stirred for 20 min at -78 °C to maximize the yield of 12. To cross-couple, 3 equiv (12 mmol) of the alkyl halide substrate was injected, neat, into the organocopper solution and the reaction continued with stirring at -78 °C for 1 h. To homocouple 12 to form 17, the temperature was maintained at -78 °C and O_2 was bubbled into the solution for 10 min. The reactions were quenched with dilute HCl and quantitated by GC. The products were identified by comparing their properties of those of authentic samples.

2-Hexanone (13): bp 129 °C (lit.[15] bp 127 °C); 2,4-DNP, mp 105-106 °C (lit.[15] mp 106 °C).

2-Nonanone (14): bp 190-193 °C (lit.[16] bp 192 °C); semicarbazone, mp 119-120 °C (lit.[16] mp 119 °C).

7-Octen-2-one (15): bp 102-104 °C (20 Torr) [lit.[17] bp 95-97 °C (12 Torr)]; lit.[17] IR matches that of the sample.

6-Phenylhexan-2-one (16): bp 105 °C (3 Torr) [lit.[18] bp 133-135 °C (13 Torr)]; lit.[18] IR matches that of the sample; ^{13}C NMR ($CDCl_3$) δ 206, 142, 128, 126, 43, 36, 32, 30, 24.

2,9-Decanedione (17): bp 105-110 °C (5 Torr) [lit.[19] bp 137 °C (12 Torr)]; IR (neat) 3000-2860, 1730, 1650, 1470, 1450, 1420, 1365 cm^{-1}. For comparison, an authentic sample was synthesized by the method of Alper, Januszkiewicz, and Smith.[20]

Formation and Reactions of 6-Cuprio-2-hexanone (19). Commercially available 6-bromo-2-hexanone (Lancaster Synthesis) was fractionally distilled shortly before use (bp 110-112 °C (20 Torr)). The procedure was the same as that given for the formation and reactions of 5-cuprio-2-pentanone with the following changes: a solution of lithium biphenylide was used in place of lithium naphthalenide, 6-bromo-2-hexanone replaced 5-bromo-2-pentanone, and the alkyl halide substrates used for cross-coupling were allyl bromide (Aldrich) to produce 8-nonen-2-one and methyl 4-bromocrotonate (Aldrich) to produce methyl (*E*)-9-oxo-2-decenoate.

8-Nonen-2-one (20): bp 102-104 °C (20 Torr) [lit.[21] 95-97 °C (12 Torr)]; 2,4-DNP, mp 47-49 °C (lit.[21] 50 °C); IR (neat) 3070, 2930, 1720, 1640, 1415, 1365, 910 cm^{-1}. For comparison, an authentic sample was synthesized by the method of Conia and Leyendecker.[21]

Methyl (*E*)-9-oxo-2-decenoate (21): bp 255 °C (20 Torr) [lit.[22] bp 86-91 °C (0.0133 mbar)]; lit.[22] IR and ^{1}H NMR match those of the sample. For comparative purposes, 21 was also synthesized by another method of our own design.[23]

Acknowledgment. We gratefully acknowledge partial support of this work by the Research Foundation of SUNY administered by the Office of Sponsored Programs at the State University College at Buffalo through their Incentive Grant program. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. Special thanks go to professor Edward M. Schulman for providing the necessary ^{13}C NMR data, to the Analytical Services Division of the Department of Chemistry at the State University of New York at Buffalo, Buffalo, NY, for providing the necessary high-resolution mass spectral data, and to professor Reuben D. Rieke for introducing G.W.E. to this field of research.

Registry No. 1, 7308-67-0; 2, 21591-31-1; 3, 7440-50-8; 4, 115591-50-9; 5, 6136-66-9; 6, 134-84-9; 7, 18220-90-1; 8, 53689-84-2; 9, 3016-97-5; 10, 13329-40-3; 11, 3884-71-7; 12, 134388-70-8; 13, 591-78-6; 14, 821-55-6; 15, 3664-60-6; 16, 14171-89-2; 17, 16538-91-3; 19, 134361-43-6; 20, 5009-32-5; 21, 1189-64-6; 6-bromo-2-hexanone, 10226-29-6; 4-bromoacetophenone, 99-90-1.

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(15) Shriner, R. L.; Fuson, R. C. *The Systematic Identification of Organic compounds*; Wiley & Sons: New York, 1948.

(16) Ruzicka, L.; Brugger, W. *Helv. Chim. Acta* **1926**, *9*, 339.

(17) Rouessac, F.; Le Perchec, P.; Conia, J. M. *Bull. Soc. Chim. Fr.* **1967**, *3*, 818.

(18) Cologne, J.; Brunil, J. C. *Compt. Rend.* **1962**, *225*, 161.

(19) Feugeas, C. *Bull. Soc. Chim. Fr.* **1963**, *11*, 2568.

(20) Alper, H.; Januszkiewicz, K.; Smith, D. J. H. *Tetrahedron Lett.* **1985**, *26*, 2263.

(21) Conia, J. M.; Leyendecker, F. *Bull. Soc. Chim. Fr.* **1967**, *3*, 830.

(22) Bestmann, H. J.; Schmidt, M.; Schobert, R. *Synthesis* **1988**, *1*, 49.

(23) Ebert, G. W. *Synth. Commun.*, in press.

Studies Dealing with Cycloaddition and Sigmatropic Reactions of Cyclopropenyl-Substituted Indenes[†]

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The thermal and photochemical reactions of a number of substituted cyclopropenylindenes have been studied. The thermolysis of these systems resulted in a series of 3,3-sigmatropic rearrangements. The product distribution parallels the expected relative order of thermodynamic stabilities of the indenes. The major product obtained upon extended heating corresponds to the isomer in which the double bonds are in conjugation with the phenyl groups on both the indene and cyclopropene rings. Direct irradiation of 1-methyl-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-3-phenylindene afforded a mixture of unsymmetrical cyclopropenes together with a cyclopropa[*cd*]pentalene. The formation of the products can be rationalized in terms of two competing pathways. One path involves σ-bond cleavage to produce a diradical pair which undergoes recombination to give the rearranged cyclopropene. The alternate pathway proceeds by ring opening of the singlet state of the cyclopropene to a vinylcarbene intermediate. Attack of the vinylcarbene carbon on the neighboring double bond produces the cyclopropa[*cd*]pentalene ring skeleton. The sensitized photolysis was found to give intramolecular [2 + 2]-cycloadducts. The observed regiospecificity of the reaction is understandable in terms of formation of the most stable diradical intermediate.

Since its discovery by Cope in the early 1940s,[1] the Cope rearrangement has become one of the most thoroughly investigated chemical reactions.[2-13] Despite all of this study, the mechanism of the 3,3-sigmatropic shift of 1,5-hexadienes still remains clouded.[14-19] At issue is whether

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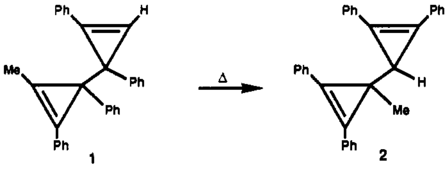
[†] Dedicated to my colleague David J. Goldsmith on the occasion of his 60th birthday.

(1) Cope, A. C.; Hardy, E. M. *J. Am. Chem. Soc.* **1940**, *62*, 441. Cope, A. C.; Hofmann, C. M.; Hardy, E. M. *Ibid.* **1941**, *63*, 1852. Cope, A. C.; Levy, H. *Ibid.* **1944**, *66*, 1684.

