stereomodel of **15** shows very large repulsion between H_a and H_b.

Although many examples of the homo-Diels–Alder reaction of norbornadiene have been reported,[10] no examples of such a reaction have yet been documented for these systems, in which the cross-type addition of ionic reagents occurs. Actually, attempted homo-Diels–Alder reactions of **1** and **2** with some electron-deficient potent dienophiles such as tetracyanoethylene, maleic anhydride, 4-phenyl-1,2,4-triazoline-3,5-dione, and dimethyl acetylenedicarboxylate were all unsuccessful.

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 spectrometer. Nmr spectra were taken with a JEOL C-60-XL spectrometer with tetramethylsilane as internal standard. Ir spectra were taken with a JASCO IR-S spectrophotometer.

Chlorination of 1. A solution of **1** (200 mg) and *tert*-butyl hypochlorite (130 mg) in acetone (10 ml) was kept at room temperature for 24 hr. After evaporation of the solvent, the residue after chromatography using chloroform–methanol (5:1) and recrystallization from ethyl acetate gave **3a** (245 mg): mp 245–247°; ir (KBr) 1770, 1690, 1270 cm^{-1}. *Anal.* Calcd for $C_{12}H_{11}O_4Cl$: C, 56.60; H, 4.32. Found: C, 56.71; H, 4.38.

Chlorination of 2. A solution of **2** (250 mg) and *tert*-butyl hypochlorite (130 mg) in ether (20 ml) was kept at room temperature for 24 hr. After evaporation of the solvent, the residue after recrystallization from benzene gave **4a** (260 mg): mp 178–180°; ir (KBr) 1760, 1735, 1300–1200 cm^{-1} (four bands). *Anal.* Calcd for $C_{13}H_{13}O_4Cl$: C, 58.11; H, 4.88. Found: C, 58.12; H, 4.83.

Esterification of 3a. To a suspension of **3a** (50 mg) in ether (10 ml), excess diazomethane was added. The reaction mixture was stirred for several hours. The resulting residue after recrystallization gave **4a** (50 mg).

Bromination of 1. A. To a solution of **1** (200 mg) in acetic acid (10 ml) an excess of bromide (300 mg) was added. The mixture was stirred for 24 hr at room temperature. Then the mixture was dissolved in 10% aqueous sodium hydroxide (30 ml) and washed with ether. After acidification, the product was extracted with ether from the aqueous layer. Drying with sodium sulfate and removal of solvent followed by recrystallization from benzene-methanol gave **3b** (280 mg): mp 232–235°; ir (KBr) 1770, 1690 cm^{-1}. *Anal.* Calcd for $C_{12}H_{11}O_4Br$: C, 48.18; H, 3.71. Found: C, 48.01; H, 3.76.

B. To a solution of **1** (200 mg) in acetonitrile (20 ml) an excess of bromine (300 mg) was added. The mixture was stirred for 24 hr at room temperature. Evaporation of the solvent followed by recrystallization from water gave **6** (290 mg): mp 250–252°; ir (KBr) 3600–2600, 1690, 1630 cm^{-1}. *Anal.* Calcd for $C_{12}H_{12}O_3NBr$: C, 48.34; H, 4.05; N, 4.70. Found: C, 48.53; H, 4.15; N, 4.95.

C. To a solution of **1** (300 mg) in acetonitrile (10 ml) and water (10 ml) an excess of bromine (450 mg) was added and the solution was stirred for 24 hr at room temperature. After evaporation of the solvent, the resulting residue was subjected to silica gel chromatography using chloroform–benzene (1:1). The first fraction gave **3b** (130 mg) and the second fraction gave **6** (30 mg).

D. To a solution of **1** (200 mg) in methanol (20 ml) an excess of bromine (300 mg) was added. The mixture was stirred for 24 hr at room temperature. After evaporation of the solvent, the residue was subjected to silica gel chromatography using chloroform. From the first fraction **5** was obtained (120 mg): mp 188–190°; ir (KBr) 1840, 1770, 1105 cm^{-1}. *Anal.* Calcd for $C_{13}H_{13}O_4Br$: C, 49.86; H, 4.18. Found: C, 49.62; H, 4.20.

