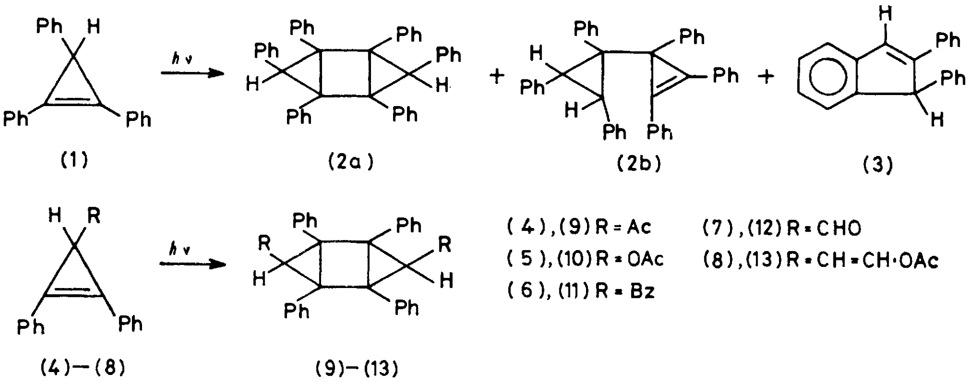
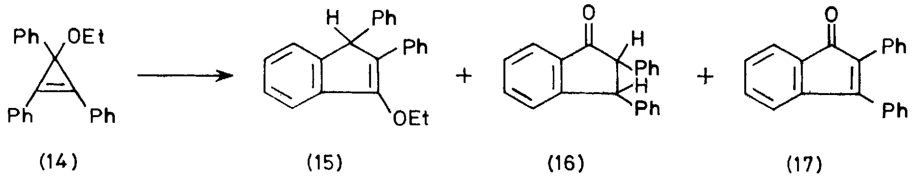
Photolytic Rearrangements in Triphenylcyclopropene Systems [1]

By **James O. Stoffer** * and **Joseph T. Bohanon**, Department of Chemistry, University of Missouri-Rolla, Rolla MO 65401, U.S.A.

Photolysis of 1,2,3-triphenylcyclopropene results in dimerization to 1,2,3,4,5,6-hexaphenyltricyclo[3.1.0.0^{2,4}]-hexane. Photolysis of 3-phenyl-, 3-benzyl-, 3-methyl-, and 3-methoxy-1,2,3-triphenylcyclopropene yields no dimeric products. All the compounds rearrange to give some of the corresponding 3-substituted 1,2-diphenylindenes. In addition to indene formation, the 3-methoxy-compound undergoes fragmentation and the 3-benzyl-compound undergoes a benzyl proton shift to form 1,2,3,4-tetraphenylbutadiene isomers. The reaction is postulated to proceed by initial excitement of the cyclopropene π bond to a π diradical followed by ring opening of the cyclopropene to form a phenyl vinyl carbene which inserts into the 3-phenyl group to form the indene and may undergo other reactions where possible.

THE photolysis of a number of 1,2-diphenyl- and 1,2,3-triphenyl-cyclopropene compounds has been reported with varying results depending on the nature of the substituents at the 3 position. The photolysis of 1,2,3-triphenylcyclopropene (1) is reported by Durr [2] to give isomers of 1,2,3,4,5,6-hexaphenyltricyclo[3.1.0.0^{2,4}]-hexane (2a) and 1,2-diphenylindene (3) in varying yields depending both on the solvent and either the presence or absence of a photosensitizer. DeBoer and Breslow [3] reported that dimer (2b) was formed in addition to the isomer (2a) upon photolysis of (1) in benzene solvent using a photosensitizer. Photolysis of 3-substituted 1,2-diphenylcyclopropenes (4)—(8) yields the analogous tricyclohexane dimers (9)—(13).[4,5]





The photolysis of the ether (14) using light of 350 nm wavelength gave the indene (15) and small amounts of the indanone (16) and indenone (17).[6]

The photolysis of 3,3-dimethyl-1,2-diphenylcyclopropene is reported [7] to give *cis*- and *trans*-isomers of 1,2-diphenyl-3-methylbutadiene *via* a carbene intermediate. Thus a study of the photolysis of the substituted cyclopropenes was initiated in order to establish the factors influencing dimerization and rearrangement (indene formation).

RESULTS

A study was undertaken to investigate the effect of photolysis on different 3-substituted 1,2,3-triphenylcyclopropenes. All compounds yielded the corresponding 3-substituted 1,2-diphenylindenes, but the yields and side-products varied with different substituted groups. Photo-

[1] Taken in part from the Ph.D. Thesis of Joseph T. Bohanon, presented at the 170th meeting of the American Chemical Society, San Francisco, CA, August 1976.