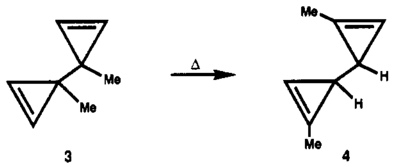
0022-3263/91/1956-4747$02.50/0

it is a concerted process proceeding via a single transition state or whether a cyclohexane-1,4-diyl is involved as an intermediate.[14-16] At the current time the mainstream view is that the Cope reaction of hexa-1,5-diene proceeds via a single transition state.[20,21] Substituents at the various positions of the diene, however, can alter the geometry of the transition state. For example, the presence of radical stabilizing groups on C_3 and C_4 as well as on C_2 and C_5 of the diene system accelerates the rate of the 3,3-shift.[13,22] In the former case the rate response suggests that the transition state resembles more two allyl radicals while in the latter case it resembles more cyclohexane-1,4-diyl. Indeed, these two extremes represent, to a first approximation, the range of transition-state structures available to the 3,3-sigmatropic shift.[22]

Since there are very few reports of Cope rearrangements involving cyclopropene moieties,[23] we decided to investigate this sigmatropic reaction in greater detail. The first example of a 3,3-shift involving a cyclopropene ring was described in 1975 by Weiss and Kölbl.[24] These authors postulated that the Cope rearrangement of bicyclopropenyl 1 to 2 was a two-step process proceeding through an *anti*-1,4-tricyclohexylene diradical. This pathway was claimed to be favorable on the basis of an estimate by the authors that the cyclohexylene diradical has 25 kcal mol^{-1} less strain energy than the pericyclic transition state. The Cope rearrangement of 3,3′-dimethyl-3,3′-bicyclopropenyl (3) to 4 was also investigated by two other research groups.[25,26]



1 2

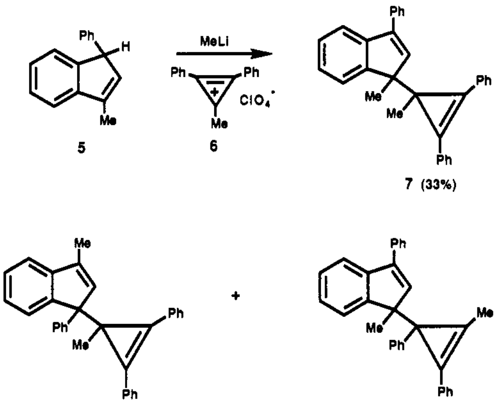


3 4

In this paper, we report the results of our studies dealing with the 3,3-sigmatropic rearrangement of several indenyl-substituted cyclopropenes. Also, in view of our interest in the photochemistry of cyclopropenes containing π-unsaturation,[27] we have examined the excited-state behavior of these indenyl-substituted cyclopropenes. Our results indicate that this system can react via several different pathways depending on the mode of energy input.

Results and Discussion

The several new indenyl-substituted cyclopropenes employed in this study were synthesized by treating 3-methyl-1-phenylindene (5)[28] with methyllithium and quenching the resulting anion with 1-methyl-2,3-diphenylcyclopropenylium perchlorate (6).[29,30] The mixture of cyclopropenes (7–9) obtained was readily separated by silica gel chromatography. The unsymmetrically substituted cyclopropene 9 consisted of a 1:1 mixture of diastereomers (9a and 9b), which could be obtained in pure form by fractional crystallization.



5 6 7 (33%)

8 (24%) 9a and 9b (33%)

Thermolysis experiments were carried out in thick wall test tubes using carbon tetrachloride as the solvent. Since trace amounts of acid are known to induce ring-opening reactions of cyclopropenes,[31] a few drops of pyridine-d_5 was added to each tube. The tubes were degassed and placed in a constant temperature bath heated at 70 ± 0.5 °C. The composition of the reaction mixture was determined at appropriate times by NMR analysis. After 2.5 h, the thermolysis of indene 8 resulted in the formation of 9b (42%) together with lesser quantities of 7 (5%) and 9a

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[2] Rhoads, S. J. In *Molecular Rearrangements*; de Mayo, P., Ed.; Interscience, New York, 1963; Vol. I. Rhoads, S. J.; Rawlins, R. N. *Org. React.* **1975**, *22*, 1.

[3] Gajewski, J. J. *Hydrocarbon Thermal Isomerization*; Academic: New York; 1978, pp 163–176.

[4] Wehrli, R.; Hansen, H. J.; Schmid, H. *Chimia* **1976**, *30*, 416.

[5] Overman, L. E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 579.

[6] Lutz, R. P. *Chem. Rev.* **1984**, *84*, 205.

[7] Doering, W. von E; Roth, W. R. *Tetrahedron* **1962**, *18*, 67.

[8] Hill, R. K.; Gilman, N. W. *J. Chem. Soc., Chem. Commun.* **1967**, 619.

[9] Goldstein, M. J.; Benzon, M. S. *J. Am. Chem. Soc.* **1972**, *94*, 5119, 7147.

[10] Hammond, G. S.; DeBoer, C. D. *J. Am. Chem. Soc.* **1964**, *86*, 899.

[11] Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 183.

[12] Berson, J. A.; Dervan, P. B. *J. Am. Chem. Soc.* **1972**, *94*, 7597. Berson, J. A.; Dervan, P. B.; Jenkins, J. A. *Ibid.* **1972**, *94*, 7598.

[13] Doering, W. von E.; Franck-Neumann, M.; Hasselmann, D.; Kaye, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 3833.

[14] Doering, W. von E.; Toscano, V. G.; Beasley, G. H. *Tetrahedron* **1971**, *27*, 5299.

[15] Dewar, M. J. S.; Wade, L. E. *J. Am. Chem. Soc.* **1973**, *95*, 290; **1977**, *99*, 4417.

[16] Dewar, M. J. S.; Ford, G. P.; McKee, M. L.; Rzepa, H. S.; Wade, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 5069.

[17] Grob, C. A.; Link, H.; Schiess, P. *Helv. Chim. Acta* **1963**, *46*, 483.

[18] Kormonicki, A.; McIver, J. W. *J. Am. Chem. Soc.* **1976**, *98*, 4553.

[19] McIver, J. W. *Acc. Chem. Res.* **1974**, *7*, 72.

[20] Marvell, E. N.; Li, T. H. C. *J. Am. Chem. Soc.* **1978**, *100*, 883.

[21] Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc.* **1978**, *100*, 6268.

[22] Wehrli, R.; Schmid, H.; Bellus, D. E.; Hansen, H. J. *Helv. Chim. Acta* **1977**, *60*, 1325; *Chimia* **1976**, *30*, 416.

[23] For an earlier report, see: Padwa, A.; Blacklock, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 2797.

[24] Weiss, R. Kolbl, H. *J. Am. Chem. Soc.* **1975**, *97*, 3222, 3224.

[25] de Wolf, W. H.; Landheer, I. J.; Bickelhaupt, F. *Tetrahedron Lett.* **1975**, 179, 349; **1974**, 2813.

[26] Davis, J. H.; Shea, K. J.; Bergman, R. G. *Angew. Chem.* **1976**, 254; *J. Am. Chem. Soc.* **1977**, *99*, 1499.

[27] For some leading references, see: Padwa, A.; Krumpe, K.; Terry, L. W.; Wannamaker, M. W. *J. Org. Chem.* **1989**, *54*, 1635.