E. To a solution of **1** (200 mg), dimethyl sulfoxide (4 ml), and water (4 ml), *N*-bromosuccinimide (360 mg) was added and the mixture was stirred for 2 hr at room temperature. Then water (50 ml) was added and the product was extracted with ether. Drying with sodium sulfate followed by silica gel chromatography using chloroform gave **1** (150 mg) and **3b** (50 mg).

F. To a solution of **1** (200 mg) in benzonitrile (5 ml) an excess of bromine (300 mg) was added. The mixture was stirred for 24 hr at room temperature. Silica gel chromatography using chloroform and methanol gave benzoic acid (90 mg) and **6** (280 mg).

Bromination of 2. To a solution of **2** (250 mg) in dry chloroform (20 ml), bromine (300 mg, drying with sulfuric acid) was added. The reaction mixture was stirred for 24 hr at room temperature. Work-up as described above gave **4b** (270 mg): mp 178–180° (benzene); ir (KBr) 1770, 1735 cm^{-1}. *Anal.* Calcd for $C_{13}H_{13}O_4Br$: C, 49.86; H, 4.18. Found: C, 49.86; H, 4.14.

Esterification of 3b. A. A solution of **3b** (100 mg) in methanol (10 ml) and sulfuric acid (2 ml) was refluxed for 1 hr. After evaporation of methanol, the reaction mixture was added to water (50 ml) and the product was extracted with ether. Drying with sodium sulfate followed by recrystallization from benzene gave **4b** (95 mg).

B. A suspension of **3b** (50 mg) in ether was treated with diazomethane. Work-up as described above gave **4b** (50 mg).

Iodination of 1. To a solution of **1** (200 mg) in methanol (50 ml), iodine chloride (165 mg) was added, and the mixture was stirred for 12 hr at room temperature under nitrogen. After evaporation of the solvent, the resulting residue was washed with water and insoluble materials were dissolved in chloroform. After evaporation of the solvent, the residue was subjected to silica gel chromatography using chloroform to give **9** (140 mg) and **8** (70 mg). **8** had mp 210° dec (benzene), ir 1740, 1705 cm^{-1}. *Anal.* Calcd for $C_{12}H_{11}O_4I$: C, 41.64; H, 3.20. Found: C, 41.64; H, 3.30.

9 had mp 162–163° (methanol), ir (KBr) 1740, 1735 cm^{-1}. *Anal.* Calcd for $C_{13}H_{13}O_4I$: C, 43.36; H, 3.64. Found: C, 43.55; H, 3.69.

Esterification of 8. A solution of **8** (30 mg), sulfuric acid (1 ml) and methanol (10 ml) was stirred for 2 hr at room temperature. Work-up as described above gave **9** (25 mg).

Reaction of 1 with Iodine Azide. To a suspension of sodium azide (325 mg) in acetonitrile (20 mg), iodine chloride (356 mg) was added. After **1** was added to the solution, the reaction mixture was stirred overnight at room temperature. Then an excess of dimethyl acetylenedicarboxylate (5 ml) was added to the reaction mixture. The mixture was evaporated under pressure and the residue was subjected to silica gel chromatography using benzene to give **11** (250 mg): mp 215° dec; ir (KBr) 1840, 1780, 1730 cm^{-1}. *Anal.* Calcd for $C_{18}H_{16}O_7N_3I$: C, 42.32; H, 3.14; N, 8.19. Found: C, 42.32; H, 3.22; N, 8.19.