[2] (*a*) H. Dürr, *Tetrahedron Letters*, 1967, 1649; (*b*) *Annalen*, 1969, 102.

[3] C. DeBoer and R. Breslow, *Tetrahedron Letters*, 1967, 1033.

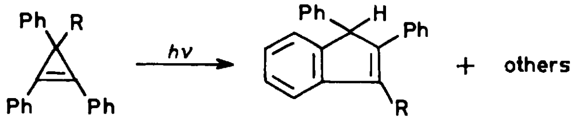
[4] (*a*) N. Obata and J. Maritani, *Bull. Chem. Soc. Japan*, 1966, **39**, 2250; (*b*) *Tetrahedron Letters*, 1966, 1503.

[5] M. I. Komendantov and I. N. Domnin, *Zhur. Org. Khim.*, 1973, **9**, 939.

[6] A. S. Monahan, J. D. Freilich, and J. J. Fong, *Tetrahedron Letters*, 1970, 1865.

[7] J. A. Pincock, R. Morchat, and D. R. Arnold, *J. Amer. Chem. Soc.*, 1974, **95**, 7536.

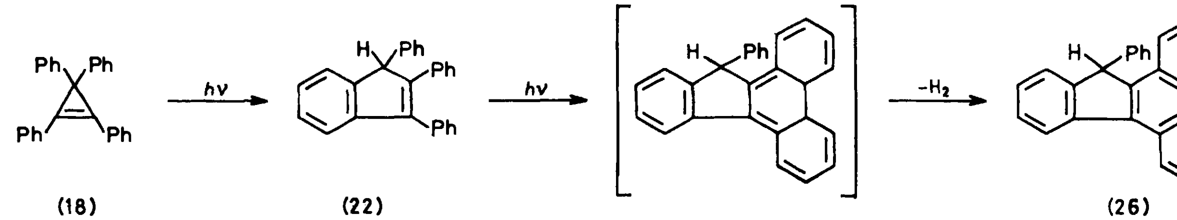
lytic investigations were conducted on the 1,2,3-triphenylcyclopropenes (18)—(21).



(18)—(21) (22)—(25)

(18),(22) R = Ph
(19),(23) R = $PhCH_2$
(20),(24) R = Me
(21),(25) R = MeO

Photolysis of the cyclopropene (18) for 24 h yielded 50—75% of the indene (22) and 5—20% of the 13*H*-indeno[1,2-*l*]phenanthrene (26). Complete conversion was observed during 24 h and no dimeric or fragmentation products were observed. The indene (22) and the phenanthrene (26) have been reported as products of photolysis of 1,1,1,3-tetraphenylpropyne *via* a 1,2,3,3-tetraphenylcyclopropene (18) intermediate.[8] The reaction probably precedes by cyclization of the 2- and 3-phenyl groups of the indene (22) followed by aerial oxidation or spontaneous dehydrogenation.



(18) (22) (26)

The formation of the phenanthrene (26) is analogous to the formation of phenanthrene (28) from stilbene (27) by photolysis in the presence of oxygen.[9]

Photolysis of the cyclopropene (19) for 24 h effected complete rearrangement of the cyclopropene. The reaction yielded 64% of the indene (23) and 2—3% of the naphthalene (29); the remaining product was assigned the identity of a mixture of *cis,cis-* (30a), *cis,trans-* (30b), and *trans,trans-* (30c) 1,2,3,4-tetraphenylbutadienes on the basis that it yielded 1,2,3,4-tetraphenylbutane (31) upon reduction with sodium in pentyl alcohol. The products are postulated to arise from an intermediate of phenyl (1,2,3-triphenylpropenyl) carbene.

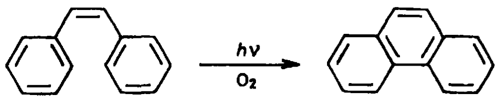
Carbene insertion into the 2-phenyl group of the intermediate would yield the indene (23). Insertion into the 3-phenyl group would yield 1,2,3-triphenyl-1,4-dihydronaphthalene (32) which could undergo aerial oxidation or dehydrogenation [10] to form the 1,2,3-triphenylnaphthalene (29). The tetraphenylbutadienes (30) can arise either by hydrogen extraction at the 3-position of the carbene intermediate or by carbene insertion at the 4-position to form 1,2,3,4-tetraphenylcyclobutene which is thermally unstable and rearranges to tetraphenylbutadienes.[11] No dimeric or fragmentation products were observed.