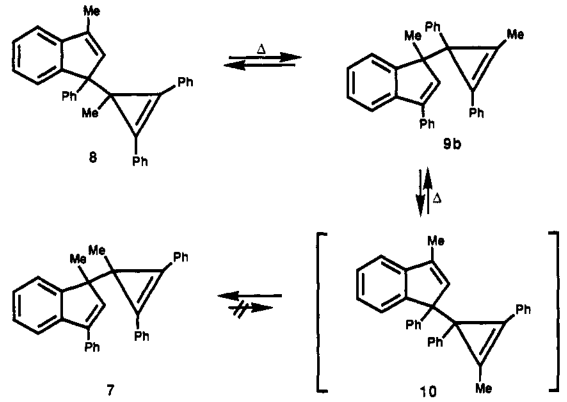
[28] Sato, T.; Watanabe, S. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 3017.

[29] Breslow, R.; Hover, H.; Chang, H. W. *J. Am. Chem. Soc.* **1962**, *84*, 3168.

[30] Padwa, A.; Blacklock, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2345.

[31] Greenberg, A.; Liebman, J. F. In *Strained Organic Molecules*; Academic Press: New York, 1978.

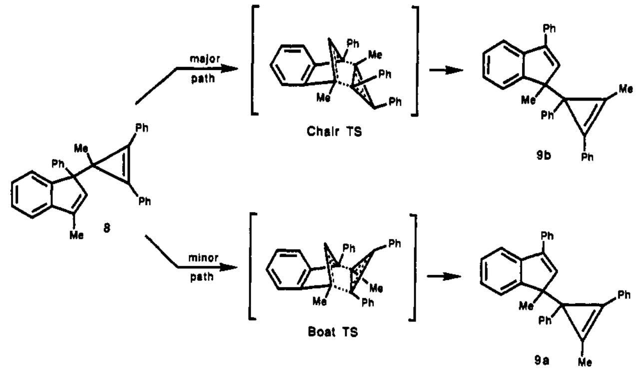
(5%). Thus, the major thermal pathway corresponds to a 3,3-sigmatropic rearrangement.



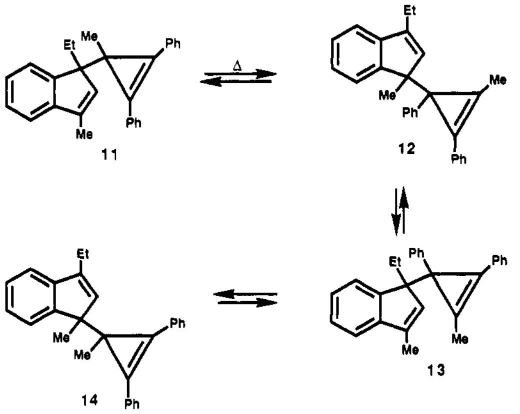
Heating a sample of **9b** at 70 °C (52% conversion) gave rise to a mixture of **8** (30%) as well as indene **7** (19%) as the two major products, together with a small amount of **9a** (3%). Continued heating of the mixture ultimately afforded indene **7** in 95% yield. A similar result was encountered upon thermolysis of the other diastereomer **9a**. Extended heating of **9a** produced indene **7** in 86% isolated yield. A short-term thermolysis of **9a**, however, afforded indenes **7**, **8**, and **9b** in 3:2:1 ratio. We believe that the other unsymmetrically substituted indene **10** is involved in the interconversion of **9a** (or **9b**) into **7**. Unfortunately, all of our attempts to detect **10** in the crude reaction mixture failed. The energetic advantage of having both double bonds in conjugation with the phenyl groups provides a significant driving force for the rapid conversion of **10** into **7**. Also, the greater stability achieved by placing the double bonds in conjugation with the phenyl groups on both the indene and cyclopropene rings nicely rationalizes why indene **7** is formed as the exclusive product upon extended heating.

Transition-state geometries for the thermal Cope rearrangement can generally be classified as either of two basic types: four-center, chairlike or six-center, boatlike.[2] The four-center geometry has the lower energy from the point of view of the unsubstituted hexa-1,5-diene carbon skeleton.[7] The six-center is nevertheless energetically accessible when required. Several independent theoretical evaluations of the relative energies of the four and six-center transition states coincide with the experimental order.[32-35] Given that the preference for the four-center transition state appears to be a moderate one, it is reasonable to expect that four- and six-center transition states for a particular rearranging molecule may have steric and electronic factors energetically balanced in such a way that both modes of rearrangement are in effect. The Cope rearrangement of cyclopropenyl indene **8** indeed behaves this way. Heating a sample of **8** produced a greater quantity of **9b** than **9a** (8:1) which is consistent with the chairlike nature of the Cope rearrangement. The minor isomer **9a** is formed via the higher energy boat transition state.

An additional point worth noting is the partial thermal interconversion of diastereomers **9a** and **9b**. This interchange implies that diastereomers **9a** and **9b** are in thermal equilibrium with indene **8**. Further reaction of **8** via a retro 3,3-sigmatropic shift which proceeds by both a chair- and boatlike orientation would account for the exchange. The facility of the sigmatropic process allows us to make some assumptions about the role of phenyl conjugation as a stabilizing factor in the interconversion of these molecules. Comparison of the structures of the various substituted cyclopropenylindenes indicates that **8** has a set of phenyl groups in conjugation with the cyclopropene π-bond. With diastereomers **9a** and **9b**, the indenyl π-bond is more extensively conjugated. Although the energy difference between the two molecules is small (i.e., **8**:**9b** = 1.6/1.0 from **9a**), phenyl conjugation of the indenyl double bond is preferred and apparently controls the distribution of indenes. Even though cyclopropene **7** is the thermodynamically most favored product, its rate of formation from **9b** is slow by comparison to the production of **8**. Most likely, this is a reflection of the fact that **7** is produced indirectly from **9b** by two consecutive 3,3-shifts rather than by any direct pathway (i.e., cleavage–recombination).



Substituent effects have historically played an important role in the elucidation of reaction mechanisms. The difficulty of this approach with the Cope rearrangement is that substituents may significantly alter the reaction pathway.[36] Nevertheless, we felt that replacement of the phenyl substituent on the indene ring with an ethyl group would diminish the stability gained by having the double bond in conjugation with the aromatic ring and might therefore influence the thermal rearrangement. With this in mind, we subjected cyclopropenyl-substituted indenes **11**–**14** to thermolysis. The mixture of products obtained from each isomer after 50% conversion were dissimilar in their distributions. This would tend to suggest that the rearrangement of this system does not proceed via a cleavage–recombination mechanism. A series of 3,3-sigmatropic shifts would most simply account for the results obtained.



The product distribution with these systems parallels the expected relative order of thermodynamic stabilities

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(32) Woodward, R. B.; Hoffmann, R. In *The Conservation of Orbital Symmetry*; Academic Press: New York, 1970.

(33) Simonetta, M.; Favini, G.; Mariani, C.; Gramaccioni, J. *J. Am. Chem. Soc.* **1968**, *90*, 1280.

(34) Fukui, K.; Fujimoto, H. *Tetrahedron Lett.* **1966**, 251.

(35) Brown, A.; Dewar, M. J. S.; Schoeller, W. *J. Am. Chem. Soc.* **1970**, *92*, 5516.