Reduction of 4b. To a solution of **4b** (600 mg) in dry tetrahydrofuran (30 ml), lithium aluminium hydride (100 mg) was added. The mixture was stirred for 3 days at room temperature. After evaporation of the solvent, 10% aqueous ammonium chloride (20 ml) was added, followed by filtration, and the resulting solution was extracted with chloroform. Evaporation of the solvent gave **12** (320 mg): mp 154–156° (acetone); ir (KBr) 3400, 3270, 1220, 1090, 1010 cm^{-1}. *Anal.* Calcd for $C_{12}H_{17}O_3Br$: C, 49.84; H, 5.92. Found: C, 49.63; H, 5.92.

Oxidation of 12. To a suspension of **12** (300 mg) in chloroform (100 ml), manganese dioxide (1 g) was added. The mixture was stirred for 24 hr at room temperature. After filtration followed by evaporation, the resulting residue was subjected to silica gel chromatography using dichloromethane. Then the resulting oily material after recrystallization from ether gave **13** (200 mg): mp 112–113°; ir ($CHCl_3$) 3640, 3600, 3300–3400, 1755, 1030 cm^{-1}; nmr ($CDCl_3$) δ 1.95–2.20 (3 H, m, simplification by irradiation at δ 4.75), 2.30–2.90 (6 H, m, D_2O exchangeable to 2 H at δ 2.40), 3.03 (1 H, t, J = 6.0, 10.0 Hz), 3.40–3.60 (3 H, m), 3.87 (1 H, s, BrCH), 4.76 (1 H, d, J = 8.0 Hz). *Anal.* Calcd for $C_{12}H_{15}O_3Br$: C, 50.19; H, 5.27. Found: C, 50.10; H, 5.20.

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Registry No.—**1**, 51447-09-7; **2**, 35211-83-7; **3a**, 51425-67-3; **3b**, 51425-68-4; **4a**, 51425-69-5; **4b**, 51425-70-8; **5**, 51425-71-9; **6**, 51425-72-0; **7**, 51425-73-1; **8**, 51425-74-2; **9**, 51425-75-3; **11**, 51425-76-4; **12**, 51425-77-5; **13**, 51425-78-6.

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Photochemistry of Dispiro-1,3-cyclobutanediones in Methylene Chloride and Methanol Solutions

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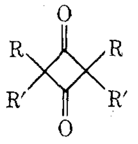
The photolysis of dione 3 ($n = 4$) in methylene chloride leads mainly to the isomeric, photolabile enol lactone 6. Diones 3 ($n = 5$, 6, or 7) on irradiation in methylene chloride solutions lead to 20, 50, and 40% yields of 4 ($n = 5$, 6, or 7), respectively. Pentamethyleneketene and hexamethyleneketene were also formed from diones 3 ($n = 6$ or 7). Little cycloelimination occurs in the case of dione 3 ($n = 5$). Small amounts of cycloalkanones are also formed from diones 3 ($n = 5$, 6, or 7) (less than 10%). Dione 3 ($n = 4$) could not be photolyzed in methanol because of its facile ring opening in this solvent to yield 7. The photolysis of 3 ($n = 5$) in a methanol solution leads to α-methoxydicyclopentyl ketone (8), methyl cyclopentanecarboxylate, cyclopentanone, and several other unidentified products. The photolysis of 3 ($n = 6$ or 7) in methanol leads to the unstable hemiketals of the dispirocyclopropanones 12 ($n = 6$ or 7), the corresponding methyl cycloalkanecarboxylates, and cycloalkanones (small amounts). On work-up the β-peroxy esters 11 ($n = 6$ or 7) were isolated from these photolyses in 43 and 25% yields, respectively. The β-peroxy esters 11 ($n = 6$ or 7) on treatment with base form the β-peroxy lactones 15 ($n = 6$ or 7), respectively. Thermolyses of 15 ($n = 6$ or 7) lead to the spiranones 14 and 17, respectively, in nearly quantitative yields.

