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(37) Diisopropylamine could also be used but a side product, diisopropylformamide, was difficult to separate from **10** by distillation.
(38) Sodium bicarbonate was added to somewhat suppress formation of **17** which apparently arises from **11** via a carbonium ion pathway. Ether **16** was the major product with and without this addition so we favor its formation via the ketocarbene.
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Molecular Design by Cycloaddition Reactions. XXIV.[1] Stereospecific Cycloaddition Reactions of Dibenzo[4,5-*c*]furotropone

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Marked differences in reactivities between [4,5-*c*]furotropone and dibenzo[4,5-*c*]furotropone in their cycloaddition reactions are observed. Reactions of dibenzo[4,5-*c*]furotropone, readily prepared from 3,6-epoxy-3,6-dihydrotribenzocycloheptatrienone with 3,6-diphenyltetrazine, with some electron-deficient and -rich dienophiles gave [4 + 2] adducts in good yields. The structures of these adducts were determined by spectral means and supported by mechanistic considerations.

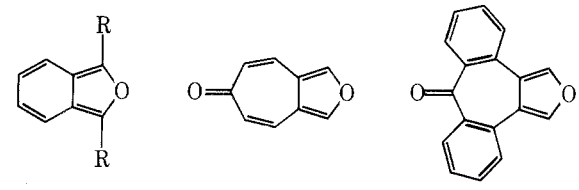
We have already investigated the photochemical and thermal cycloaddition reactions of benzoheterocycles such as isobenzofuran derivatives with some cyclic diene and triene compounds.[2]

Synthesis of a highly reactive isobenzofuran (**1a**) has also been reported; however, it rapidly polymerizes.[3] 1,3-Diphenylisobenzofuran (**1b**) is commercially available and has been used extensively as a trapping agent for reactive dienes but is very sensitive to oxygen.[4] By contrast, [4,5-*c*]furotropone (**2**) has proved to be inert to the Diels–Alder reactions even with a highly reactive dienophile as tetracyanoethylene.[5]

Therefore, it was of interest to prepare derivatives of these ring systems and to examine their reactivities.

The present paper describes a ready method for the preparation of dibenzo[4,5-*c*]furotropone (**3**) (dibenzo[*a*,*e*]furo[3,4-*c*]-8*H*-cycloheptatrienone),[6] and its reactivity in cycloaddition reactions with some dienophiles.

Chart I



1a, R = H
b, R = Ph

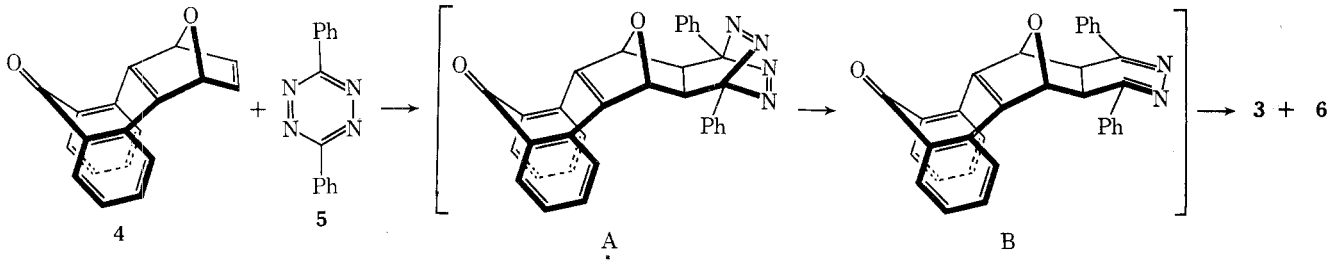
2

3

Results and Discussion

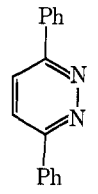
Preparation of Dibenzo[4,5-*c*]furotropone. Reaction of 3,6-epoxy-3,6-dihydrotribenzocycloheptatrienone (**4**)[6] with 3,6-diphenyltetrazine (**5**) under reflux in benzene afforded dibenzo[4,5-*c*]furotropone (**3**) in a high yield together with 3,6-diphenylpyridazine (**6**) as evidenced by the immediate disappearance of the purple color of the solution. Presumably the formation of **3** might proceed via initially

Scheme I



4 **5** **A** **B** → **3** + **6**

produced [4 + 2] adduct (A) followed by loss of nitrogen to give an unstable intermediate (B) which decomposed rapidly to **3** and **6** as shown in Scheme I. These intermediates