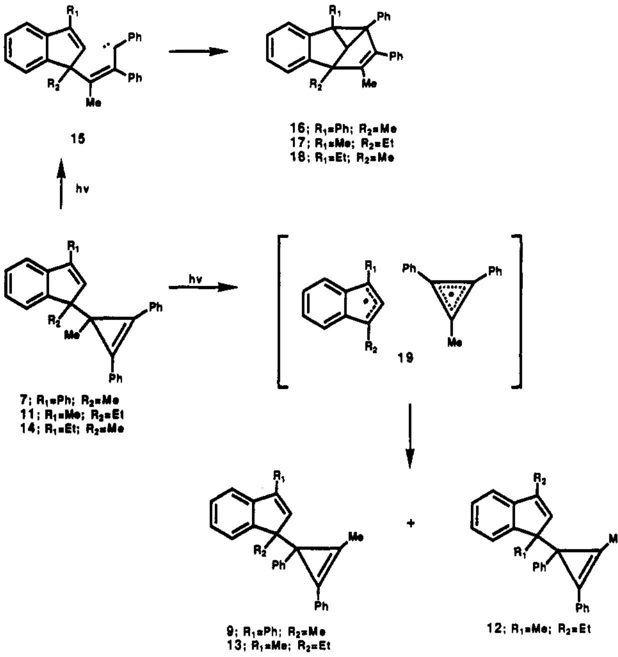
(36) Gajewski, J. J. *Acc. Chem. Res.* **1980**, *13*, 142.

of the cyclopropenyl-substituted indenes. Each compound has available to it two possible conformations for the transition state, namely a chair- or a boatlike orientation. We assume that the indene derived from the boatlike transition state will be formed in lesser amounts than that derived from the chairlike conformation. This expectation is predicated on the assumption that there are no stereoelectronic effects destabilizing the chair confirmation in comparison to the boat conformation.

It should be noted that the thermolysis of indene **13** afforded a mixture of **12a**/**12b** (26%) together with indenes **11** (13%) and **14** (46%). More than a single 3,3-sigmatropic shift would be required to produce the mixture of diastereomers **12a** and **12b** from **13**. Also, the fact that **13** affords **14** as the major product provides good support for the involvement of the related phenyl analogue (i.e. **10**) in the thermal rearrangement of **9b** to **7**. The experimental results obtained here are most consistent with a pathway where the bond-making and bond-breaking steps are occurring in concert.

The photochemistry of cyclopropene derivatives has attracted considerable interest mainly because of the high strain energy associated with the unsaturated three-membered ring.[37] The relief of ring strain combined with resonance stabilization of the corresponding ring-opened species accounts for the relatively facile ring-opening reaction of this system.[31] The excited behavior of this highly strained ring system has been shown to be remarkably dependent on the multiplicity of the excited state involved.[38,39] Singlet states react by σ-bond cleavage to give products which are explicable in terms of the chemistry of vinyl carbenes[40,41] while triplet states, generated by sensitization techniques, give high yield of cyclopropene dimers[42–46] or [2 + 2]-cycloadducts.[47] During the course of our studies dealing with the thermal Cope rearrangement of the above cyclopropenes, it occurred to us that these compounds might also undergo some interesting photochemistry. Toward this end, we examined the direct irradiation of indene **7**. Photolysis of **7** in benzene for 1 h afforded a 1:1 mixture of cyclopropenes **9a** and **9b** (50%) and cyclopropa[*cd*]pentalene **16** (39%). A related reaction was also encountered on photolysis of cyclopropenes **11** and **14**. The direct irradiation of **11** and **14** afforded a mixture of unsymmetrical cyclopropenes **12** and **13** together with the benzosemilbullvalene derivatives **17** and **18**. The most reasonable explanation to account for the formation of benzosemibullvalenes **16–18** involves ring opening of the electronically excited singlet state of the cyclopropene to a vinylcarbene intermediate (**15**). Attack of the vinylcarbene carbon on the neighboring double bond produces the cyclopropa[*cd*]pentalene ring skeleton. A similar photochemical rearrangement of related allyl-substituted cylcopropenes has been reported in the literature and provides good chemical analogy for this reaction.[47,48]

We propose a mechanism analogous to that accepted for the type I reaction of ketones[50] to account for the formation of the rearranged cyclopropenes from the irradiation of indenes **7**, **11**, and **14**. The exclusive formation of the unsymmetrical cyclopropenes can nicely be accommodated by a disassociation–reassociation path. Breslow and coworkers had previously shown that alkyl groups stabilize cyclopropenyl cations more than phenyl groups.[29] This reversal of substituent effects was rationalized by assuming that the aromatic cyclopropenyl cation would not accept more electrons into its π-system as required for assistance by a phenyl group. The cation can be stabilized by an inductive effect in which electron shifts occur within the σ-bond. Such an effect is presumably responsible for the fact that nucleophilic attack on a diphenylalkyl-substituted cyclopropenyl cation occurs at the alkylated carbon atom.[50] Phenyl groups, on the other hand, will stabilize a radical located on a cyclopropene ring while alkyl groups will destabilize the radical center.[51] Thus, the formation of cyclopropenes **9**, **12**, and **13** from the irradiation of **7**, **11**, and **14** is to be expected since the transition state of these systems prefers to localize the odd electron on the phenylated carbon.



15

16; R_1=Ph; R_2=Me
17; R_1=Me; R_2=Et
18; R_1=Et; R_2=Me

7; R_1=Ph; R_2=Me
11; R_1=Me; R_2=Et
14; R_1=Et; R_2=Me

19

9; R_1=Ph; R_2=Me
13; R_1=Me; R_2=Et

12; R_1=Me; R_2=Et

It should be noted that the same mixture of diastereomers (**9a**/**9b**) was also obtained from the photolysis of cyclopropene **8** providing additional support for the diradical pair mechanism. In this case, cleavage of the σ-bond to generate the diradical pair **19** proceeds at a faster rate than ring cleavage to the vinylcarbene. Possible cage reactions of the initially formed radical pair **19** include recombination to give ground-state cyclopropene and diffusion to give separated free radicals. Noncage radical reactions should include recombination or hydrogen abstraction from an appropriate hydrogen atom donor.[52,53] No effect on the quantum efficiency (Φ = 0.1) of cyclopropene **9a**/**9b** was noted when the irradiation was carried out in the presence of 0.03 M 1-dodecanethiol. This would

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(37) Padwa, A. *Org. Photochem.* **1979**, *4*, 261.

(38) DeBoer, C. D.; Wadsworth, D. H.; Perkins, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 861.

(39) Pincock, J. A.; Moutsokapas, L. *Can. J. Chem.* **1977**, *55*, 979.

(40) Arnold, D. R.; Pincock, J. A.; Morchat, R. *J. Am. Chem. Soc.* **1973**, *95*, 7536.

(41) Padwa, A.; Blacklock, T. J.; Loza, R.; Poliniaszek, R. *J. Org. Chem.* **1980**, *45*, 2181.

(42) DeBoer, C. D.; Breslow, R. *Tetrahedron Lett.* **1967**, 1033.

(43) Stechl, H. H. *Chem. Ber.* **1964**, *97*, 2681.

(44) Obata, N.; Moritani, I. *Tetrahedron Lett.* **1966**, 1503.

(45) Arnold, D. R.; Humphreys, R. W.; Leigh, W. J.; Palmer, G. E. *J. Am. Chem. Soc.* **1976**, *98*, 6225.

(46) Pincock, J. A.; Boyd, R. J. *Can. J. Chem.* **1977**, *558*, 2482.

(47) Padwa, A.; Blacklock, T. J.; Cordova, D. M.; Loza, R. *J. Am. Chem. Soc.* **1981**, *103*, 7202.