The photolysis of tetramethyl-1,3-cyclobutanedione 1 ($R = R' = Me$) in inert solvents such as benzene or methylene chloride produces tetramethylethylene. A competitive cycloelimination also occurs to yield some dimethylketene.[2,3] A low yield of the isomeric enol β-lactone 2 has been obtained when 1 ($R = R' = Me$) is irradiated in ether, dioxane, or tetrahydrofuran.[4] The irradiation of this dione in dioxane containing some acetic acid or in propionic acid leads to α-acyloxy ketones.[5]



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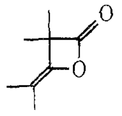

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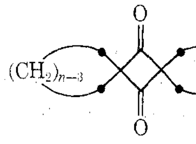

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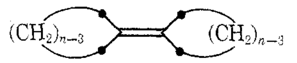
The intermediacy of tetramethylcyclopropanone in the photolysis of 1 ($R = R' = Me$) has been supported by its isolation,[2d] its trapping on photolysis of the dione in furan,[3,6] and the isolation of hemiketals of the cyclopropanone when the photolysis is performed in alcohols as solvents.[2,6,7] The irradiation of 1 ($R = R' = Me$) or 2 in methanol leads to similar products and the dione and lactone 2 were not measurably interconverted under the conditions utilized.[7d]

Diones 1 ($R = R' = Et$) and 1 ($R = R' = n\text{-Pr}$) also yield the corresponding olefins on photolysis in inert solvents.[2a] The dispiro-1,3-cyclobutanedione 3 ($n = 6$) on irradiation in methylene chloride yields 4 ($n = 6$) (50%) along with the cycloelimination product pentamethyleneketene.[2b,8] Irradiation of 5 in aqueous THF yields bicyclo[2.2.1]heptane-7-carboxylic acid (53%).[9]

In connection with another study,[10] it was of interest to study the effect of ring size on the products of the photolysis of a series of dispiro-1,3-cyclobutanediones 3 ($n = 4$, 5, 6, or 7) in inert solvents. Since the photolysis of 3 ($n = 6$) leads to 4 ($n = 6$),[2b,8] a similar double decarbonylation of the other diones would be a useful synthetic route to cycloalkylidenecycloalkanes of various ring size. In addition the photolysis of 3 ($n = 4$, 5, 6, or 7) in a reactive solvent such as methanol would be of interest in order to hopefully isolate and investigate the stabilities of the hemiketals of the dispirocyclopropanones which might be produced in the photolysis.



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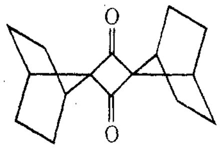

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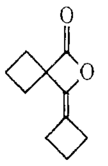

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Syntheses of the Diones 3 ($n = 4$, 5, 6, and 7). The diones 3 ($n = 4$, 5, 6, and 7) can readily be prepared by dehydrohalogenation of the cycloalkanecarbonyl chlorides of the proper ring size with triethylamine.[10,11]

Spectral Characteristics of the Tetrasubstituted 1,3-Cyclobutanediones. The ultraviolet spectrum of dione 1 ($R = R' = Me$) exhibits two distinct $n\text{-}\pi^*$ transitions.[2a,12] The ultraviolet spectra for diones 1 ($R = R' = Me$) and 3 ($n = 4$, 5, 6, and 7) are tabulated in Table I. All diones except 3 ($n = 4$) exhibit two $n\text{-}\pi^*$ transitions. These two bands can be attributed to 1,3-π interactions in the excited states of these diones.[2c]

Results and Discussion

All irradiations were performed through Pyrex or by use of a Pyrex filter to ensure that the initial absorption was restricted to $n\text{-}\pi^*$ excitation. Photolyses were performed using a Rayonet RPR-208 reactor or a Hanovia medium-pressure lamp (see Experimental Section).

A. Dispiro[3.1.3.1]decane-5,10-dione (3, $n = 4$). (a) Methylene Chloride. A 0.08 *M* solution of 3 ($n = 4$) in methylene chloride was irradiated (Rayonet) and the progress of the photolysis was periodically monitored by ir analysis of aliquots. The original carbonyl absorption peak