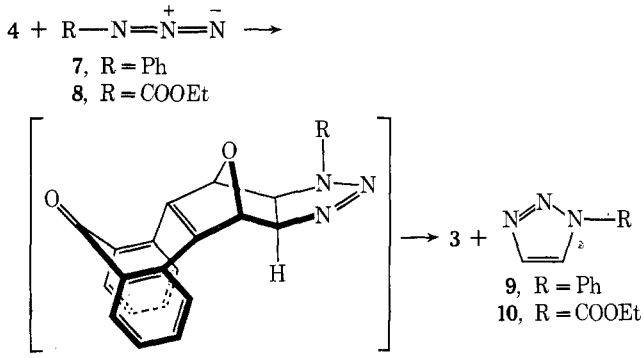


6

could not be isolated directly from the reaction mixture owing to their extreme thermal lability even under mild conditions.

Similarly, the reactions of **4** with phenyl azide (**7**) or ethoxycarbonyl azide (**8**) under the same conditions gave also compound **3** in a moderate yield (Scheme II).

Scheme II



7, R = Ph
8, R = COOEt

9, R = Ph
10, R = COOEt

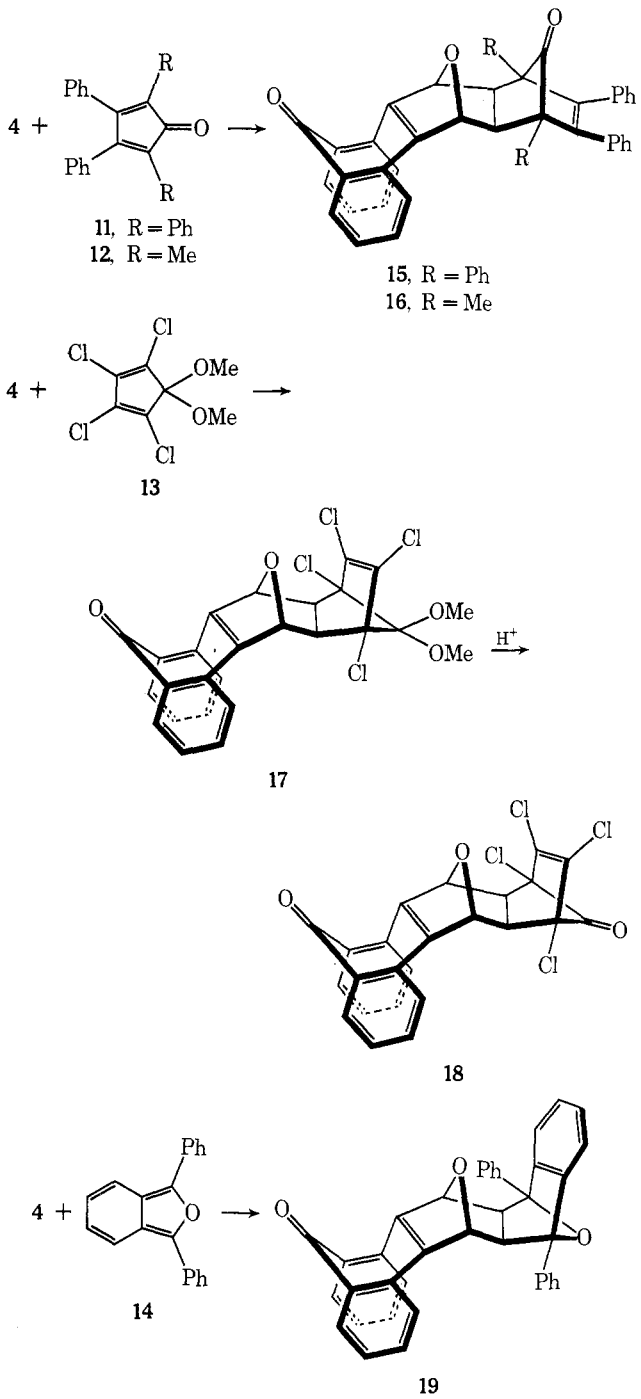
By contrast, the cycloaddition reactions of **4** with tetracyclone (**11**),[6] 2,5-dimethyl-3,4-diphenylcyclopentadienone (**12**), 1,1-dimethoxy-2,3,4,5-tetrachloropentadienone (**13**), and 1,3-diphenylisobenzofuran (**14**) under reflux in benzene gave [2 + 4] adducts, **15**, **16**, **17**, and **19**, respectively (Scheme III). The NMR data for these adducts are summarized in Table I;[7] the adducts **15** and **16** were confirmed by their NMR spectra to take the exo,exo configuration by the absence of vicinal couplings.[8] On the other hand, the adduct **17** was assigned to be the exo,endo configuration by the absence of vicinal coupling and by hydrolysis of **17** with 80% sulfuric acid to give compound **18**, which showed an endo methine proton signal at δ 1.60 due to influence of the bridged carbonyl group. Similarly, the exo,endo configuration of compound **19** was determined by the NMR inspection, which will be discussed separately (see Chart III).

