TABLE VIII

CHLORINATION OF 2,3-DIHYDROXYPYRAZINES **3**[a]

2,3-Dihydroxy-pyrazine	Reaction time, hr	Yield of **9**, %	Mp, °C (lit.)
3a	33	63.5	22–25 (22–24)[b]
3b	28	86.1	12[c]
3c	43	70.9	79–80[d] (80–81[4])
3d	90	77.1	106–107[e] (102)[f]
3e	96	79.8	69–70[g]
3f	48	69.9	182[h] (182–183[4])

[a] Satisfactory analytical values (±0.3% for C, H, N, and Cl) were reported for all compounds in the table: Ed. [b] American Cyanamide Co., British Patent 612,385 (1948); *Chem. Abstr.*, **44**, 1537 (1950). [c] Bp 100–101° (20 mm); n^{25}D 1.5498. [d] Recrystallized from hexane and [e] ethanol. [f] S. T. Minovici and V. Th. Bente, *Bull. Sect. Sci. Acad. Roumaine*, **4**, 185 (1915); *Chem. Abstr.*, **10**, 606 (1916). [g] Recrystallized from petroleum ether (bp 30–50°). [h] Recrystallized from acetone.

TABLE IX

AMINATION OF 2,3-DICHLOROPYRAZINES **9**[a]

Starting material	Conditions		Product	Yield, %	Mp, °C
	Temp, °C	Time, hr			
9a	130–140[b]	50	**11a**	61	167[f]
9b	150–160[c]	70	**11b**	77	113[g]
9b	200–220[d]	60	**10b**	66	178[h]
9d	200–210[e]	85	**10d**	59	173[i]
9e	200–220[e]	72	**10e**	28	167–168[i]

[a] Satisfactory analytical values (±0.3% for C, H, and N) were reported for all compounds in the table: Ed. [b] Amination were carried out with activated copper powder in liquid ammonia, [c] ammonium hydroxide (*d* 0.880), [d] activated copper powder in ammonium hydroxide (*d* 0.880), and [e] activated copper powder and potassium bromide in ammonium hydroxide (*d* 0.880), respectively. [f] Recrystallized from water (lit.[15] mp 169°). The melting point of a mixture with an authentic sample[15] undepressed and ir spectra were identical. The authors are grateful to Mr. T. Kohagizawa for the synthesis of an authentic sample. [g] Recrystallized from ethanol. Mp 113°: G. Palamidassi, *Farmaco, Ed. Sci.*, **18**, 557 (1963); *Chem. Abstr.*, **59**, 13975 (1963). [h] Recrystallized from ethyl acetate and [i] benzene, respectively.

Acknowledgment.—The authors wish to thank Mr. K. Kishimoto, Mr. K. Kaneko, Mr. M. Ichinose, Mr. K. Ikeda, and Mr. Y. Nagatsu for their experimental assistances and Mr. A. Ito for nmr measurement. The authors are also grateful to Dr. T. Nakagawa for his helpful suggestions.

Derivatives of Thiacyclobutene (Thiete). V.[1] Molecular Reorganization in the Reaction of Thiete Sulfone and Tetraphenylcyclopentadienone[2-4]

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Thiete sulfone (**1**) and tetracyclone react in refluxing *m*-xylene to yield 1,2,6,7-tetraphenylcycloheptatriene (65%, **2**) and a bicyclic ketone (15%), 1,5,6,7-tetraphenylbicyclo[3.2.1]octa-2,6-dien-8-one (**3**). When 1,2,3,4-tetraphenylcyclopentadiene and thiete sulfone are refluxed in *m*-xylene, a 77% yield of the Diels-Alder adduct is obtained in addition to 1,5,6,7-tetraphenylbicyclo[3.2.1]octa-2,6-diene (13%). Thiete sulfone and phencyclone give a 69% yield of a cycloheptatriene (**4**) but no carbonyl compound. An alternate structure (**6**) for ketone **3** was abandoned on the basis of physical data and the conversion of the ketone to 1,5,6,7-tetraphenylbicyclo-[3.2.1]octene-6 (**8**). In dioxane a low (8%) yield of the Diels-Alder adduct **9** of thiete sulfone and tetracyclone is obtained. Decomposition of this adduct in refluxing *m*-xylene gives only cycloheptatriene **2**. A pathway for formation of bicyclic ketone **3** through the intermediacy of vinyl carbene (or some species which resembles it) derived from thiete sulfone is discussed. Reaction of a vinyl carbenoid species, obtained by the Simmons-Smith procedure from 3,3-dichloro-1-propene, with tetracyclone gives a 4% yield of bicyclic ketone **3**.

α,β-Unsaturated sulfones usually react normally as dienophiles in the Diels–Alder cycloaddition reaction[5] and a number of additions to thiete sulfone (thiacyclobutene 1,1-dioxide) (**1**) proceed normally.[6] A logical route to thiete sulfones containing a fused benzene ring involves the Diels–Alder addition of tetracyclone (tetraphenylcyclopentadienone) to thiete sulfone followed by loss of carbon monoxide and two hydrogens. In fact, a number of tetraphenylbenzene derivatives are obtained from Diels–Alder adducts of tetracyclone.[7] We have found that butadiene, furan, and 2,5-dimethylfuran, in addition to the dienes reported earlier,[6a] add normally to thiete sulfone. This report is about an anomalous reaction of thiete sulfone with tetracyclone.

Product Identification. A Cycloheptatriene and a Bicyclic Ketone.—When thiete sulfone and tetracyclone were refluxed in *m*-xylene (139°) until the color of tetracyclone was discharged (*ca.* 85 hr), two gases identified as sulfur dioxide and carbon monoxide were produced. The major organic products were two solids of empirical formulas $C_{31}H_{24}$ (65% yield) and

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[1] Paper IV: D. C. Dittmer, R. S. Henion, and N. Takashina, *J. Org. Chem.*, **34**, 1310 (1969).

[2] This research was supported in part by National Science Foundation Grants GP 726, 5513 and 8086, and by National Institutes of Health Grant CA 08250, for which the authors are grateful.

[3] A preliminary report on some of this work has been given: D. C. Dittmer and J. M. Balquist, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Abstract K 37. The structure of compound **3** was given incorrectly at that time.

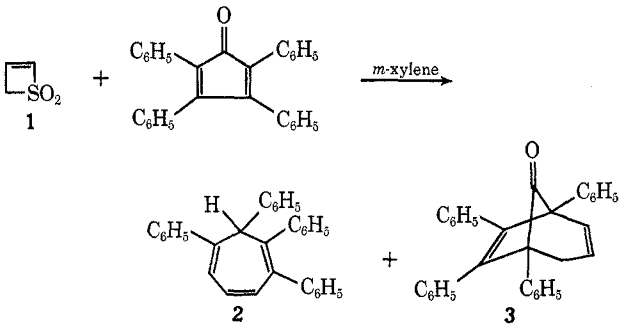
[4] Taken in part from the Ph.D. thesis of J. M. Balquist, Syracuse University, 1966.