Photolysis of the cyclopropene (20) for 24 h yielded 40% of the indene (24). The remaining substance recovered was starting material. No evidence of formation of a triphenylbutadiene by hydrogen extraction from the methyl group by the carbene was observed. Increasing the time of photolysis to 68 h increased the yield of the indene (24) to 78%, but unchanged starting material was still present. No dimeric or fragmentation products were recovered. Thus for the 3-methyl compound, the quantum yield must be considerably lower than for the other compounds studied.

Photolysis of the ether (21) for 48 h yielded 15% of the indene (25), 3.5% of diphenylacetylene (33), 3.5% of benzoic acid (34), 3% of the indene (35), a trace of the propen-1-one (36), and a polymer of average molecular weight of 910.

Keyton *et al.*[8] report that photolysis of 1 methoxy-1,1,3-triphenylpropyne yields the indene (25) *via* a postulated cyclopropene (21) intermediate.

The vinyl carbene intermediate analogue postulated for the previous reactions accounts for the products. Carbene insertion into the 3-phenyl group would yield the indene (25) while loss of the methoxy methyl group would lead to the indenone (35). The propenone (36) can arise from loss of a methyl radical followed by hydrogen extraction. Fragmentation of the radical intermediate would lead to diphenylacetylene (33) and the phenacyl radical which may react with atmospheric oxygen to form benzoic acid. The intermediate (37a) is sterically oriented for insertion into the phenyl group to form the indene (24) while the isomer (37b) is not and thus reverts to the starting cyclopropene (20) by carbene addition across the double bond. The cyclopropene (20) did not yield any triphenylbutadiene analogous to the tetraphenylbutadiene (30) from the 3-benzyl-1,2,3-triphenylcyclopropene (19), possibly because a radical intermediate is stabilized by the additional phenyl group in the latter compound and not in the former.



(27) (28)

The fragmentation of methyl 1,2,3-triphenylcyclopropenyl ether (21) probably occurs from the isomer (21b) intermediate where the carbene is *cis* to the methoxy-group while carbene insertion into the phenyl group to form the indene (25b) occurs with the intermediate (21a) where the carbene is *cis* to the phenyl group. Monahan, Freilich, and Fong,[6] who photolysed the analogous ethyl ether (14) in benzene do not report fragmentation products from the

---

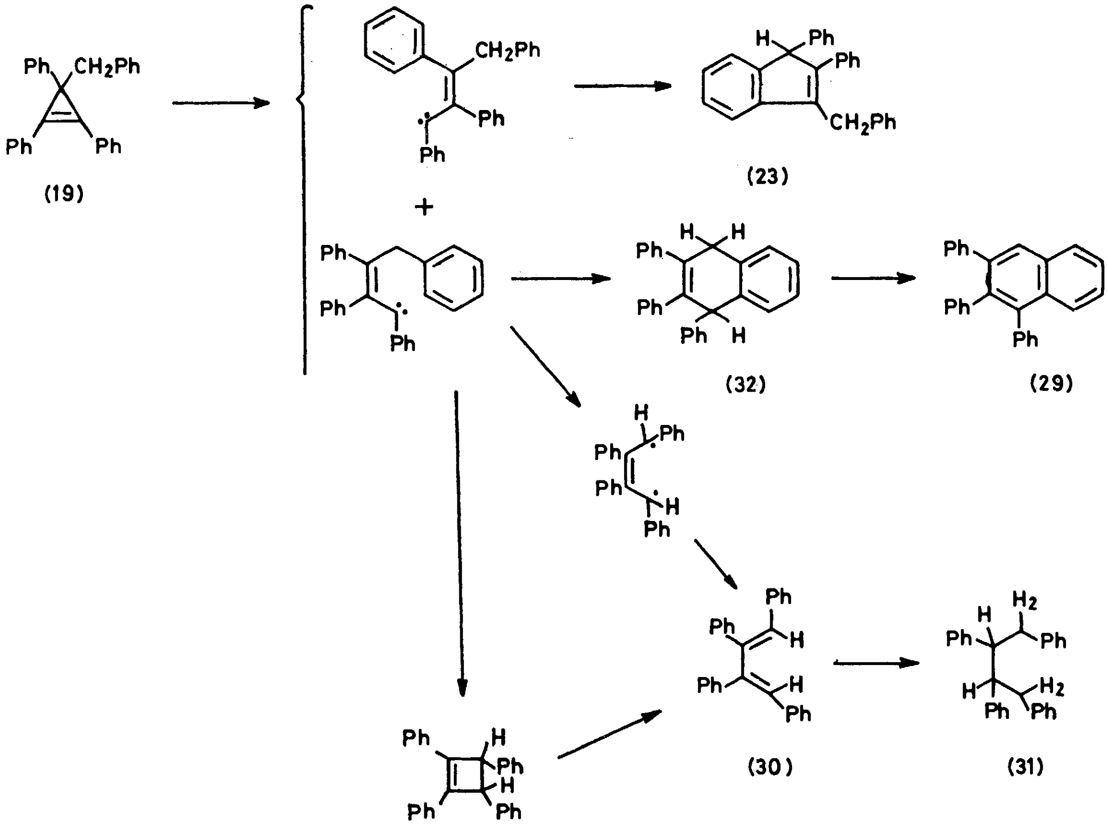
[8] D. J. Keyton, J. J. Brophy, G. W. Griffin, M. Kulig, and M. A. Battiste, presentation at 160th meeting, American Chemical Society, Chicago, Ill., September 1970.