Further heating of these adducts, **15**, **16**, and **18**, in chlorobenzene at 120 °C gave compound **3** in a moderate yield, but heating of the adduct **19** gave only the starting material even under more drastic conditions for much longer times.

From these results, it is concluded that the reaction of **4** with **5** proceeded at lower temperature than that of **4** with the cyclopentadienone derivatives and it is a convenient preparation of the dibenzo[4,5-*c*]furotropone (**3**) in a high yield.

Cycloaddition Reaction of Dibenzo[4,5-*c*]furotropone. The cycloaddition of dibenzo[4,5-*c*]furotropone (**3**) with *N*-phenylmaleimide (**20**), *p*-benzoquinone (**21**), dimethyl acetylenedicarboxylate (**22**), and tetracyanoethylene (**23**) as electron-deficient dienophiles afforded [4 + 2] cycloadducts, **24** (75%), **25** (50%), **26** (88%), and **27** (90%), respectively (Scheme IV).

Scheme III



11, R = Ph
12, R = Me

15, R = Ph
16, R = Me

13

17

18

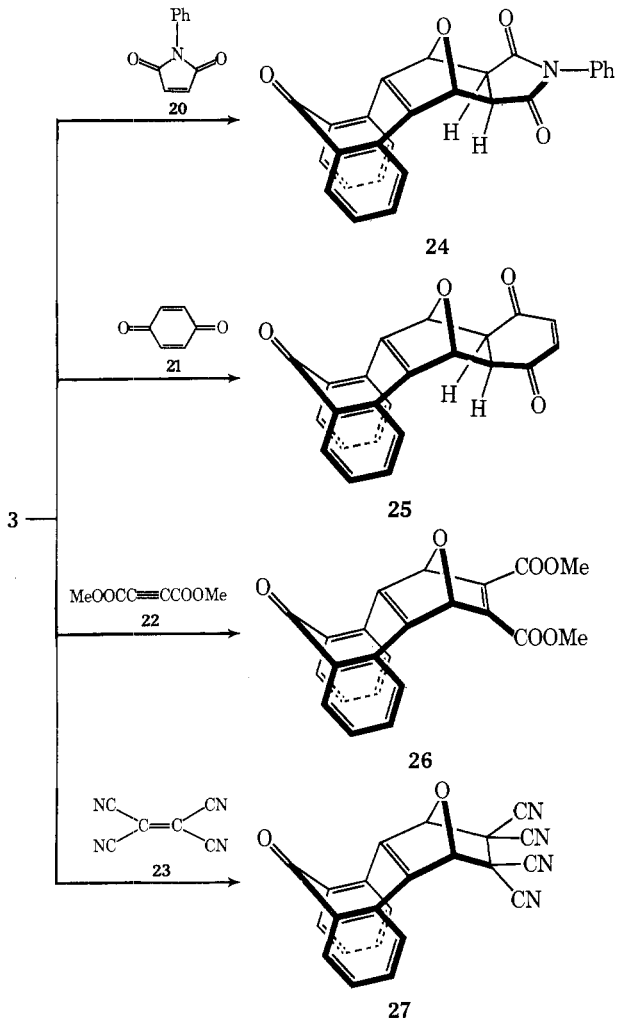
14

19

The absence of appreciable coupling between two methine proton signals in compounds **24** and **25** indicates the exo configuration.