[5] For example, see K. Alder, H. F. Rickert, and E. Windemuth, *Ber.*, **71**, 2451 (1938); H. R. Snyder, H. V. Anderson, and D. P. Hallada, *J. Amer. Chem. Soc.*, **73**, 3258 (1951); H. R. Snyder and D. P. Hallada, *ibid.*, **74**, 5595 (1952).

[6] (a) D. C. Dittmer and M. E. Christy, *ibid.*, **84**, 399 (1962); D. C. Dittmer and N. Takashina, *Tetrahedron Lett.*, 3809 (1964); L. A. Paquette, *J. Org. Chem.*, **30**, 629 (1965); L. A. Paquette and T. R. Phillips, *ibid.*, **30**, 3883 (1965). (b) Cycloaddition of diazoalkanes to thiete sulfone also occurs normally although certain adducts lose sulfur dioxide at 150°: D. C. Dittmer and R. Glassman, *ibid.*, **35**, 999 (1970).

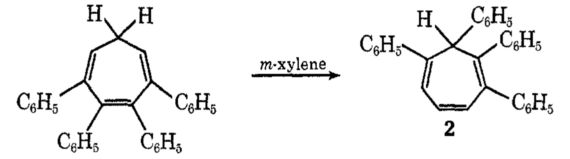
[7] See the review by M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 261 (1965).

$C_{32}H_{24}O$ (15% yield). These were separated and identified as 1,2,6,7-tetraphenylcycloheptatriene (**2**) and 1,5,6,7-tetraphenylbicyclo[3.2.1]octa-2,6-dien-8-one (**3**).

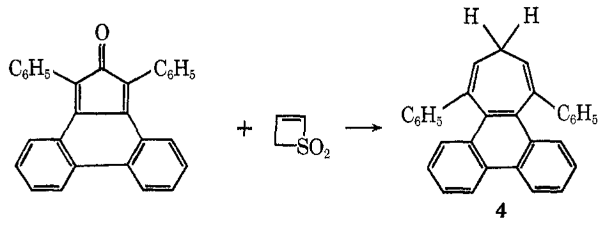


The cycloheptatriene $C_{31}H_{24}$ was dimorphous, exhibiting mp 69–70 and 127–128°.[8] The form melting at 127–128° can be converted to the form melting at 69° by a cycle of melting and solidification. The ultraviolet spectrum in acetonitrile [231 (4.27), 274 (4.29), 324 nm (log ϵ 3.94)] is similar to that of other cycloheptatrienes, *e.g.*, heptaphenylcycloheptatriene.[9] In the proton nmr spectrum the C-7 proton appears as a singlet, τ 4.40,[10] the C-5 proton appears as a complex multiplet, τ 3.10–3.35, and the C-3 and C-4 protons appear as a complex multiplet, τ 3.35–3.75.

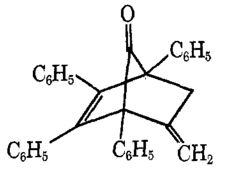
Further evidence for the structure of **2** is obtained by refluxing 2,3,4,5-tetraphenylcycloheptatriene[11] in *m*-xylene. A 1,5-hydrogen shift[12] occurs to give **2**.



The usefulness of thiete sulfone in the synthesis of tetrasubstituted cycloheptatrienes is illustrated further by the reaction of phencyclone (1,3-diphenyl-2*H*-cyclopenta[*l*]phenanthren-2-one) and thiete sulfone. A 69% yield of cycloheptatriene **4** was obtained. The absence of product from a 1,5-hydrogen migration may be explained by the resistance to disruption of the conjugation in the phenanthrene part of the molecule.



The absorption at 1761 cm^{-1} in the infrared spectrum of the compound of formula $C_{32}H_{24}O$ indicates the presence of a bridged carbonyl group.[13] Structure **6** was considered in addition to **3**. The proton nmr spectrum, in particular, indicated that the structure was not **6**, the spectrum, however, being consistent with **3**. Double and triple irradiation experiments established that one olefinic proton (absorption centered at τ 4.02) was coupled to the methylene protons, $J = 3.5$ Hz, and to another olefinic proton (centered at τ 3.2), $J = 9.5$ Hz. Decoupling of the methylene protons ($-CH_2-$) absorbing at τ 6.94 reduced the six-line multiplet at τ 4.02 to a doublet, and further irradiation (triple resonance) at τ 3.02 reduced the doublet to a singlet.[14] The pattern and magnitude of the coupling of the protons in the ketone are difficult to interpret on the basis of structure **6**. For instance, the large coupling constant of 9.5 Hz between the olefinic protons is about three times greater[15] than is observed normally for a coupling constant between geminal olefinic protons such as occur in **6**. The rather low-field absorption (τ 3.02) for the proton at C-2 is an indication of deshielding by the neighboring phenyl group.[16] The mass spectrum of the ketone showed that carbon monoxide was lost readily and that ions corresponding to tropylium ions are formed. Hydrogenation of one double bond in the bicyclic ketone gave a compound which lacked absorption in the infrared at 1370–1385 cm^{-1}, characteristic of the symmetric deformations of a methyl group, and had no absorption in the nmr spectrum which could be attributed to a methyl group.



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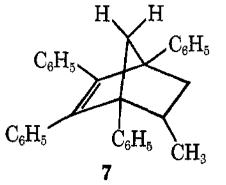
In order to dispose of any ambiguity in the interpretation of the spectra of the bicyclic ketone, compound **7** was prepared; it was *not* identical with the product obtained from the bicyclic ketone by reduction of both the carbonyl group and the less conjugated double



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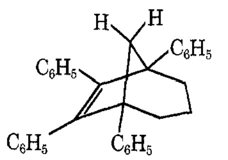

8

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(8) X-Ray powder patterns of the two forms are indistinguishable. We wish to thank Professor Harry Brumberger for obtaining these data for us. Infrared, ultraviolet, and proton nmr spectra of both forms are identical.

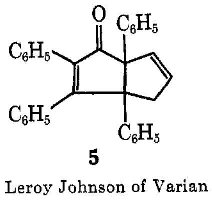
(9) M. A. Battiste, *Chem. Ind. (London)*, 550 (1961).

(10) The C-7 proton of heptaphenylcycloheptatriene appears at τ 4.73: R. Breslow and H. W. Chang, *J. Amer. Chem. Soc.*, **84**, 1484 (1962).

(11) M. A. Battiste and T. J. Barton, *Tetrahedron Lett.*, 2951 (1968).