[9] F. B. Mallery, C. S. Wood, J. T. Gordon, L. C. Lindquist, and M. Savitz, *J. Amer. Chem. Soc.*, 1962, **84**, 5361.

[10] L. I. Smith and H. H. Hoohn, *J. Amer. Chem. Soc.*, 1941, **63**, 1184.

[11] H. H. Freeman, G. A. Doorakian, and V. R. Sandel, *J. Amer. Chem. Soc.*, 1965, **87**, 3019.

use of 350 nm light; however, 30% of the material is not accounted for. Since none of the other compounds investigated were fragmented under identical conditions, one must assume that the fragmentation is initiated at the alkoxy-bond of the ether.



DISCUSSION

Photolysis of a 1,2-diphenyl- or 1,2,3-triphenyl-cyclopropene proceeds by initial excitation of the 1,2 π-bond electrons to the π^* orbital. If a hydrogen is present at the 3-position, the excited intermediate dimerizes with another cyclopropene to give the corresponding tricyclo[3.1.0.0^{2,4}]hexane.[1-5] If both substituents at the 3-position are larger than hydrogen, steric hindrance prevents dimerization and the excited state intermediate follows a lower energy reaction pathway, proceeding with ring opening to a phenyl vinyl carbene. When 1,2,3-triphenylcyclopropene (1) is photolysed in the presence of photosensitizer, 1,3-diphenylindene (3) is formed and in the absence of photosensitizer the tricyclohexane (2) is formed. The presence of a photosensitizer presumably results in energy transfer with formation of a cyclopropene π,π^* triplet excited state which then undergoes a bond cleavage reaction with initial formation of the triplet phenyl vinyl carbene. Where dimerization of the singlet excited state is prevented by steric hindrance, then the singlet excited state may either undergo bond cleavage leading to formation of the singlet phenyl vinyl carbene or it may possibly undergo inner system crossing to the triplet which is then converted into the triplet phenyl vinyl carbene.