(48) Padwa, A.; Blacklock, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 3390.

(49) Padwa, A.; Blacklock, T. J.; Cordova, D. M.; Loza, R. *J. Am. Chem. Soc.* **1980**, *102*, 5648.

(50) Johnson, R. W.; Widlanski, T.; Breslow, R. *Tetrahedron Lett.* **1976**, 4685.

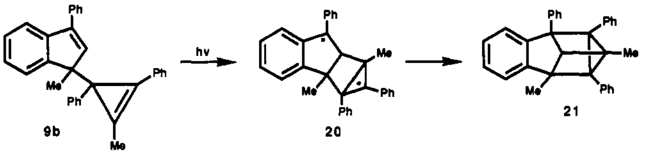
(51) Wasielewski, M. R.; Breslow, R. *J. Am. Chem. Soc.* **1976**, *98*, 4222.

(52) Yang, N. C.; Chen, R. H. K. *J. Am. Chem. Soc.* **1971**, *93*, 530.

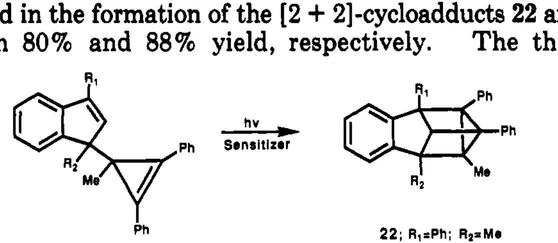
(53) Barltrop, J. A.; Coyle, J. D. *J. Chem. Soc., Chem. Commun.* **1969**, 1081.

tend to suggest that noncage recombination of the cyclopropenyl–indenyl radical pair from cyclopropenes **7** and **8** is not very important.

Since the photochemical α-cleavage process is known to occur with both the cyclopropenyl[49] and indenyl system,[54] it is not clear as to where the excitation energy is localized with the above systems. We were surprised to find that the extended irradiation of cyclopropene **9b** afforded a single product in 72% yield whose structure is assigned as cycloadduct **21** on the basis of its spectral properties. The formation of **21** is the consequence of an intramolecular [2 + 2]-cycloaddition probably involving diradical intermediate **20**. Photocycloaddition across the double bond of cyclopropenes generally proceed smoothly from the triplet state[37] since this reaction reduces ring strain by 26 kcal/mol.[55] Since photocycloaddition of the singlet excited state of an aryl-substituted cyclopropene is extremely rare, we assume that the indenyl π-bond represents the electronically excited chromophore. Initial bond formation between the C_2 carbon atom of the indene ring and the cyclopropene carbon bearing the methyl substituent produces the more stable diradical intermediate **20**. Coupling of the radical centers affords the observed product. Cycloadduct **21** was also formed form the sensitized photolysis of cyclopropene **9b**. In contrast to the direct photolysis, the sensitized irradiation of **7** and **8** resulted in the formation of the [2 + 2]-cycloadducts **22** and **23** in 80% and 88% yield, respectively. The thioxanthenone sensitized irradiation of indenes **11** and **14** also afforded the intramolecular [2 + 2]-cycloadducts **24** and **25** in high yield. Triplet states of 1,2-diphenyl-substituted cyclopropenes possess a large barrier (13 kcal/mol) for ring opening to a vinylcarbene.[46] This would account for the difference in the photochemical behavior of the singlet and triplet excited states. It should also be noted that with the unsymmetrically substituted cyclopropene system **13**, only cycloadduct **26** was formed in 93% yield. No signs of the other regioisomer (i.e. **27**) could be found in the crude reaction mixture. There is clearly a distinct preference for that product arising from bonding between the C_2-indenyl carbon and the cyclopropene bearing the methyl group. This is undoubtedly related to the fact that π–π bridging will give the most stable biradical and thus lead to the preferential formation of cycloadduct **26**.

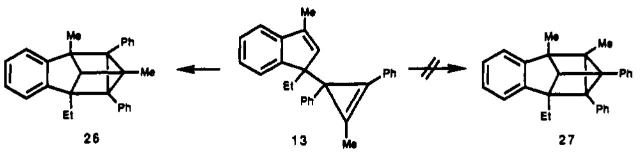


9b 20 21



7; R_1=Ph; R_2=Me
8; R_1=Me; R_2=Ph
11; R_1=Me; R_2=Et
14; R_1=Et; R_2=Me

22; R_1=Ph; R_2=Me
23; R_1=Me; R_2=Ph
24; R_1=Me; R_2=Et
25; R_1=Et; R_2=Me



26 13 27

In conclusion, the photochemical and ground-state behavior of indenyl-substituted cyclopropenes is especially rich in the varied types of reactions encountered. The subtle variation of behavior as a function of the nature of the substituent group attached to the π-bond continues to provide mechanistic challenge. Further studies on the thermal and photobehavior of unsaturated cyclopropenes are in progress and will be reported in due course.

Experimental Section

Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70 eV. Unless otherwise noted, all reactions were performed in oven-dried glassware under extra dry N_2. Flash silica gel chromatography was used to separate and purify the crude reaction mixtures.

Reaction of 3-Methyl-1-phenylindene (5) with Methyllithium and 1-Methyl-2,3-diphenylcyclopropenylium Perchlorate (6). A solution containing 12 mL of a 1.8 M CH_3Li–LiBr complex in ether was added under N_2 to a solution containing 4.44 g of 3-methyl-1-phenylindene (**5**) and 2.55 g of TMEDA in 50 mL of THF at −78 °C. The red solution was allowed to warm to rt with stirring over 3 h. This solution was added to 6.59 g of perchlorate **6** in 150 mL of THF at −78 °C. The mixture was stirred at rt for 9 h and was then quenched with water. The solvent was removed under reduced pressure, and the residue was extracted with ether, washed with water and a saturated salt solution, and dried over $MgSO_4$. Removal of the solvent under reduced pressure left a crude oil, which was purified by silica gel chromatography using a 6% benzene–hexane mixture as the eluent. The first component isolated from the column contained 2.91 g (33%) of a white solid whose structure was assigned as **1-methyl-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-3-phenylindene (7)** on the basis of the following data: mp 123–124 °C; NMR ($CDCl_3$, 100 MHz) δ 1.22 (s, 6 H), 6.57 (s, 1 H), and 7.1–7.7 (m, 19 H); IR (KBr) 1805, 1590, 1435, 1380, 1070, 750, 725, and 685 cm^{-1}; uv (cyclohexane) 339 nm (ϵ = 15 700), 324 (ϵ = 22 300), 300 (ϵ = 16 400), 292 (ϵ = 14 700), 267 (ϵ = 13 400) and 226 (ϵ = 41 600); m/e 410 (M^+), 395, 380, 204 (base), 191 and 101. Anal. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.57; H, 6.40.

The second component isolated from the column contained 2.11 g (24%) of a solid whose structure was assigned as **1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-3-methyl-1-phenylindene (8)** on the basis of the following data: mp 118–119 °C; NMR ($CDCl_3$, 100 MHz) δ 1.52 (s, 3 H), 1.96 (s, 3 H), 6.46 (br s, 1 H), and 7.0–7.6 (m, 19 H); IR (KBr) 1820, 1610, 1500, 1390, 815, 760, and 695 cm^{-1}; UV (cyclohexane) 324 nm (ϵ = 16 700), 298 (ϵ = 11 800), 289 (ϵ = 10 900), 277 (ϵ = 10 600), and 222 (ϵ = 34 400); m/e 410 (M^+), 204 (base), 191 and 101. Anal. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.53; H, 6.43.