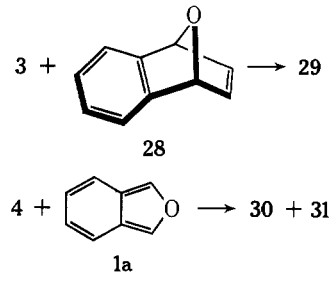
The reaction of **3** with oxabenzonorbornadiene (1,4-epoxy-1,4-dihydronaphthalene, **28**) as an electron-rich and strained olefin gave a 1:1 adduct **29** in 85% yield (Scheme V). This adduct was thermally stable even under more drastic conditions for much longer times, suggesting no interconversions to the isomers. The NMR spectrum of compound **29** showed bridgehead protons at δ 2.78 (2 H, d, J = 4.1 Hz), 4.95 (2 H, s) and 5.77 (2 H, d, J = 4.1 Hz), and aromatic protons at δ 7.60–8.15 (12 H, m). However, the exact configuration for **29** could not be determined based on the NMR inspection, for which the two possible stereoisomeric structures (endo,exo and exo,endo configurations) are assumable. Therefore, the reaction of **4** with isobenzofuran, generated from thermal decomposition of the Diels–Alder

Scheme IV



adduct of **28** and **11**,[9] was attempted, and a mixture of isomeric 1:1 adducts **30** and **31** was obtained in the ratio of 1:1.1 in total yield of 54%. Interestingly, significant shifts of the chemical shifts and coupling constants for the oxygen bridgehead protons and the center bridgehead protons are observed in the NMR spectra of these adducts as summarized in Table II.[7]

Scheme V



Among the possible stereoisomers (C–F) as shown in Chart II, only the exo,exo isomer (C) was assigned for the adduct **31** because of the absence of appreciable coupling between H_a and H_b and between H_b and H_c;[10] the center bridgehead proton H_b lying over the aromatic rings showed at δ 2.19 due to the benzene ring current effect. The structures of the exo,endo (D) and endo,exo isomers (E) were examined by the stereomodel.[10] In the exo,endo isomer (D), the H_a proton lying over the oxabenzonorbornene moiety will be shielded by the benzene ring current effect and should appear as a singlet with no vicinal couplings. Therefore, the structure **30** was assigned to be the exo,endo cycloadduct. In the endo,exo isomer (E), the H_a proton will be deshielded by the anisotropic effect of the bridge oxygen atom in comparison with H_c and should be coupled with the vicinal hydrogen H_b, while the H_c proton lying over the dibenzo groups will be shielded by the benzene ring current effect and should appear as a singlet with no vicinal couplings.

Thus, the structure **29** was assigned to have the endo,exo configuration. By contrast, the adduct **19** was assigned to have the exo,endo configuration by the absence of vicinal coupling, which showed the center bridgehead proton H_b at δ 3.0 similar to that of compound **30** (δ 3.03).

On these evidences, it is concluded that the cycloaddition reactions of the dibenzo[4,5-*c*]furotropone with dienophiles under thermal conditions would proceed by a directive influence on the incoming dienophiles by steric interactions as depicted in Chart III; only two structures G and K might be formed by most favorable approaches of the dienophiles.

The above results show that the dibenzo[4,5-*c*]furotropone (**3**) is a valuable trapping agent for a number of ethyl-