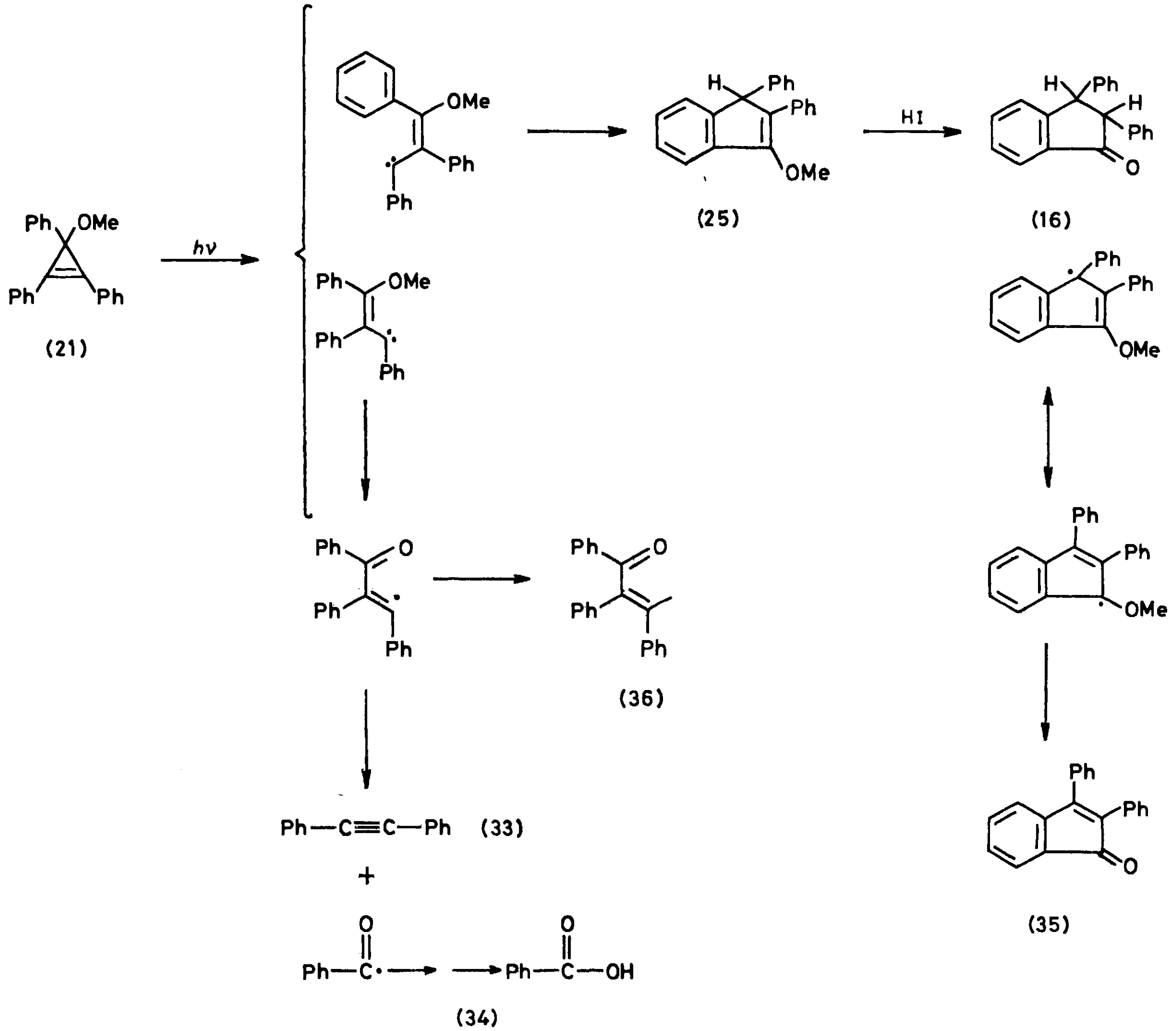
The phenyl vinyl carbene intermediate is capable of undergoing carbene addition across the vinyl double bond to reform the starting cyclopropene. Pincock, Morchat, and Arnold[7] report quantum yields of only 3—15% upon photolysis of 3,3-dimethyl-1,2-diphenylcyclopropene. In the present work, the photolysis of 3-methyl-1,2,3-triphenylcyclopropene (20) for 68 h resulted in only 78% conversion and photolysis of methyl 1,2,3-triphenylcyclopropenyl ether (21) is also incomplete after 48 h. The other photolyses were complete within 24 h. The intermediate phenyl vinyl carbenes may exist in *cis*- and *trans*-forms (37a),(21a), and (37b),(21b).

EXPERIMENTAL

M.p.s were determined on a Mel–Temp apparatus of a Fisher Melting Block and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer model 337 spectrophotometer; u.v. spectra were made on a Beckman DK2A or a Carey 14 spectrophotometer; n.m.r. spectra were obtained with a Varian A 56/60 or Varian 360 n.m.r. spectrometer using tetramethylsilane (TMS) as an internal standard.

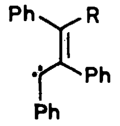
Photolyses were conducted in a 1 000 ml cylindrical vessel constructed with a nitrogen inlet at the bottom, a nitrogen outlet at the top, and a ground-glass neck. Into the neck was inserted a water-cooled quartz immersion well with a ground glass joint. Into the immersion well was inserted a 450 W Hanovia u.v. lamp surrounded by a Pyrex filter.

t-Butyl Triphenylcyclopropenyl Ether and Triphenylcyclopropenium Bromide.—The synthesis of t-butyl 1,2,3-triphenylcyclopropenyl ether and 1,2,3-triphenylcyclopropenium bromide was carried out by the procedure of Breslow and Chang.[12] The cyclopropenyl ether was subjected to further recrystallization from diethyl ether to yield white prisms, m.p. 142.5—144 °C (lit.,[12] 143—144.5 °C).

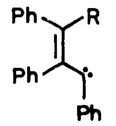


Synthesis and Photolysis of 1,2,3,3-Tetraphenylcyclopropene (18).—A solution of phenylmagnesium bromide from bromobenzene (15.7 g) and magnesium (2.4 g) in ether (200 ml) was treated with 1,2,3-triphenylcyclopropenium bromide (6.0 g). The solution was refluxed 1.5 h, set aside overnight, and then quenched with 5% aqueous ammonium chloride solution (250 ml). The aqueous phase was extracted with ether (2 × 100 ml) and the ethereal phases were combined, dried (Na_2SO_4), and stripped of solvent. The residue was crystallized from 10% benzene–hexane and recrystallized from diethyl ether to give white prisms, m.p. 176—177 °C (lit.,[13] 177—178 °C); yield of 1,2,3,3-tetraphenylcyclopropene (18) (5.5 g). Chromatography on silicic acid yielded a further 0.2 g of (21) to yield a total of 5.7 g (95%).