(12) A. P. ter Borg, H. Kloosterziel, and N. van Meurs, *Recl. Trav. Chim. Pays-Bas*, **82**, 717 (1963); A. P. ter Borg and H. Kloosterziel, *ibid.*, **82**, 741 (1963).

(13) Absorption of the carbonyl group of bicyclo[3.2.1]octa-2-en-8-one is at 1758 cm^{-1}: N. A. LeBel and L. A. Spurlock, *Tetrahedron*, **20**, 215 (1964). A structure for the ketone such as **5** is unlikely because dihydrotetracyclone has ir absorption for the carbonyl group at 1709 cm^{-1}: N. O. V. Sonntag, S. Linder, E. I. Becker, and P. E. Spoerri, *J. Amer. Chem. Soc.*, **75**, 2283 (1953).



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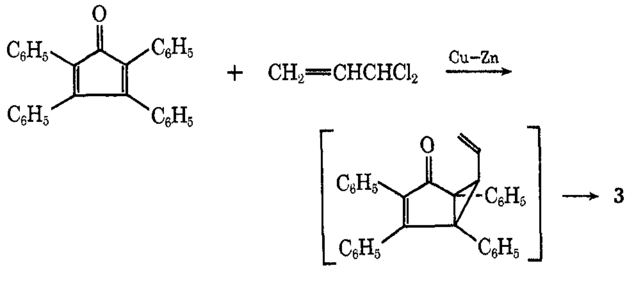
(14) We are indebted to Leroy Johnson of Varian Associates for assistance in obtaining and interpreting the spectra.

(15) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, Wiley, New York, N. Y., 1967.

(16) The vinyl protons of 3,6-biphenyl-7,7-dimethylnorbornadiene absorb at τ 2.93: L. A. Paquette and L. M. Leichter, *J. Amer. Chem. Soc.*, **92**, 1765 (1970).

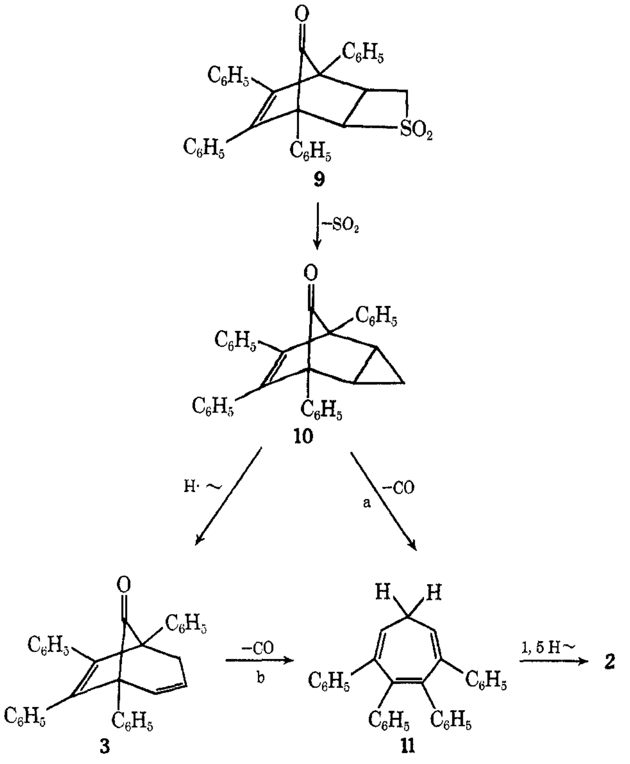
bond. The properties of this product were consistent with structure **8**.

A possible route to the independent synthesis of structure **3** was suggested by the reported rearrangement of *syn*-6-vinyl[3.1.0]bicyclohex-2-ene to bicyclo-[3.2.1]octa-2,6-diene.[17] Accordingly, tetracyclone was treated with the carbenoid species obtained from 3,3-dichloropropene. After 3 days, a 4% yield of a compound identical with the bicyclic ketone, $C_{32}H_{24}O$, was isolated.



Possible Mechanisms.—The formation of cycloheptatriene **2** and bicyclic ketone **3** conceivably could proceed through the Diels-Alder adduct **9** as a common intermediate (Scheme I).

Scheme I

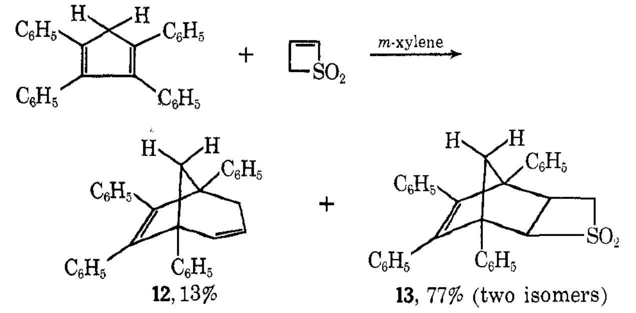


Path b for the formation of the cycloheptatriene, while plausible, is unlikely since **3** did not yield cycloheptatriene **2** when heated. Several products were obtained but none could be identified as **2**. Path a is reasonable since *endo*-1,5,6,7-tetraphenyltricyclo-$[3.2.1.0^{2,4}]$-6-octen-8-one (**10**) yields 2,3,4,5-tetraphenylcycloheptatriene (**11**) in refluxing acetonitrile.[11] This cycloheptatriene derivative gives **2** when it is refluxed in *m*-xylene.

Compound **10** (endo) is not an intermediate in the formation of bicyclic ketone **3** since only cycloheptatriene and no ketone is obtained from it. Possibly *exo*-**10** could yield the ketone, except for the report that both *exo*- and *endo*-tricyclo$[3.2.1.0^{2,4}]$-6-octen-8-ones decompose to cycloheptatrienes, the endo decomposing faster.[18] The temperature (139°) at which the reaction of thiete sulfone and tetracyclone was done is sufficiently high so that both isomers would readily decarbonylate according to the rate measurements given in the literature.[18]

In view of these data, divergent pathways must exist for formation of **2** and **3**. To determine if the divergence occurs before or after the formation of the Diels-Alder adduct **9**, this adduct was prepared in dioxane solvent from thiete sulfone and tetracyclone in 8% yield. Decomposition of **9** in refluxing *m*-xylene gave 76% of cycloheptatriene **2**. *No* ketone **3** was detected. Formation of **3** must occur by a pathway which does not involve the Diels-Alder adduct **9**.[19]

Another observation which bears on the mechanism of the reaction is the absence of any cycloheptatriene in the reaction of thiete sulfone and tetraphenylcyclopentadiene. A bicyclic derivative (**12**) analogous to the bicyclic ketone **3** is formed in about the same yield as the latter and a good yield of the Diels-Alder adduct **13** is obtained. The latter is formed in an amount approximately equivalent to the amount of cycloheptatriene **2** produced in the original reaction. Both isomers of **13** were stable at 139°. At 300° they yielded tetraphenylcyclopentadiene, an unidentified substance and tar, but no **12**.