The third component isolated from the column contained 2.91 g (33%) of an oily residue whose NMR spectrum revealed it to be a 1:1 diastereomeric mixture of **1-methyl-1-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-3-phenylindenes (9a and 9b).** The diastereomers were obtained pure by fractional crystallization from benzene–hexane. **9a**: mp 139–140 °C; NMR ($CDCl_3$, 100 MHz) δ 1.34 (s, 3 H), 2.40 (s, 3 H), 6.46 (s, 1 H), and 6.9–7.6 (m, 19 H); IR (KBr) 1835, 1600, 1490, 1385, 1075, 840, 760, and 700 cm^{-1}; UV (cyclohexane) 269 (ϵ = 16 800), 262 (ϵ = 16 500), and 225 nm (ϵ = 30 100); m/e 410 (M^+), 204 (base), 191 and 101. Anal. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.51; H, 6.45.

Diastereomer **9b**: mp 133–134 °C; NMR ($CDCl_3$, 90 MHz) δ 1.26 (s, 3 H), 2.40 (s, 3 H), 6.59 (s, 1 H), and 6.7–7.8 (m, 19 H); IR (KBr) 1835, 1600, 1490, 1400, 940, 770, and 700 cm^{-1}; UV (cyclohexane) 265 nm (ϵ = 14 100); m/e 410 (M^+), 204 (base), and 191. Anal. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.48; H, 6.27.

Thermal Rearrangement of 1-(1-Methyl-2,3-diphenyl-2-cyclopropen-1-yl)-3-methyl-1-phenylindene (8). A solution containing 180 mg of indene **8** in 5.0 mL of CCl_4 containing a drop of pyridine-d_5 was degassed and placed in a thick wall test tube. The tube was heated at 70 °C for 2.5 h. The NMR spectrum of the crude reaction mixture consisted of indenes **7** (5%), **9a** (5%),

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(54) Padwa, A.; Goldstein, S.; Pulwer, M. *J. Org. Chem.* **1982**, *47*, 3893.
(55) Wilberg, K. B.; Bartley, W. J. *J. Am. Chem. Soc.* **1960**, *82*, 6375.

and **9b** (42%) and recovered starting material (48%).

In a related manner, a solution containing 160 mg of indene **9b** in 2.0 mL of CCl_4 was heated for 6 h at 70 °C (52% conversion). The crude reaction mixture consisted of indenes 7 (19%), 8 (30%), and **9a** (3%). After heating for an additional 133 h, the solution contained mostly indene 7 (95%) as the major product. A related rearrangement also occurred when 162 mg of indene **9a** was heated in 2.0 mL of CCl_4 at 70 °C. After heating for 1 h (8% conversion), the reaction mixture consisted of indenes 7 (5%) and 8 (3%). After heating for 92 h, the major product (86%) was indene 7. Identification of each indene was made by isolation of pure samples derived from chromatographic workup.

Reaction of 3-Ethyl-1-methylindene with Methyllithium and 1-Methyl-2,3-diphenylcyclopropenylium Perchlorate. To a sample containing 1.04 g of 3-ethyl-1-methylindene in 100 mL of dry THF at −78 °C was added 5.6 mL of a 1.18 M CH_3Li–ether solution and 1.0 mL of TMEDA. The yellow solution was warmed to 0 °C for 2 h, cooled to −78 °C and was then slowly added to a mixture containing 2.0 g of perchlorate **6** in 20 mL of THF at −78 °C. The mixture was allowed to stir at 0 °C for 2 h and then at rt for an additional 12 h before being hydrolyzed by the addition of 10 mL of water. The solvent was removed under reduced pressure, and the residue was extracted with ether. The ether extracts were washed with a saturated NH_4Cl solution and then dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the resulting oil was chromatographed on a silica gel column using hexane as the eluent. The first component isolated contained 180 mg (8%) of a white solid whose structure was assigned as **1-ethyl-3-methyl-1-(1-methyl-2,3-diphenyl-2-cyclopropen-3-yl)indene (11)**: mp 107–108 °C; IR (KBr) 1820, 1600, 1450, 1250, 1075, 825, and 690 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 0.30 (t, 3 H, J = 9 Hz), 1.20 (s, 3 H), 1.70 (q, 2 H, J = 9 Hz), 2.20 (s, 3 H), 6.10 (s, 1 H), and 7.0–7.89 (m, 14 H); UV (95% ethanol) 340 nm (ϵ = 16 380), 325 (ϵ = 22 220), 260 (ϵ = 12 840), 240 (ϵ = 20 580), and 230 nm (ϵ = 23 380); *m/e* 362 (M$^+$), 332, and 205. Anal. Calcd for $C_{28}H_{26}$: C, 92.77; H, 7.23. Found: C, 92.74; H, 7.24.

The second component isolated from the column contained 450 mg (19%) of **3-ethyl-1-methyl-1-(1-methyl-2,3-diphenyl-2-cyclopropen-3-yl)indene (14)**: mp 89–90 °C; IR (KBr) 1800, 1600, 1360, 1075, 915, 795, 690 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 0.99 (s, 3 H), 1.00 (s, 3 H), 1.02 (s, 3 H), 1.10 (t, 3 H, J = 9 Hz), 2.50 (q, 2 H, J = 9 Hz), 6.21 (s, 1 H), and 7.00–7.80 (m, 14 H); uv (95% ethanol) 340 nm (ϵ = 15 300), 325 (ϵ = 22 100), 240 (ϵ = 21 200), and 230 nm (ϵ = 24 300); *m/e* 363 (M$^+$), 299, 205 (base). Anal. Calcd for $C_{28}H_{26}$: C, 92.77; H, 7.23. Found: C, 92.66; H, 7.27.

The third component obtained from the column contained 420 mg (18%) of **1-ethyl-3-methyl-1-(2-methyl-1,3-diphenyl-2-cyclopropen-3-yl)indene (13)**: mp 119–120 °C; IR (KBr) 1850, 1550, 1450, 1390, 875, 820, 775, and 705 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 0.40 (t, 3 H, J = 9 Hz), 1.80 (q, 2 H, J = 9 Hz), 1.90 (s, 3 H), 2.45 (s, 3 H), 6.05 (s, 1 H), and 6.80–7.80 (m, 14 H); UV (95% ethanol) 273 (ϵ = 18 340) and 265 nm (ϵ = 17 850); *m/e* 363 (M$^+$), 348, 334, 319, and 203 (base). Anal. Calcd for $C_{28}H_{28}$: C, 92.77; H, 7.23. Found: C, 92.62; H, 7.29.

The fourth component isolated from the column contained 483 mg (20%) of yellow oil which consisted of a 1:1 mixture of the two diastereomers of **3-ethyl-1-methyl-1-(2-methyl-1,3-diphenyl-2-cyclopropen-3-yl)indene (12a and 12b)**. Repeated chromatography of the oil failed to separate the two diastereomers. Characterization data of the diastereomeric mixture: IR (neat) 1960, 1850, 1695, 1610, 1085, 950, 765, and 700 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 1.05 (s, 6 H), 1.23 (t, 6 H, J = 9 Hz), 2.36 (q, 4 H, J = 9 Hz), 2.40 (s, 6 H), 6.05 (s, 1 H), 6.20 (s, 1 H), and 6.80–7.60 (m, 28 H); UV (95% ethanol) 263 nm (ϵ = 13 160) and 275 nm (ϵ = 11 410). Anal. Calcd for $C_{28}H_{28}$: C, 92.77; H, 7.23. Found: C, 92.56; H, 7.05.