A solution of 1,2,3,3-tetraphenylcyclopropene (18) (2.0 g) in alumina-washed hexane (550 ml) was photolysed for 24 h. The solution was stripped of solvent and crystallized from 5% benzene–hexane to yield 13-phenyl-13*H*-indeno-[1,2-*l*]phenanthrene (26) (100 mg, 5%),[8] and 1,2,3-triphenylindene (22) (1.5 g, 75%). Recrystallization of the indene (22) from diethyl ether yielded white prisms, m.p. 128—130 °C (lit.,[14] 133—134°) undepressed when mixed with an authentic sample.



(37a) R = Me
(21a) R = OMe



(37b) R = Me
(21b) R = OMe

---

[12] R. Breslow and H. W. Chang, *J. Amer. Chem. Soc.*, 1961, **83**, 2367.

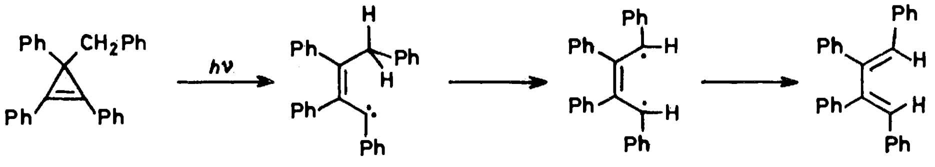
[13] J. A. Berson and M. Pomerantz, *J. Amer. Chem. Soc.*, 1964, **86**, 3896.

[14] C. F. Koelsch and P. R. Johnson, *J. Amer. Chem. Soc.*, 1943, **65**, 567.

[15] R. C. Fuson and S. J. Stryckner, *J. Amer. Chem. Soc.*, 1957, **79**, 2633.

Recrystallization of the phenanthrene (26) from toluene–ethanol yielded white needles, m.p. 205—208 °C (slight decrease) (lit.,[15] 212—213 °C). The n.m.r. and u.v. spectra [15] are consistent with the assigned structure as is the analysis (Found: C, 94.5; H, 5.4%; *M*, 360. Calc. for $C_{27}H_{18}$: C, 94.70; H, 5.30%; *M*, 342).

Repetition of the photolysis without a nitrogen purge produced 0.4 g (20%) of the phenanthrene (26) and 1.0 g (50%) of the indene (22).



(19) (30)

Synthesis and Photolysis of 3-*Benzyl*-1,2,3-*triphenylcyclopropene* (19).—A solution of benzylmagnesium chloride from benzyl chloride (32 g) and magnesium (6.0 g) in ether (450 ml) was treated with 1,2,3-triphenylcyclopropenium bromide (19.0 g) over a 30 min period. The solution was refluxed for 2 h and then quenched with 10% aqueous ammonium chloride solution (300 ml). The aqueous phase was extracted with ether (2 × 100 ml). The ethereal phases were combined, dried (Na_2SO_4), stripped of solvent, crystallized from 10% benzene–hexane, and recrystallized from diethyl ether to yield white needles of 3-benzyl-1,2,3-triphenylcyclopropene (19), m.p. 105—106 °C; yield 17 g (87%) (Found: C, 93.65; H, 6.0. Calc. for $C_{28}H_{22}$: C, 93.81; H, 6.19%).

Several photolytic reactions were conducted on the product (19). Initially, a solution of 3-benzyl-1,2,3-triphenylcyclopropene (19) (2.0 g) in alumina-washed hexane (550 ml) was photolysed for 24 h. The solvent was stripped and the residue was crystallized from 10% benzene–hexane to yield 0.80—0.88 g (44%) of 3-benzyl-1,2-diphenylindene (23) which was recrystallized from diethyl ether to yield white prisms, m.p. 116—117.5 °C (lit.,[16] 118—119°) undepressed when mixed with an authentic sample. Subsequent n.m.r. analysis of the residue indicated that it contained a further 0.39 g of indene (23) to give a total yield of 1.27 g (64%). Several investigations were made to isolate and identify the remainder of the residue.

Chromatography of the residue on silicic acid yielded 5 mg of white needles, m.p. 149—152 °C. The u.v. spectrum of the product shows $\lambda_{max.}$(hexane) at 245 nm and was identical to that of 1,2,3-triphenylnaphthalene (29) (m.p. 153—154 °C).[17] The middle fraction of the eluant from silicic acid was stripped of solvent and analysed; the material was found to be monomeric and isomeric with the starting material (Found: C, 93.5; H, 6.05%; *M*, 345. Calc. for $C_{28}H_{22}$: C, 93.81; H, 6.19%; *M*, 358).