The inference from the above observations is that cycloheptatriene **2** is produced *via* the Diels-Alder adduct **9** while bicyclic ketone **3** and also **12** are not. Scheme II is a rationalization of the reaction path in which cycloheptatriene is produced by decomposition of a Diels-Alder adduct; the bicyclic ketone is formed

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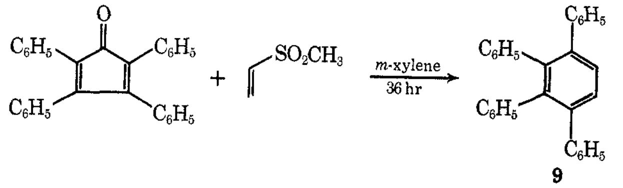
(17) C. Cupas, W. E. Watts, and P. v. R. Schleyer, *Tetrahedron Lett.*, 2503 (1964); J. M. Brown, *Chem. Commun.*, 226 (1965).

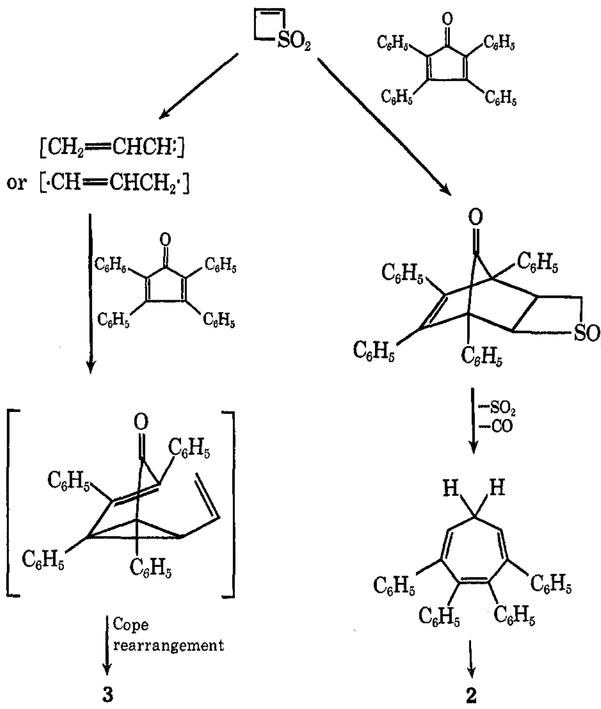
(18) B. Halton, M. A. Battiste, R. Rehberg, C. L. Deyrup, and M. E. Brennan, *J. Amer. Chem. Soc.*, **89**, 5964 (1967).

(19) The loss of sulfur dioxide and carbon monoxide from adduct **9** is probably thermodynamically sound since three quite stable molecules are formed. We have observed that the Diels-Alder reaction of methyl vinyl sulfone and tetracyclone gives a 77% yield of 1,2,3,4-tetraphenylbenzene, presumably formed in an aromatization by loss of methanesulfinic acid.



Unfavorable electrostatic interaction between the sulfone group and the carbonyl group in **9** (especially in the exo isomer) may contribute to the instability.

SCHEME II



from a diradical or vinyl carbenoid species, C_3H_4, derived from the decomposition of thiete sulfone.[20] Under the reaction conditions, thiete sulfone alone is decomposed completely to tar. Ketone **3** also could be formed from vinyl sulfene[20] *via* its adduct with tetracyclone; the adduct then can undergo loss of sulfur dioxide to give a diradical precursor to **3**.

Experimental Section[21]

Diels–Alder Adducts of Thiete Sulfone. A. With Butadiene.—Butadiene (3 ml) was transferred by means of a vacuum line into a reaction tube containing thiete sulfone[22] (1.04 g, 0.01 mol) in benzene (10 ml); a total of 10 tubes was prepared, sealed *in vacuo* at liquid nitrogen temperature, and placed in an oil bath at 110°. After 60 hr the tubes were opened and the contents combined. Solvent was removed on a rotary evaporator and the residue was treated with 100 ml of methanol to precipitate polymer which was removed by filtration. Evaporation of the methanol left an oil which solidified on standing. Two recrystallizations from ethanol gave 10.3 g (0.065 mol, 65%) of white needles with the structure of 7-thiabicyclo[4.2.0]-3-octene 7,7-dioxide.

Anal. Calcd for $C_7H_{10}O_2S$: C, 53.16; H, 6.37; S, 20.24. Found: C, 53.40; H, 6.42; S, 20.24.

B. With Furan.—Five sealed tubes each containing furan (5 ml) and thiete sulfone (2.08 g, 0.02 mol) in 20 ml of benzene were prepared as in A. After 40 hr in the oil bath at 110°, the tubes were opened, the contents were combined, and the solvent was evaporated. The residue was treated with ethanol and insoluble material was removed by filtration. The ethanol was removed by evaporation, and the product was recrystallized twice to yield small white crystals (12 g, 0.07 mol, 70%), mp 130°. Spectroscopic data were consistent with the structure, 9-oxa-3-thiatricyclo[$4.2.1.0^{2,5}$]non-7-ene 3,3-dioxide. The stereochemistry (exo or endo) of the product was not determined.

Anal. Calcd for $C_7H_8O_3S$: C, 48.84; H, 4.68; S, 18.60. Found: C, 48.77; H, 4.78; S, 18.67.

C. With 2,5-Dimethylfuran.—Five sealed tubes each containing 2,5-dimethylfuran (5 g) and thiete sulfone (2.08 g, 0.02 mol) in 20 ml of benzene were prepared as in A and placed in an oil bath at 110° for 40 hr. Combination of the reaction mixtures, evaporation of the solvent, and recrystallization from benzene–ethanol gave white crystals, mp 131° (4.55 g, 0.0228 mol, 23%). Spectroscopic data were in accord with the structure, 7,8-dimethyl-9-oxa-3-thiatricyclo[$4.2.1.0^{2,5}$]non-7-ene 3,3-dioxide. The stereochemistry (exo or endo) of the product was not determined.

Anal. Calcd for $C_9H_{12}O_3S$: C, 53.99; H, 6.04; S, 15.99. Found: C, 53.75; H, 6.14; S, 16.15.