Thermolysis of 1-Ethyl-3-methyl-1-(1-methyl-2,3-diphenyl-2-cyclopropen-3-yl)indene (11). A mixture containing 70 mg of indene **11** in 0.7 mL of a 20% pyridine-d_5–80% benzene-d_6 mixture was degassed and sealed in a 5-mm thick wall test tube. The tube was heated at 150 °C for 60 h at which time the system had completely equilibrated. The ratio of the various indene isomers was established by HPLC using a reverse-phase C^{18}-Corasil column and a 9:1 methanol–water mixture as the eluent at a flow rate of 0.5 mL/min to give indene **11** (27%), indene **14** (50%), indene **13** (8%), and indenes **12a** and **12b** (in 15% combined yield). The same compounds were also obtained from the thermolysis of each cyclopropenyl-substituted indene.

Direct Irradiation of 1-Methyl-1-(1-methyl-2,3-diphenyl-2-cyclopropen-3-yl)-3-phenylindene (7). A solution containing 390 mg of indene 7 in 250 mL of benzene was irradiated through a Pyrex filter sleeve for 1 h. The solvent was removed under reduced pressure, and the resulting brown residue was chromatographed on a silica gel medium-pressure column using hexane as the eluent. The first component eluted contained 143 mg (33%) of a white solid whose structure was assigned as **1,6b-dimethyl-2,2a,2b-triphenyl-2a,2b,6b,6c-tetrahydrobenzo[*a*]cyclopropa[*cd*]pentalene (16)** on the basis of its spectral data: mp 146–147 °C; NMR ($CDCl_3$, 90 MHz) δ 1.12 (s, 3 H), 1.77 (s, 3 H), 3.36 (s, 1 H), 6.6–6.7 (m, 2 H), and 7.0–7.3 (m, 17 H); IR (KBr) 1600, 1485, 1455, 1380, 740, and 690 cm^{-1}; UV (cyclohexane) 257 nm (ϵ = 13 700) and 247 (ϵ = 16 500); *m/e* 410 (M$^+$, base) 396, and 380; ^{13}C NMR ($CDCl_3$, 20 MHz) δ 8.2, 14.2, 48.3, 48.8, 56.1, 67.1, 120.7, 129.4, 136.6, 137.7, 139.2, 148.1, and 148.7. Anal. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.57; H, 6.43.

The second fraction eluted from the column contained 181 mg (50%) of a 1:1 mixture of **9a** and **9b**. In a similar manner indenes 8 and **9b** were subjected to direct irradiation. The major product (85%) consisted of a 1:1 mixture of the diastereomers **9a** and **9b**.

A solution containing 178 mg of indene **9b** in 250 mL of benzene was irradiated through a Corex filter sleeve for 30 min. The solvent was removed under reduced pressure, and the resulting residue was chromatographed on a silica gel medium pressure column using hexane as the eluent. The major fraction contained 135 mg (72%) of a clear oil whose structure was assigned as **2,2a,7,7a-tetrahydro-1,2a-dimethyl-2,7,8-triphenyl-1,7-methano-1*H*-cyclobut[*a*]indene (21)**: NMR ($CDCl_3$, 100 MHz) δ 1.11 (s, 3 H), 1.61 (s, 3 H), 3.19 (s, 1 H), 6.25–6.35 (m, 1 H), 6.40–6.65 (m, 2 H), and 6.7–7.5 (m, 16 H); IR (neat) 1600, 1570, 1465, 1365, 1020, 745, 725, and 690 cm^{-1}; UV (cyclohexane) 273 nm (ϵ = 7900) and 222 (ϵ = 17 700); *m/e* 410 (M$^+$, base), 395, 380, 315, 302, 232, 219, 215, 202, 178, 165, 151, 115, 91, and 77. Anal. Calcd for $C_{32}H_{26}$: C,93.62; H, 6.38. Found: C, 93.47; H, 6.26. The same cycloadduct was obtained in 74% yield from the irradiation of **9b** using thioxanthen-9-one as the triplet sensitizer.

Direct Irradiation of 1-Ethyl-3-methyl-1-(1-methyl-2,3-diphenyl-2-cyclopropen-3-yl)indene (11). A solution containing 250 mg of indene **11** in 300 mL of dry benzene was irradiated under Ar for 30 min using a 550-W Hanovia medium-pressure mercury arc lamp in a Pyrex well. The solvent was removed under reduced pressure, and the resulting oil was passed through a silica gel column using hexane as the eluent. The first component isolated contained 78 mg (31%) of a clear oil whose structure was assigned as **6b-ethyl-2a,2b,6b,6c-tetrahydro-1,2b-dimethyl-2,2a-diphenylbenzo[*a*]cyclopropa[*cd*]pentalene (17)** on the basis of its spectral properties: IR (neat) 1600, 1465, 1380, 1020, 820, and 700 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.05 (m, 6 H), 1.57 (s, 3 H), 2.15 (m, 2 H), 2.97 (s, 1 H), and 6.60–7.45 (m, 14 H); UV (95% ethanol) 251 (ϵ = 16 310) and 224 nm (ϵ = 19 500); *m/e* 362, 347, 334, 333 (base), 319, 318, 315, and 302. Anal. Calcd for $C_{28}H_{26}$: C, 92.77; H, 7.23. Found: C, 92.54; H, 7.33.

The second component contained 78 mg (31%) of **1-ethyl-3-methyl-1-(2-methyl-1,3-diphenyl-2-cyclopropen-3-yl)indene (13)**. The third component contained 92 mg (37%) of an oil, which was identified as a clear oil whose structure was assigned as a 1:1 mixture of **12a** and **12b**.

Direct Irradiation of 3-Ethyl-1-methyl-1-(1-methyl-2,3-diphenyl-2-cyclopropen-3-yl)indene (14). A solution containing 200 mg of indene **14** in 500 mL of benzene was irradiated under Ar for 30 min using a 550-W Hanovia medium-pressure mercury arc lamp in a Pyrex well. The solvent was removed under reduced pressure, and the resulting oil was chromatographed on a silica gel column using hexane as the eluent. The first component isolated contained 59 mg (29%) of **2b-ethyl-2a,2b,6b,6c-tetrahydro-1,6b-dimethyl-2,2a-diphenylbenzo[*a*]cyclopropa[*cd*]pentalene (18)**: mp 113–114 °C; IR (KBr) 1605, 1455, 1075, 745, and 690 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.96 (t, 3 H, J = 9 Hz), 1.03 (s, 3 H), 1.65 (s, 3 H), 2.06 (q, 3 H, J = 9 Hz), 2.96 (s, 1 H), and 6.56–7.36 (m, 14 H); UV (95% ethanol) 250 nm (ϵ = 15 700); *m/e* 362 (M$^+$), 361, 334, 333 (base), and 318. Anal. Calcd for $C_{28}H_{26}$: C, 92.77; H, 7.23. Found: C, 92.69; H, 7.28.

The second component contained 46 mg (23%) of **13**. The third component contained 72 mg (36%) of diastereomers **12a** and **12b**.