The u.v. spectrum of the material showed $\lambda_{max.}$(hexane) at 255 nm. The n.m.r. analysis displayed a multiplet at τ 2.7, a singlet at τ 3.12, and a singlet at τ 3.21 which overlapped so that no integral could be taken. The u.v. and n.m.r. spectra resemble those reported for *cis,trans*-1,2,3,4-tetraphenylbutadiene (30).[18]

Chromatography of the residue on alumina, silica gel, and Fluorsil failed to isolate other products.

The residue (1.06 g) of one of the photolyses was dissolved in pentyl alcohol (30 ml) and treated with sodium (3.0 g) in small pieces during 3 h; the mixture was then quenched with water and the pentyl alcohol steam distilled off; the residue was extracted with diethyl ether and carbon tetrachloride to yield a solution which was dried, stripped of solvent, and chromatographed on alumina (100 g). Elution with hexane yielded 0.25 g of an unidentified oil, and 0.20 g of 1-benzyl-2,3-diphenylindane [the reduction product of indene (23) [19]], m.p. 138—141 °C (lit.,[19] 143—144 °C), undepressed when mixed with an authentic sample. Ether–hexane eluted 0.20 g of 1,2,3,4-tetraphenylbutane, m.p. 182.5—183.5 °C (lit.,[10] 179—180 °C), undepressed when mixed with an authentic sample. [The tetraphenylbutane is the reduction product of tetraphenylbutadiene (30).[10]] Ether eluted another 0.25 g of an unidentified residue.

In a further reaction with the residue of the photolysis after crystallization of the indene (23), the residue was treated with sulphur (0.16 g) and heated at 240—250 °C for 4 h. The product was dissolved in chloroform and treated with pentane; the solution was chilled to yield 0.08 g of a dark brown residue, m.p. 60—100 °C. The filtrate was stripped of solvent and chromatographed on alumina. Hexane eluted 0.05 g of sulphur and 0.04 g of 1-benzyl-2,3-diphenylindene.[10]

Photolysis of 3-*Methyl*-1,2,3-*triphenylcyclopropene* (20).—A solution of 3-methyl-1,2,3-triphenylcyclopropene (20) (2.0 g) [20] in alumina-washed hexane (550 ml) was photolysed for 24 h. The solution was stripped of solvent and crystallized from 5% benzene–hexane to yield 3-methyl-1,2-diphenylindene (24) (0.8 g, 40%). Recrystallization of (24) from diethyl ether yielded white prisms, m.p. 88—90 °C (lit.,[14] 90—91 °C) undepressed when mixed with an authentic sample. Chromatography of the residue failed to separate the components. The n.m.r. analysis of the residue indicated that it consisted of starting material and some of the indene (27).

The reaction was repeated with a 68 h period of photolysis. A yield of 1.4 g (70%) of product was obtained and n.m.r. analysis of the residue indicated a further 0.15 g of the indene (27) to give a total yield of 1.55 g (78%). The n.m.r. analysis also indicated the presence of starting material (23).

Preparation of Methyl 1,2,3-*Triphenylcyclopropenyl Ether* (21) *and Analogous Ethers*.—Semi-pure t-butyl 1,2,3-triphenylcyclopropenyl ether (200 mg) was dissolved in methanol (25 ml) and refluxed for 45 min. The solvent was evaporated to 2 ml and cooled. Crystals of starting

---

[16] F. Bergman and Y. H. Herschberg, *J. Amer. Chem. Soc.*, 1943, **65**, 1429.

[17] H. H. Freeman, G. A. Deerakian, and V. R. Sandel, *J. Amer. Chem. Soc.*, 1965, **87**, 3015.

[18] R. N. McDonald and C. E. Reineke, *J. Amer. Chem. Soc.*, 1964, **87**, 3019.

[19] E. Bergman and W. Schreiber, *Annalen*, 1963, **500**, 118.

[20] R. Breslow and P. Dowd, *J. Amer. Chem. Soc.*, 1963, **85**, 2779.

material (50 mg) formed followed by methyl 1,2,3-triphenylcyclopropenyl ether (21) (100 mg, 57%), m.p. 69—70 °C (lit.,[21] 69—70 °C).[21]

Similar refluxing of solutions of t-butyl triphenylcyclopropenyl ether in ethanol and propan-2-ol yielded the respective ethyl 1,2,3-triphenylcyclopropenyl ether (14) and the 1-methylethyl 1,2,3-triphenylcyclopropenyl ether. Recrystallization of the ethyl ether (14) from diethyl ether yielded white prisms, m.p. 127—128 °C (lit.,[22] 121—122 °C crystallized from aqueous ethanol). The i.r., u.v., and n.m.r. spectra are consistent with the assigned structure. The methylethyl ether was recrystallized from diethyl ether to give white prisms, m.p. 102—103 °C. The n.m.r. spectrum and the analysis were consistent with the assigned structure (Found: C, 88.0; H, 6.9. Calc. for $C_{24}H_{20}O$: C, 88.21; H, 6.80%).