Reaction of Thiete Sulfone and Tetracyclone.—A solution of 5.3 g (13.7 mmol) of tetracyclone (Aldrich Chemical Co.), 1.60 g (15.6 mmol) of thiete sulfone,[22] and 75 ml of *m*-xylene (Matheson Coleman and Bell) was refluxed for 85 hr in an apparatus fitted with a gas-tight syringe to collect the evolved gases. During the reaction, the color of the solution changed from purple to yellow. The solution was cooled to room temperature, and an insoluble residue (0.1 g, mp 250°) was removed by filtration. The solvent was removed by means of a rotary evaporator and the residue was chromatographed on a Florisil (Fischer-F-101) column. The first fraction, eluted with a hexane–benzene (2:1) mixture, was identified as 1,2,6,7-tetraphenylcycloheptatriene (**2**) (3.80 g, 65%). Recrystallization from ethanol gave pale yellow crystals, mp 69–70°.

Occasionally, especially with shorter reaction times, a second form of 1,2,6,7-tetraphenylcycloheptatriene, mp 127–128°, was isolated. The infrared spectrum (KBr), ultraviolet spectrum (CH_3CN), proton nmr spectrum ($CDCl_3$), X-ray powder pattern, and behavior on thin layer chromatography (silica gel sheets, 4:1 petroleum ether–benzene) are identical with those of the lower melting isomer. The high melting polymorph can be converted to the low melting one by melting and resolidification but not vice versa.

Anal. Calcd for $C_{31}H_{24}$: C, 93.90; H, 6.10; mol wt, 396. Found: C, 93.87; H, 6.17; mol wt, 396 (obtained from mass spectrum.

The following spectroscopic observations were made: ir 3047 (sh), 3003 (w), 2959 (sh), 796 (s, C═CH), 747 (s, C_6H_5), 730 (s, C_6H_5), 687 cm^{-1} (s, HC═CH, C_6H_5); uv (CH_3CN) log $\epsilon_{231}^{\max}$ 4.27, log $\epsilon_{274}^{\max}$ 4.29, log $\epsilon_{324}^{\max}$ 3.94; proton nmr (100 MHz in $CDCl_3$) τ 2.45–3.03 (multiplet, C_6H_5), 3.03–3.26 (complex multiplet, C-5 H), 3.44–3.65 (complex multiplet, C-3, C-4 H), 4.29–4.42 (singlet, C-7 H); mass spectrum (250°, direct inlet 70 eV)[23] *m/e* 397 (35.5), 396 (100, P), 319 (27, P − C_6H_5), 318 (19, P − C_6H_6), 242 (8, P − $2C_6H_5$), 241 (36, P − $2C_6H_5$ − H), 167 (5, P − $3C_6H_5$), 165 (14.5, P − $3C_6H_5$ − 2H).

The second compound, eluted with benzene, was identified as 1,5,6,7-tetraphenylbicyclo[3.2.1]octa-2,6-dien-8-one (**3**) (0.86 g, 2.05 mmol, 15%). Recrystallization from chloroform–ethanol gave colorless crystals, mp 192.5–193.5°.

Anal. Calcd for $C_{32}H_{24}O$: C, 90.63; H, 5.66; mol wt, 424. Found: C, 90.32; H, 5.89; mol wt, 424 (obtained from mass spectrum).

The following spectroscopic observations were made: ir 3074 (sh), 3030 (sh), 3024 (m), 2980 (sh), 1761 (vs, C═O), 1605 (m), 695 cm^{-1} (vs); uv (CH_3CN) log $\epsilon_{254}^{\max}$ 3.99, log $\epsilon_{260}^{\max}$ 4.00, log $\epsilon_{265}^{\max}$ 4.00, log $\epsilon_{270}^{\max}$ 4.00; proton nmr (100 MHz in $CDCl_3$) τ 2.52–3.30 (complex multiplet, 19 H, 18 aromatic protons and one olefinic proton at τ 3.02), 3.37–3.60 (multiplet, 2 H, aromatic protons), 3.84–4.30 (two sets of triplets, J = 9.5, 3.5 Hz, 1 H, C═CH), and 6.79–6.95 (complex multiplet, 2 H, CH_2); mass spectrum (250°, direct inlet, 70 eV)[23] *m/e* 425 (33.3), 424 (100, P), 396 (83.5, P − CO), 395 (13.9, $[C_7H_3(C_6H_5)_4]^+$), 319 (44.5, $[C_7H_4(C_6H_5)_3]^+$), 305 (30.5, $[C_6H_3(C_6H_5)_3]^+$).

The gases which were evolved during the reaction were transferred to a gas infrared cell. An infrared spectrum comparison

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(20) Thermal decompositions of thiete sulfones have been reported to yield cyclic sulfinates or sultines: R. W. Hoffmann and W. Sieber, *Angew. Chem., Int. Ed. Engl.*, **4**, 786 (1965); D. C. Dittmer, R. S. Henion, and N. Takashina, Abstracts of Papers, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April, 1967, 101-0 and ref 1; J. F. King, K. Piers, D. J. H. Smith, C. L. McIntosh, and P. de Mayo, *Chem. Commun.*, 31 (1969).

(21) Melting points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 137 or 521 spectrometer and ultraviolet spectra on a Perkin-Elmer Model 202 spectrometer. Nmr spectra were obtained on a Varian A-60 or HA-100 spectrometer with TMS as an internal standard. Mass spectra were obtained on a Perkin-Elmer Hitachi RMU 6 E instrument. Analyses for elements were done by Galbraith Laboratories, Inc., Knoxville, Tenn., or by Alfred Bernhardt Mikroanalytisches Laboratorium in Max Planck Institut für Kohlenforschung, Mulheim, West Germany.

(22) D. C. Dittmer and M. E. Christy, *J. Org. Chem.*, **26**, 1324 (1961); P. L. F. Chang and D. C. Dittmer, *ibid.*, **34**, 2791 (1969).

(23) Percentage of base peak is given in parenthesis. P = parent ion.

showed these gases to be carbon monoxide[24] and sulfur dioxide.[25]

Hydrogenation of 1,5,6,7-Tetraphenylbicyclo[3.2.1]octa-2,6-dien-8-one (3).—The bicyclic ketone **3** (0.4 g, 0.94 mmol) and platinum oxide (40 mg) in 50 ml of ethyl acetate were hydrogenated at room temperature under atmospheric pressure. After the hydrogen absorption ceased, the catalyst was removed by filtration and the solvent was removed.

The residue was recrystallized from ethanol–chloroform to give a monoolefinic ketone (0.3 g, 0.7 mmol, 77%): mp 184–186°; uv (CH_3CN) 213 nm (log ϵ 4.73), 227 (4.34), 250 (4.06), 258 (4.03), 265 (3.99); ir (KBr disk), 3080 (sh), 3063 (w), 3030 (w), 2952 (m), 2870 (m), 1758 (vs, C=O), 1600 (m), 1447 (s, CH_2), 695 cm^{-1} (vs); proton nmr (60 MHz in $CDCl_3$) τ 2.68–3.2 (complex multiplet, 20 H) and 7.25–7.85 (complex multiplet, 6 H); mass spectrum (250°, direct inlet, 70 eV) m/e 426 (5.4, P).