Chart II

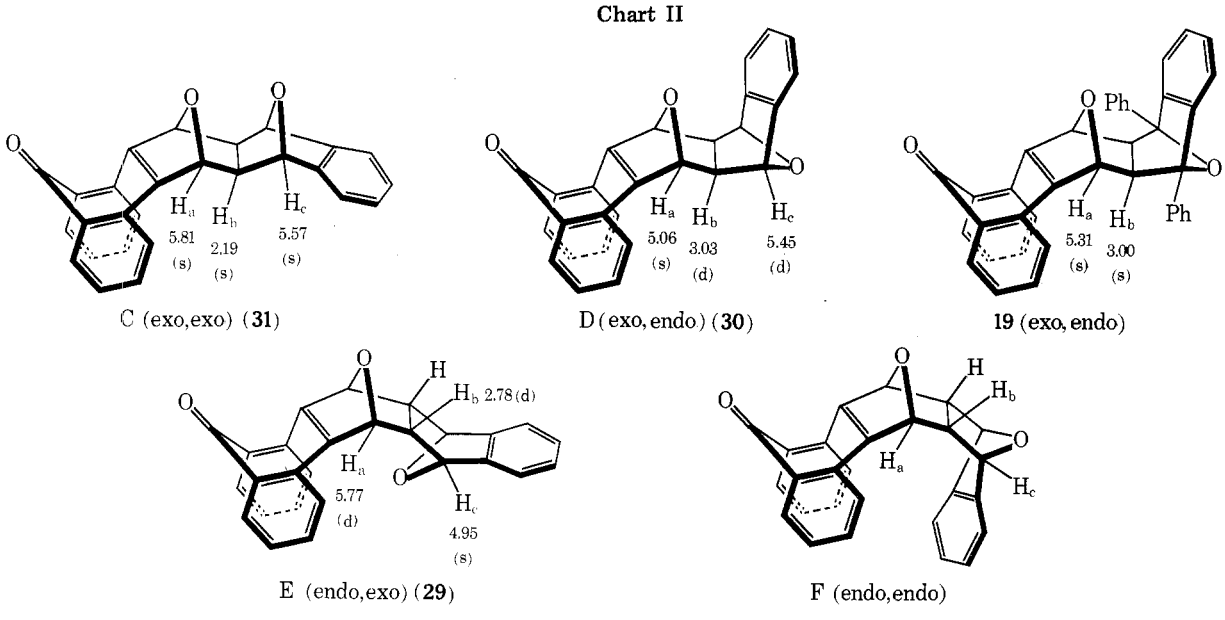
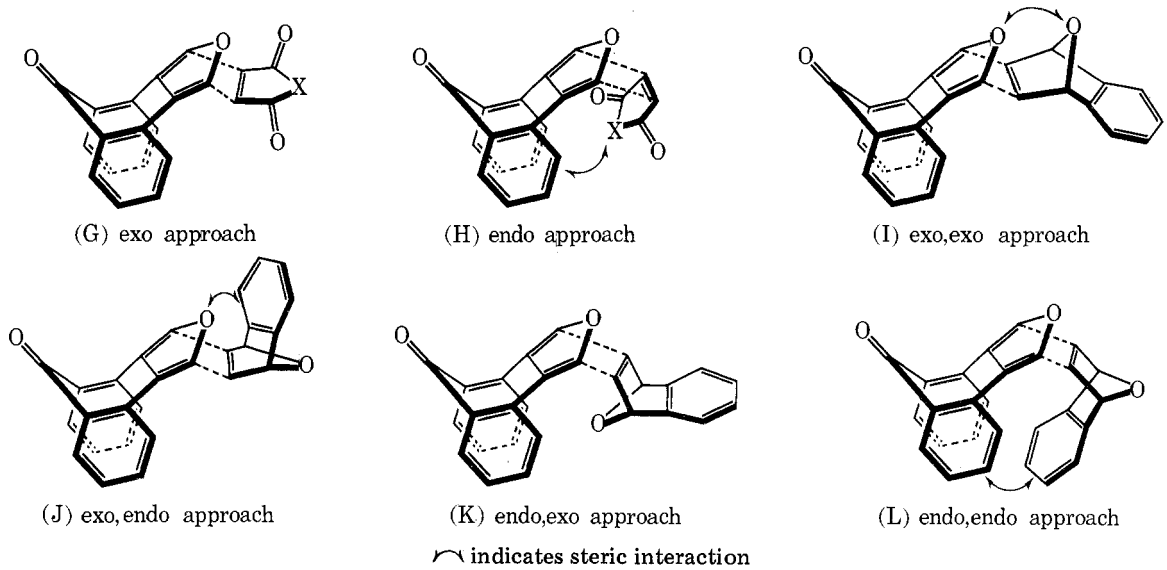


Chart III. Possible Approaches in Cycloaddition Reactions of Diene with Dienophile



(G) exo approach (H) endo approach (I) exo,exo approach

(J) exo,endo approach (K) endo,exo approach (L) endo,endo approach

⌒ indicates steric interaction

enic dienophiles and more reactive than the [4,5-*c*]furotropone (**2**) in the cycloaddition reactions.

Experimental Section

The melting points were measured with a Yanagimoto micromelting point apparatus. Microanalyses were performed with a Perkin-Elmer 240 elemental analyzer. The NMR spectra were taken with a JEOL C-60-XL recording spectrometer with tetramethylsilane as an internal standard and the chemical shifts are expressed in δ values. The ir spectra were taken with a Jasco Model IRA-1 grating infrared spectrophotometer.

Reaction of 3,6-Epoxy-3,6-dihydrotribenzocycloheptatrienone (4) with 3,6-Diphenyl-1,2,4,5-tetrazine (5). A solution of compound **4** (2.18 g) and 3,6-diphenyl-1,2,4,5-tetrazine (**5**, 1.87 g) in benzene (80 ml) was refluxed for 3 h. Then 3,6-diphenylpyridazine (**6**, 1.79 g, 94%) was precipitated in the cooled solution. The filtrate was evaporated to dryness and recrystallization from methanol gave dibenzo[4,5-*c*]furotropone (**3**, 1.52 g, 82%) as colorless needles, mp 105–106 °C (lit.[6] 100–102 °C).