The i.r. spectrum of each of the ethers showed a cyclopropene absorption at 5.5 μm and the u.v. spectrum shows $\lambda_{max.}$(hexane) 223, 230, 289sh, 301, and 319 nm of nearly equal absorbance.

When the t-butyl ether was subjected to multiple recrystallization or treatment with diethylamine its ether exchange activity ceased. [The addition of a small quantity of triphenylcyclopropenium bromide or anhydrous HCl reactivated this property indicating that the exchange is catalysed by traces of triphenylcyclopropenium chloride, an intermediate in the synthesis of the t-butyl ether.

Photolysis of Methyl 1,2,3-*Triphenylcyclopropenyl Ether* (21).—The methyl ether (21) (2.0 g) in alumina-washed hexane (550 ml) was photolysed for 48 h with a nitrogen purge and then stripped of solvent to leave 1.9 g of residue. The residue was extracted with 2 × 50 ml of hexane. The undissolved residue was dissolved in ether (10 ml) and hexane (100 ml) was added to the solution to precipitate 0.2 g (10%) of a light yellow powder, m.p. 154 °C (decomp.), *M*, 910; and solution A. Solution A and the hexane extracts were stripped of solvent, dissolved in ether (150 ml) (soln. B), and extracted with 4 × 50 ml of saturated $NaHCO_3$ solution (soln. C). The aqueous layer (soln C). was acidified with HCl and extracted with 2 × 50 ml of ether (soln. D). The ethereal solution D was dried (Na_2SO_4) and stripped of solvent to yield 0.07 g (3.5%) of benzoic acid (34) which was crystallized from hexane and identified by a mixed m.p. (In a parallel experiment, the photolysis solution was chromatographed directly on 100 g of silicic acid to yield benzoic acid with ether–hexane elution.)

The ethereal solution B was dried (Na_2SO_4) and stripped of solvent to leave 1.6 g (80%) of residue. The residue was dissolved in 5% ether–hexane (15 ml) (soln. E) and chilled overnight to yield a further 0.1 g (5%) of polymer.

Solution E was stripped of solvent, dissolved in hot ethanol (soln. F), chilled, and allowed to warm to room temperature to precipitate ethyl 1,2,3-triphenylcyclopropenyl ether (14) (0.090 g) [formed by the alcohol exchange of ethanol with unchanged starting methyl ether (21)].

Solution F was stripped of solvent to leave 1.1 g (55%) of residue. The residue was chromatographed on silicic acid (100 g). It was eluted with hexane and ether–hexane. The first fraction eluted diphenylacetylene (33) identified by i.r. analysis and mixed m.p. comparison with an authentic sample. The next fraction consisted of 0.3 g (15%) of 3-methoxy-1,2-diphenylindene (25) recrystallized from ether to m.p. 96.5—97.5 °C. The n.m.r. and u.v. spectra and the analysis are consistent with the assigned structure (Found: C, 88.7; H, 6.1. Calc. for $C_{22}H_{18}O$: C, 88.89; H, 6.08%).

Hydrolysis of the ether (25) with HI yielded 2,3-diphenylindanone (25a) identified by its i.r. spectrum which is identical to that of an authentic sample.[23]

Following the indene (25), the chromatography yielded 0.15 g (7.5%) of a mixture of the indene (25) and the ethyl ether (14) identified by n.m.r. spectroscopy.

The next fraction eluted consisted of 0.04 g (2%) of 2,3-diphenylindenone (35), m.p. 149—151 °C, which was identified by its identical i.r. spectrum and its undepressed mixed melting point when compared with an authentic sample.[12]

The next fraction eluted consisted of 0.14 g (7%) of viscous oils. The i.r. spectrum of the oils showed bands at 5.8, 6.0, and 6.1 mμ. [In a parallel experiment, a trace of 1,2,3-triphenylpropen-1-one (36) was isolated, m.p. 98.5—100 °C undepressed when mixed with an authentic sample.[21])

Elution of the column with ether yielded another 0.11 g (5.5%) of unidentified viscous oils, the i.r. spectrum of which had no carbonyl absorption between 5.7 and 6.1 μm.

[7/1090 *Received*, 23*rd June*, 1977]

---

[21] R. Breslow and C. Yuan, *J. Amer. Chem. Soc.*, 1958, **80**, 5991.

[22] A. Padwa and D. Eastman, *J. Org. Chem.*, 1969, **34**, 2728.

[23] C. F. Koelsch, *J. Amer. Chem. Soc.*, 1934, **56**, 1338.