Anal. Calcd for $C_{32}H_{26}O$: C, 90.14; H, 6.1. Found: C, 90.25; H, 6.28.

Thermal Rearrangement of 2,3,4,5-Tetraphenylcycloheptatriene (11) to 1,2,6,7-Tetraphenylcycloheptatriene (2).—2,3,4,5-Tetraphenylcycloheptatriene (**11**) (0.6 g, 1.48 mmol)[11] was refluxed in *m*-xylene for 1.5 hr. The solvent was removed and the residue was recrystallized from benzene–hexane to yield **11**, (0.2 g, 0.5 mmol, 34%), mp 169–170°. The recovered starting material was removed by filtration and the residue was recrystallized from acetone to yield the high melting form of 1,2,6,7-tetraphenylcycloheptatriene (0.2 g, 0.5 mmol, 34%), mp 127–129°.

Conversion of 1,5,6,7-Tetraphenylbicyclo[3.2.1]octa-2,6-dien-8-one (3) to 1,5,6,7-Tetraphenylbicyclo[3.2.1]octa-6-ene (8).—The bicyclic ketone **3** (1 g, 2.36 mmol) was dissolved in ethanedithiol (10 ml). Boron trifluoride etherate (10 ml) was added with cooling by ice–water. The solution immediately became deep red and the mixture was kept at room temperature for 2 days. The precipitate was removed by filtration and washed with methanol to give white crystals (0.3 g, 0.6 mmol, 22.8%), mp 275–278°.

Anal. Calcd for $C_{34}H_{28}S_2$: C, 81.6; H, 5.6; S, 12.8. Found: C, 81.73; H, 5.78; S, 12.80.

The thioketal was suspended in dioxane (20 ml) and W-5 Raney nickel (5 g) was added. The Ni catalyst was removed after a 14-hr reflux period and the dioxane was removed. The residue was recrystallized from methanol–acetone (50 mg, 0.12 mmol, 20.3%): mp 113–115°; ir (KBr disk) 3080 (sh) 3033 (w), 2950 (m), 2930 (m), 2903 (w), 2862 (w), 1600 (m), 1443 (s, CH_2), and 698 cm^{-1} (vs); uv (CH_3CN) 225 nm (log ϵ 4.27), 256 (4.02), and 267 (4.00); nmr (60 MHz in $CDCl_3$) complex τ 2.54–3.22 (complex multiplet, 20 H), 6.95 (perturbed doublet, 1 H), 7.5–8.25 (complex multiplet, 7 H); mass spectrum (300°, direct inlet, 70 eV) m/e 413 (36.7), 412 (100, P), 384 (21.6, P − C_2H_4), 370 (13.3, P − C_3H_6), 306 (30, $[C_6H_3(C_6H_5)_3]$), 178 (21.6, $C_6H_5C{\equiv}CC_6H_5$), metastable ion at m/e 357.9 (P − $CH_2{=}CH_2$).

Anal. Calcd for $C_{32}H_{28}$: C, 93.20; H, 6.79. Found: C, 93.07; H, 6.70.

5-Methyl-1,2,3,4-tetraphenyl-2-norbornene (7). A. 5-Cyano-1,2,3,4-tetraphenyl-2-norbornene.—Tetraphenylcyclopentadiene (8 g, 0.022 mol), acrylonitrile (6 g, 0.14 mol), and a small amount of hydroquinone were heated in benzene solution for 2 days. The solvent was removed and the residue was recrystallized from chloroform–ethanol (8 g, 0.019 mol), mp 187–189°, ir (KBr disk) 2230 cm^{-1}.

Anal. Calcd for $C_{32}H_{25}N$: C, 90.77; H, 5.91; N, 3.31. Found: C, 91.02; H, 5.89; N, 3.26.

B. 5-Aminomethyl-1,2,3,4-tetraphenyl-2-norbornene.—An equimolar $LiAlH_4$ ether solution was added at room temperature to the above nitrile (4 g, 9.7 mmol) in dry ether (200 ml). The reaction mixture was refluxed 2 hr and hydrolyzed with 3 *N* sodium hydroxide solution. The ether layer was separated and the aqueous layer was extracted with benzene. The solvent was removed and the residue was recrystallized from benzene–hexane (3.2 g, 7.5 mmol, 77.5%), mp 80–82°, ir (neat) 3400 cm^{-1}.

Anal. Calcd for $C_{32}H_{29}N$: C, 89.92; H, 6.79; N, 3.28. Found: C, 89.80; H, 6.67; N, 3.18.

C. 5-*N,N*-Dimethylaminomethyl-1,2,3,4-tetraphenyl-2-norbornene.—The amine prepared in B (7 g, 0.016 mol) was added slowly to formic acid (10 g, 90%) cooled with tap water. Formaldehyde (5 ml, 37% solution) was added and the reaction mixture stirred for 2 hr at room temperature and then heated to 90–100° for 14 hr. Hydrochloric acid (2 ml of 4 *N*) was added, and the solvent was removed by a rotary evaporator. A small amount of water and 2 ml of 18 *N* sodium hydroxide were added, and the mixture was extracted with benzene. After removal of solvent, the mixture was separated on silica gel (Will, Grade 950, 60–200 mesh). The dimethylated amine was eluted with ether and recrystallized from benzene–acetone (2.5 g, 5.45 mmol, 34%): mp 198–200°; ir (KBr disk) 2880, 2760 cm^{-1}; nmr (60 MHz, $CDCl_3$) τ 2.5–3.5 (complex multiplet 20 H), 7.5–7.68 (complex multiplet, 5 H), 7.5 (singlet, 6 H), 7.75–8.17 (multiplet, 2 H).

Anal. Calcd for $C_{34}H_{33}N$: C, 89.92; H, 6.79; N, 3.28. Found: C, 89.80; H, 6.67; N, 3.13.

Another isomer, most probably endo, was eluted with methanol from the silica gel column (2 g, 4.3 mmol, 27%): mp 81–85°; nmr (60 MHz, $CDCl_3$) τ 2.35–3.6 (complex multiplet, 20 H), complex 6.3–8.4 (complex multiplet, 7 H), 7.83 (singlet, 6 H, endo CH_3).

D. 5-*N,N*-Dimethylaminomethyl-1,2,3,4-tetraphenyl-2-norbornene Methiodide.—The *exo*-dimethylamine from C (2.5 g, 5.5 mmol) was dissolved in benzene (40 ml). Excess methyl iodide was added and the reaction mixture kept at room temperature for 7 hr, after which a white crystalline precipitate was removed by filtration, washed with benzene, and recrystallized from ethanol–acetone to give 2.7 g (4.45 mmol, 81%) of product, mp 255–260° dec. A methiodide (mp 191–196°) also could be prepared from the endo isomer; the reaction was much slower.