Reaction of 4 with Phenyl Azide (7). A solution of **4** (545 mg) and phenyl azide (**7**, 238 mg) in benzene (20 ml) was stirred at room temperature for 4 h. Evaporation to dryness and chromatography on silica gel using benzene–chloroform (1:1) gave **3** (340 mg, 77%) and phenyltriazole (**9**, 180 mg, 69%).

Reaction of 4 with Ethoxycarbonyl Azide (8). A solution of **4** (545 mg) and ethoxycarbonyl azide (**8**, 230 mg) in benzene (20 ml) was refluxed for 5 h. Similar work-up gave **3** (270 mg, 47%) and *N*-ethoxycarbonyltriazole (**10**, 100 mg, 40%).

Reaction of 4 with Tetracyclone (11). A solution of **4** (545 mg) and tetracyclone (745 mg) in benzene (30 ml) was refluxed for 1 day. Recrystallization from benzene gave a 1:1 adduct (**15**, 940 mg, 83%) as colorless needles: mp 210–212 °C; ir (KBr) 1780, 1640 cm^{-1}.

Anal. Calcd for $C_{48}H_{32}O_3$: C, 89.43: H, 5.01. Found: C, 89.30; H, 5.14.

Reaction of 4 with 2,5-Dimethyl-3,4-diphenylcyclopentadienone (12). A solution of **4** (545 mg) and a dimer of **12** (520 mg) in benzene (30 ml) was refluxed for 1 day. Recrystallization from benzene gave a 1:1 adduct (**16**, 430 mg, 68%) as colorless needles: mp 239–240 °C; ir (KBr) 1640, 1780 cm^{-1}.

Anal. Calcd for $C_{38}H_{28}O_3$: C, 85.70; H, 5.30. Found: C, 85.45; H, 5.35.

Reaction of 4 with 1,1-Dimethoxy-2,3,4,5-tetrachlorocyclopentadienone (13). A solution of **4** (272 mg) and the ketal **13** (300 mg) in benzene (30 ml) was refluxed for 15 h. Evaporation to dryness and chromatography on silica gel using benzene–chloroform (1:1) gave a 1:1 adduct (**17**, 390 mg, 90%) as colorless needles: mp 285–289 °C (benzene–chloroform); ir (KBr) 1640 cm^{-1}.

Anal. Calcd for $C_{26}H_{18}O_4Cl_4$: C, 60.82; H, 3.51. Found: C, 60.66; H, 3.49.

Hydrolysis of Compound 17. The adduct **17** (390 mg) was added to 80% H_2SO_4 (5 ml), and stirred at room temperature for 5 h. The solution was neutralized with aqueous $NaHCO_3$ (20 ml), and extracted with benzene (40 ml). Evaporation to dryness and recrystallization gave **18** (130 mg, 35%) as colorless needles: mp 235–237 °C ($CHCl_3$); ir (KBr) 1780, 1640 cm^{-1}.

Anal. Calcd for $C_{24}H_{12}O_3Cl_4$: C, 58.80; H, 2.47. Found: C, 58.82; H, 2.50.

Reaction of 4 with 1,3-Diphenylisobenzofuran (14). A solution of **4** (408 mg) and 1,3-diphenylisobenzofuran (**14**, 405 mg) in benzene (30 ml) was refluxed for 4 h. Evaporation to dryness and recrystallization gave a 1:1 adduct (**19**, 740 mg, 91%) as colorless needles: mp >300 °C (benzene–$CHCl_3$); ir (KBr) 1640 cm^{-1}.

Anal. Calcd for $C_{39}H_{26}O_3$: C, 86.32; H, 4.83. Found: C, 86.12; H, 5.06.

Pyrolysis of 15. A solution of the adduct **15** (300 mg) in chlorobenzene (10 ml) was heated in a sealed tube at 120 °C for 4 days. Chromatography on silica gel using benzene gave compound **3** (78 mg, 70%) and 1,2,3,4-tetraphenylbenzene (154 mg, 90%).

Pyrolysis of 16. A solution of the adduct **16** (300 mg) in chlorobenzene (10 ml) was heated in a sealed tube at 120 °C for 4 days. Similar work-up gave compound **3** (70 mg, 50%) and 1,4-dimethyl-2,3-diphenylbenzene (56 mg, 39%).