Triplet-Sensitized Irradiation of 1-Methyl-1-(1-methyl-2,3-diphenyl-2-cyclopropen-3-yl)-3-phenylindene (7). A solution containing 300 mg of indene **7** and 55 mg of thioxanthen-9-one in 250 mL of benzene was irradiated through a Uranium filter sleeve for 30 min. The solvent was removed under reduced pressure, and the resulting residue was passed through a small silica gel column using hexane as the eluent. The major fraction (80%) was a clear oil whose structure was assigned as **2,2a,7,7a-tetrahydro-2,2a-dimethyl-1,7,8-triphenyl-1,7-methano-1*H*-cyclobut[*a*]indene (22)**: NMR ($CDCl_3$, 90 MHz) δ 1.50 (s, 3 H), 1.70 (s, 3 H), 3.82 (s, 1 H), and 6.5–7.6 (m, 19 H); IR (neat) 1590, 1495, 1370, 1165, 1065, 740, and 705 cm^{-1}; UV (cyclohexane) 273 nm (ϵ = 5500) and 277 (ϵ = 17 400); *m/e* 410 (M^+, base), 396, 395, 380, 319, 318, 317, 303, 302, 232, 217, 216, 215, 205, 151 and 91. Anal. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.38; H, 6.17.

The following compounds were prepared by triplet sensitized irradiations as described above for **7** with the indene, sensitizer, solvent and irradiation times specified. Photoproducts **24–26** were purified by medium-pressure silica gel chromatography with hexane.

2,2a,7,7a-Tetrahydro-2,7-dimethyl-1,2a,8-triphenyl-1,7-methano-1*H*-cyclobut[*a*]indene (23). Indene **8** (240 mg) and thioxanthen-9-one (60 mg) in benzene (250 mL) was irradiated for 15 min to give **23** (88%): NMR ($CDCl_3$, 100 MHz) δ 1.43 (s, 6 H), 3.07 (s, 1 H), 6.40–6.65 (m, 2 H), and 6.9–7.5 (m, 17 H): IR (neat) 1595, 1445, 1060, 780, 715, and 695 cm^{-1}; UV (cyclohexane) 272 nm (ϵ = 3900) and 216 (ϵ = 15 900); *m/e* 410 (M^+, base), 396, 380, 317, 302, 239, 232, 217, 202, 191, 178, 165, 151, 115, 91, and 77. Anal. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.54; H, 6.13.

2-Ethyl-2a,7-dimethyl-1,8-diphenyl-1,7-methano-1*H*-cyclobut[*a*]indene (24). Indene **11** (126 mg) and thioxanthen-9-one (23 mg) in benzene (250 mL) was irradiated for 35 min to give 91 mg (72%) of **24**: IR (neat) 1600, 1520, 1385, 1075, 750, 725, and 695 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.07 (t, 3 H, *J* = 8 Hz), 1.43 (s, 6 H), 1.97 (q, 2 H, *J* = 8 Hz), 3.07 (s, 1 H), and 6.37–7.43 (m, 14 H); UV (95% ethanol) 227 nm (ϵ = 22 700); *m/e* 362 (M^+), 360, 347, 332, and 319. Anal. Calcd for $C_{28}H_{26}$: C, 92.77; H, 7.23. Found: C, 92.61; H, 7.05.

2-Ethyl-7,8-dimethyl-1,2a-diphenyl-1,7-methano-1*H*-cyclobut[*a*]indene (25). Indene **14** (297 mg) and thioxanthen-9-one (53 mg) in benzene (500 mL) was irradiated to give 287 mg (97%) of **25**: IR (KBr) 1610, 1500, 1390, 1075, 755, and 700 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.80 (t, 3 H, *J* = 8.0 MHz), 1.43 (s, 3 H), 1.58 (s, 3 H), 2.30 (sex, 2 H, *J* = 8.0 Hz), 2.97 (s, 1 H), and 6.38–7.47 (m, 14 H); UV (95% ethanol) 272 (ϵ = 6260) and 228 nm (ϵ = 24 870); *m/e* 362 (M^+), 333, 255, 215, 205, 184, and 178. Anal. Calcd for $C_{28}H_{26}$: C, 92.77; H, 7.23. Found: C, 92.50; H, 7.28.

2-Ethyl-1,7-dimethyl-1a,8-diphenyl-1,7-methano-1*H*-cyclobut[*a*]indene (26). Indene **13** (110 mg) and thioxanthen-9-one (20 mg) in benzene (200 mL) was irradiated to give 102 mg (93%) of **26**: IR (KBr) 1600, 1390, 1075, 910, 770, 755, and 705 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.96 (t, 3 H, *J* = 8 Hz), 1.43 (s, 3 H), 1.82 (s, 3 H), 1.83 (q, 2 H, *J* = 8 Hz), 2.62 (s, 1 H), and 6.20–7.46 (m, 14 H); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 9.9, 15.5, 16.9, 23.9, 45.5, 47.7, 48.6, 60.4, 68.1, and 120.1–150.2; UV (95% ethanol) 272 nm (ϵ = 10 950); *m/e* 362 (M^+), 347, 334, and 318. Anal. Calcd for $C_{28}H_{26}$: C, 92.77; H, 7.23. Found: C, 92.72; H, 7.27.

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Synthesis and Reactions of 9,10,11-Triptindantrione and Some Other Functionalized Tribenzo[3.3.3]propellanes (9*H*,10*H*-4b,9a-([1,2]Benzenomethano)indeno[1,2-*a*]indenes)[1]

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A new and efficient route to the tribenzo[3.3.3]propellane **1** (triptindan) and to some interesting derivatives such as 9-triptindanone (**13**) and 9,10,11-triptindantrione (**3**) has been developed. The propellane framework of **13** is accessible from 1,3-indandione in only two steps. Triketone **3**, a versatile substrate with formal C_{3v} molecular symmetry, is obtained from **13** in two further steps. First examples are presented for reactions of **3** leading to more complex benzoannelated centropolyquinanes (centropolyindans).

Mutual annelation of several indan units along the bonds of the five-membered rings leads to centropolyquinanes[2] bearing several benzo nuclei at the molecular periphery. This new group of centropolycyclic aromatic hydrocarbons ("centropolyindans")[3] thus combine the rich three-dimensional structural variety of polyquinanes[4] with the well-known chemical features of arenes. The synthetic access to higher centropolyindans with up to six centrically fused indan units has been reported recently.[5]

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(1) Benzoannelated Centropolyquinanes. 8. Parts 6 and 7: refs 5d and 3, respectively. Presented, in part, at the 200th ACS National Meeting, Washington, DC, August 26–31, 1990; American Chemical Society: Washington, DC, 1990; ORGN 316.

(2) Gund, P.; Gund, T. M. *J. Am. Chem. Soc.* 1981, *103*, 4458.

(3) Kuck, D. In *Quasicrystals, Networks, and Molecules of Fivefold Symmetry*; Hargittai, I., Ed.; VCH Publishers: New York, 1990; Chapter 19.

(4) (a) Paquette, L. A.; Doherty, A. M. *Polyquinane Chemistry, Synthesis and Reactions*; Springer-Verlag: Berlin, 1987. (b) Paquette, L. A. *Top. Curr. Chem.* 1984, *119*, 1–160. (c) Paquette, L. A. *Ibid.* 1979, *79*, 41–165.

(5) (a) Kuck; D. *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 508. (b) Kuck, D.; Bögge, H. *J. Am. Chem. Soc.* 1986, *108*, 8107. (c) Kuck, D.; Schuster, A. *Angew. Chem., Int. Ed. Engl.* 1988, *27*, 1192. (d) Kuck, D.; Schuster, A.; Ohlhorst, B.; Sinnwell, V.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* 1989, *28*, 595.

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