Anal. Calcd for $C_{35}H_{36}NI$: C, 70.35; H, 6.03; N, 2.34. Found: C, 70.49; H, 6.22; N, 2.48.

E. 5-Methylene-1,2,3,4-tetraphenyl-2-norbornene.—The quaternary ammonium iodide (1 g, 1.6 mmol) was dissolved in tetrahydrofuran and a volume of water equal to the volume of tetrahydrofuran was added. Freshly prepared silver oxide (1 g) was added and stirred for 50 min at room temperature. The excess silver oxide and silver iodide were removed by filtration and the solvent was removed by means of a rotary evaporator. The light brown salt was heated at 240° for 1.5 hr under vacuum (water aspirator). The product mixture was dissolved in benzene and separated on silica gel. The first compound, eluted with hexane–benzene (1:1), was tetraphenylcyclopentadiene (50 mg, 0.13 mmol, 8.4%), mp 181° (lit.[26] mp 180°). The second compound, eluted with the same solvent, was 5-methylene-1,2,3,4-tetraphenyl-2-norbornene (recrystallized from methanol–chloroform) (0.5 g, 1.21 mmol, 76%): mp 154–156°; ir (KBr disk) 3040, 1658, and 887 cm^{-1} ($C{=}CH_2$); uv (CH_3CN) 221 nm (log ϵ 4.35), 237 (4.05), 261 (4.05), 340 (3.83); nmr (60 MHz in $CDCl_3$) τ 2.65–3.5 (complex multiplet, 20 H), 4.77 (apparent doublet, 2 H), 6.95 (broadened singlet, 2 H), 7.26, 7.77 (AB quartet, J = 8.5 Hz, 2 H).

Anal. Calcd for $C_{32}H_{26}$: C, 93.65; H, 6.35. Found: C, 93.67; H, 6.24.

F. Hydrogenation of 5-Methylene-1,2,3,4-tetraphenyl-2-norbornene.—The olefin (0.5, 1.2 mmol) was hydrogenated in ethyl acetate (50 ml) with 50 mg of platinum oxide at room temperature and under atmospheric pressure. The reaction was completed in 5 min. The catalyst was removed by filtration and the solvent was removed. The residue was recrystallized from benzene–hexane mixed solvent to give 5-methyl-1,2,3,4-tetraphenyl-2-norbornene (**7**) (0.28 g, 0.67 mmol, 56%): mp 203°; ir (KBr disk) 2962, 1458, and 1374 cm^{-1}; uv (CH_3CN) 222 nm (log ϵ 4.31), 237 (4.13), and 273 (3.99); nmr (60 MHz in $CDCl_3$) τ 2.55–3.5 (complex multiplet, 20 H), 6.52–7.12 (multiplet, 1 H), 7.15–7.65 (complex multiplet, 2 H), 7.95 (doublet, J = 9 Hz, 1 H), 8.15–8.5 (complex multiplet, 1 H), 8.59 (doublet, 3 H)

Anal. Calcd for $C_{32}H_{28}$: C, 93.20; H, 6.79. Found: C, 92.34; H, 6.78.

1,5,6,7-Tetraphenylbicyclo[3.2.1]octa-2,6-dien-8-one from Tetracyclone and 3,3-Dichloropropene.—3,3-Dichloropropene (1.43 g, 0.013 mol) and a trace amount of iodine catalyst were added to 0.91 g (0.014 g-atom) of zinc, treated as described by Shank and Shechter,[27] in 50 ml of ether. The mixture was refluxed for 10 min and tetracyclone (5 g, 0.013 mol) suspended in 150 ml of ether was added. The refluxing was continued for 3 days. The mixture was filtered through Celite, the solvent was removed, and the residue was separated on an alumina column. The

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(24) "The Sadtler Standard Spectra," Sadtler Research Laboratories, Philadelphia, Pa., 1965, infrared spectrum 1142.

(25) Reference 24, infrared spectrum 841.

(26) See the paper of Sonntag, *et al.*, cited in ref 13.

(27) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

products were mainly recovered tetracyclone (3 g, 7.5 mmol, 60%), a ketone (0.2 g, 0.5 mmol, 4.2%), and an unidentified compound (1 g). The melting point and infrared and nmr spectra of the ketone were identical with those of 1,5,6,7-tetraphenylbicyclo[3.2.1]octa-2,6-dien-8-one (**3**), which was obtained from tetracyclone and thiete sulfone.

1,6,7,8-Tetraphenyl-3-thiatricyclo[4.2.1.0^{2,5}]non-7-en-9-one 3,3-Dioxide (9).—Tetracyclone (3 g, 7.5 mmol) and thiete sulfone (1 g, 9.6 mmol) were refluxed in dioxane (30 ml) for 1 week. The solvent was removed and the residue was separated on a silica gel column. The tetracyclone–thiete sulfone adduct (**9**) was eluted with ether and recrystallized from benzene–hexane mixed solvent (0.3 g, 0.6 mmol, 7.8%): mp 140–150° (it resolidified at 190–200° followed by decomposition at 220–221°); ir (KBr disk) 1785, 1310, and 1120 cm^{-1}; uv (dioxane) 237 nm (log ϵ 4.04) and 270 (3.96); nmr (60 MHz in CDCl$_3$) τ 2.7 (singlet, 10 H), 2.9–3.42 (complex multiplet, 10 H), 4.6 (perturbed doublet, 1 H), 5.6–5.96 (multiplet, 1 H), 6.1–6.6 (multiplet, 2 H). Adduct **9** (0.2 g, 0.4 mmol) was refluxed in *m*-xylene (Eastman Kodak Co.) and the decomposition was followed by thin layer chromatography (silica gel). After 3 hr, the adduct completely decomposed. *m*-Xylene was removed and the residue was separated on a silica gel column. 1,2,6,7-Tetraphenylcycloheptatriene (**2**) (0.12 g, 0.302 mmol, 76%), mp 64–66°, was eluted with hexane–benzene (2:1).

Anal. Calcd for $C_{32}H_{24}O_3S$: C, 78.68; H, 4.92; S, 6.56. Found: C, 78.81; H, 5.10; S, 6.38.