Pyrolysis of 18. A solution of the adduct **18** (100 mg) in chlorobenzene (5 ml) was heated in a sealed tube at 120 °C for 18 h. Evaporation to dryness and chromatography on silica gel using benzene gave compound **3** (25 mg, 58.6%) and 1,2,3,4-tetrachlorobenzene (40 mg, 95%).

Reaction of Dibenzo[4,5-*c*]furotropone (3) with *N*-Phenylmaleimide (20). A solution of **3** (246 mg) and *N*-phenylmaleimide (**20**, 207 mg) in chlorobenzene (10 ml) was heated at 120 °C for 7 h in a sealed tube. After evaporation to dryness chromatography on silica gel using benzene–chloroform gave a 1:1 adduct (**24**, 310 mg, 74%) as colorless needles: mp 278–279 °C ($CHCl_3$); ir (KBr) 1790, 1720, 1640 cm^{-1}.

Anal. Calcd for $C_{27}H_{17}O_4N$: C, 77.32; H, 4.09; N, 3.34. Found: C, 77.05; H, 4.00; N, 3.51.

Reaction of 3 with *p*-Benzoquinone (21). A solution of **3** (246 mg) and *p*-benzoquinone (**21**, 115 mg) in chlorobenzene (20 ml) was heated at 120 °C for 19 h. Similar work-up gave a 1:1 adduct (**25**, 120 mg, 50.3%) as yellow needles: mp 151–154 °C ($CHCl_3$); ir (KBr) 1665, 1640 cm^{-1}.

Anal. Calcd for $C_{23}H_{14}O_4$: C, 77.96; H, 3.98. Found: C, 78.10; H, 3.88.

Reaction of 3 with Dimethyl Acetylenedicarboxylate (22). A solution of **3** (246 mg) and dimethyl acetylenedicarboxylate (**22**, 170 mg) in chlorobenzene (10 ml) was heated at 120 °C for 7 h. Similar work-up gave a 1:1 adduct (**26**, 230 mg, 88%) as yellow needles: mp 199–201 °C ($CHCl_3$); ir (KBr) 1730, 1710, 1640 cm^{-1}.

Anal. Calcd for $C_{23}H_{16}O_6$: C, 71.13; H, 4.15. Found: C, 71.45; H, 4.26.

Reaction of 3 with Tetracyanoethylene (23). A solution of **3** (123 mg) and tetracyanoethylene (**23**, 64 mg) in benzene (20 ml) was stirred at room temperature for 1 day. Evaporation to dryness and recrystallization from benzene gave a 1:1 adduct (**27**) in a quantitative yield: mp 110–114 °C (benzene); ir (KBr) 1640 cm^{-1}. This compound was thermally unstable.

Anal. Calcd for $C_{23}H_{10}O_2N_4$: C, 73.77; H, 2.67; N, 14.42. Found: C, 73.70; H, 2.70; N, 14.51.

Reaction of 3 with Oxabenzonorbornadiene (28). A solution of **3** (246 mg) and oxabenzonorbornadiene (**28**, 144 mg) in chlorobenzene (4 ml) was heated in a sealed tube at 100 °C for 11 h. Evaporation to dryness and chromatography on silica gel using benzene–chloroform (1:1) gave a 1:1 adduct (**29**, 330 mg, 85%), mp 250–252 °C (benzene–$CHCl_3$).

Anal. Calcd for $C_{27}H_{18}O_3$: C, 83.06; H, 4.65. Found: C, 83.24; H, 4.51.

Reaction of 3 with Isobenzofuran (1a). A solution of the 1:1 adduct[9] of **28** and tetracyclone (275 mg) and **4** (136 mg) in *p*-xylene (10 ml) was heated in a sealed tube at 170 °C for 1 day. Work-up as described above gave compound **30** (50 mg) and **31** (55 mg) (total yield of 54%), and 1,2,3,4-tetraphenylbenzene (190 mg, 99.4%).

30: mp 294–295 °C ($CHCl_3$).

Anal. Calcd for $C_{27}H_{18}O_3$: C, 83.06; H, 4.65. Found: C, 82.96; H, 4.94.

31: mp > 300 °C ($CHCl_3$).

Anal. Calcd for $C_{27}H_{18}O_3$: C, 83.06; H, 4.65. Found: C, 82.99; H, 4.70.

Registry No.—**1a**, 270-75-7; **3**, 20457-17-4; **4**, 16567-36-5; **5**, 6830-78-0; **6**, 891-22-5; **7**, 622-37-7; **8**, 817-87-8; **11**, 479-33-4; **12**, 26307-17-5; **13**, 2207-27-4; **14**, 5471-63-6; **15**, 58241-44-4; **16**, 58241-45-5; **17**, 58241-53-5; **18**, 58241-46-6; **19**, 58241-52-4; **20**, 941-69-5; **21**, 106-51-4; **22**, 762-42-5; **23**, 670-54-2; **24**, 58241-47-7; **25**, 58241-48-8; **26**, 58241-49-9; **27**, 58241-50-2; **28**, 573-57-9; **29**, 58241-51-3; **30**, 58267-64-4; **31**, 58267-65-5.

Supplementary Material Available. Tables I and II, NMR data (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part XXIII of this series: T. Sasaki, K. Kanematsu, and N. Okamura, *J. Org. Chem.*, **40**, 3322 (1975).
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(7) Tables I and II (NMR spectra) appear in the microfilm edition; see paragraph at end of paper regarding supplementary material.
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Gas Phase, Uncatalyzed Thermolysis of 3-Homoadamantyl Acetate

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3-Homoadamantyl acetate has been shown to undergo unimolecular gas phase thermolysis with $E_a = 48.1 \pm 0.4$ kcal/mol. The variation in product distribution with temperature, and upon 4 deuteration, has been taken as evidence for parallel pathways of thermal decomposition. A mechanistic scheme has been proposed involving competition of well-precedented six-membered and seven-membered transition states giving rise to two products (**3** and **4**) and one unique product (**2**), respectively. Moreover, substrates, such as **8** and **9**, which are structurally incapable of realizing a low energy seven-membered or a six-membered cyclic pathway which does not result in bridgehead olefin formation, seem to be completely stable under conditions which lead to extensive decomposition of **1**. However, the formation of an exocyclic cyclopropane at a bridgehead or an equivalent (relatively) stable diradical leading to **2a** or **2b**, stemming from the thermolysis of **1**, appears to take place readily via a seven-membered transition state.

Recently Kovacic and Adams[1] have disclosed that the gas phase thermolysis of 3-homoadamantyl acetate (**1**) in a Vycor (quartz)-packed reactor tube at 500–600 °C produces two olefinic products in a combined yield of ca. 30–40%, accompanied by a host of other products, each in very small amounts. Their report was particularly intriguing because the predominant products, 4-methyleneprotoadamantane (**2**) and 3-vinylnoradamantane (**3**), obtained in a ratio of ca. 2.5:1, obviously resulted from skeletal rearrangements.

We have for some time been interested in the course of the normal, six-centered, retroene thermolysis reaction by which the usual, unrearranged olefins are formed, as well as that of the less common thermolysis from which only rearranged products originate through the operation of a seven-centered or homoretroene pathway.[2] The data of Kovacic and Adams,[1] who did not provide any mechanistic interpretation, indicated that the relative quantities of **2** and **3** in the complex product mixture varied somewhat. This suggested the possibility that the multiplicity of products may arise from either a competition of reaction mechanisms or rate-determining formation of a common intermediate with more than one rapid, product-forming pathway available to it. In the search for evidence to elucidate the reaction routes producing **2** and **3**, under highly reproducible, noncatalytic, thermolysis conditions, a kinetic investigation of the thermolysis of **1** and related substrates was undertaken.

Results and Discussion

In contrast to the preparative scale, quartz-packed, hot tube previously employed[1] the kinetic studies of interest were carried out with a micro, gas phase, flow system utilizing a gold-coil reactor which has been established[3] to minimize or eliminate the wall-catalyzed reactions commonly found to take place in glass or quartz reactors. This system has been shown to exhibit even less catalytic activity in ester thermolysis than the well-seasoned reactor of Maccoll[4] which is most widely employed[5] as a means of *diminishing* the recognized catalytic activity of glass and quartz-based reactors.

The thermal decomposition of **1** studied in the gold-coil microreactor over the temperature range 445–500 °C followed a simple, unimolecular rate law. The rate data gathered from these measurements are compiled in Table I. In sharp contrast to the results obtained[1] with the use of the (apparently) catalytic Vycor reactor in the temperature range of 500–600 °C, only three, clean products are ob-