Reaction of Tetraphenylcyclopentadiene and Thiete Sulfone.—Tetraphenylcyclopentadiene (5 g, 0.014 mol) and thiete sulfone (1.8 g, 0.015 mol) were refluxed in *m*-xylene (Eastman Kodak Co.) (70 ml) for 2 days. The solvent was removed by a rotary evaporator, and the residue was dissolved in benzene and chromatographed on silica gel. The first compound, eluted with hexane–benzene (1:1), was 1,5,6,7-tetraphenylbicyclo[3.2.1]-octa-2,6-diene (**12**) which was recrystallized from ethanol–acetone (1.4 g, 5.2 mmol, 12.7%): mp 140–142°; ir (KBr disk) 3040, 1638, and 904 cm^{-1}; uv (CH$_3$CN) 218 nm (log ϵ 4.35), 229 (4.27), 235 (4.24), 345 (3.29); nmr (60 MHz in CDCl$_3$) τ 2.6–3.57 (complex multiplet, 21 H), 4.15 (two sets of triplets, J = 10 and 3 Hz, 1 H), 7.36 (quartet, J = 10 Hz, 2 H), 7.45 (complex multiplet, 2 H).

Anal. Calcd for $C_{32}H_{26}$: C, 93.65; H, 6.35. Found: C, 93.75; H, 6.28.

The second compound, 1,6,7,8-tetraphenyl-3-thiatricyclo-[4.2.1.0^{2,5}]non-7-en-9-one 3,3-dioxide (**13**), was eluted with ether and recrystallized from ethanol–acetone (2.4 g, 5.1 mmol, 36.3%): mp 236°; ir (KBr disk) 1323 and 1130 cm^{-1}; uv (CH$_3$CN) 217 nm (log ϵ 4.24), 235 (shoulder, 4.11), 260 (3.91); nmr (60 MHz in CDCl$_3$) τ 2.6–3.55 (complex multiplet, 20 H), 4.7 (perturbed doublet, 1 H), 5.95–6.8 (complex multiplet, 3 H), 6.89 (singlet, 2 H).

Anal. Calcd for $C_{32}H_{26}O_2S$: C, 81.01; H, 5.48; S, 6.75. Found: C, 81.16; H, 5.49; S, 6.67.

A third compound was separated from the other sulfone by recrystallization and is an isomer of it (2.7 g, 5.6 mmol, 40.7%): mp 115–120°; uv (CH$_3$CN) 213 nm (log ϵ 4.27) and 264 (3.88); nmr (60 MHz in CDCl$_3$) τ 2.4–3.6 (complex multiplet, 20 H), 5.6–6.1 (perturbed doublet, 1 H), 6.45–6.95 (complex multiplet, 3 H), 6.95–7.8 (complex multiplet, 2 H). The displacements of some of these absorptions to lower field suggests that this isomer is the exo. The ir spectra of the two sulfones are almost identical.

Anal. Calcd for $C_{32}H_{26}O_2S$: C, 81.01; H, 5.48; S, 6.75. Found: C, 81.14; H, 5.50; S, 6.51.

Hydrogenation of 1,5,6,7-Tetraphenylbicyclo[3.2.1]octa-2,6-diene (12).—The olefin (0.5 g, 1.2 mmol) was hydrogenated in ethyl acetate solvent over platinum oxide. After 5 min the hydrogenation was complete and the catalyst was separated. The solvent was removed and the residue was recrystallized from ethanol–acetone (0.48 g, 1.15 mmol, 96%). This compound was identical with the Raney nickel reduction product from 1,5,6,7-tetraphenylbicyclo[3.2.1]octa-2,6-dien-8-one (**3**).

Anal. Calcd for $C_{32}H_{28}$: C, 93.20; H, 6.79. Found: C, 93.07; H, 6.70.

Reaction of Tetracyclone and Methyl Vinyl Sulfone to Give 1,2,3,4-Tetraphenylbenzene.—A solution of tetracyclone (3.86 g, 10 mmol) and methyl vinyl sulfone (1.59 g, 15 mmol, K and K Laboratories) in *m*-xylene (100 ml) was refluxed for 36 hr. The reaction mixture was poured into an evaporating dish and allowed to evaporate to dryness. The residue was dissolved in benzene–chloroform and chromatographed on a column of Florisil. Elution with petroleum ether (bp 35–60°) and evaporation of the eluent gave 1,2,3,4-tetraphenylbenzene (2.96 g, 77%), mp 189–190° (lit.[28] mp 190–191°). The infrared and ultraviolet spectra are in accord with data given in the literature.[29]

1,5-Diphenyl-3*H*-cyclohepta[*l*]phenanthrene (4).—A solution of thiete sulfone (1.25 g, 12 mmol) and phencyclone[30] (3.82 g, 10 mmol) in *m*-xylene (100 ml) was refluxed for 12 hr. The *m*-xylene was removed by evaporation and the residue chromatographed on a column of Florisil and eluted with 1:1 benzene–petroleum ether (bp 65–75°). The solvent was evaporated and the residue was recrystallized from benzene–ethanol to yield a white, fluorescent product: mp 242–244° (2.75 g, 69%); ir (KBr disk) 3000 (w), 1600 (m), 1480 cm^{-1} (m); uv (CH$_3$CN) 252 nm (log ϵ 4.75), 261 (4.81), 275 (4.61), 310 (4.06), 340 (3.16); nmr (60 MHz, CDCl$_3$) τ 2.00–3.03 (complex multiplet, 20 H), 3.20–3.56 (triplet, J = 7 Hz, 2 H).

Anal. Calcd for $C_{31}H_{22}$: C, 94.38; H, 5.62; mol wt, 394. Found: C, 94.27; H, 5.67; mol wt (osmometric), 400.

Registry No.—**1**, 7285-32-7; **2**, 32513-31-8; **3**, 32513-32-9; **4**, 32513-33-0; **7**, 32513-56-7; **8**, 32513-57-8; **9**, 32513-58-9; **12**, 32513-59-0; *endo*-**13**, 32513-60-3; *exo*-**13**, 32513-61-4; tetracyclone, 479-33-4; 7-thiabicyclo[4.2.0]-3-octene 7,7-dioxide, 32513-62-5; 9-oxa-3-thiatricyclo[4.2.1.0^{2,5}]non-7-ene 3,3-dioxide, 32476-23-6; 7,8-dimethyl-9-oxa-3-thiatricyclo[4.2.1.-0^{2,5}]non-7-ene 3,3-dioxide, 32513-63-6; monoolefinic ketone from **3**, 32506-29-9; thioketal from **3**, 32513-64-7; 5-cyano-1,2,3,4-tetraphenyl-2-norbornene, 32513-65-8; 5-aminomethyl-1,2,3,4-tetraphenyl-2-norbornene, 32513-66-9; *exo*-5-*N*,*N*-dimethylaminomethyl 1,2,3,4-tetraphenyl-2-norbornene, 32527-25-6, 32513-68-1 (methiodide); *endo* - 5 - *N*,*N* - dimethylaminomethyl-1,2,3,4-tetraphenyl-2-norbornene, 32513-67-0, 32513-69-2 (methiodide); 5 methylene-1,2,3,4-tetraphenyl-2-norbornene, 32513-70-5.

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