obtaining the 300-MHz NMR and mass spectral measurements.

Registry No. **4** (R_1 = SCH_3; R_2 = PNB; R_3 = H), 71001-38-2; **4** (R_1 = SCH_3; R_2 = 9-AM; R_3 = H), 71001-39-3; **4** (R_1 = $SCH_2CH_2NHCO_2PNB$; R_2 = PNB; R_3 = H), 71001-40-6; **4** (R_1 = $SCH_2CH_2NHCO_2TCE$; R_2 = PNB; R_3 = H), 71001-41-7; **4** (R_1 = Ph; R_2 = PNB; R_3 = $(CH_2)_5$), 71001-42-8; **4** (R_1 = *p*-OMePh; R_2 = PNB; R_3 = $(CH_2)_5$), 71001-43-9; **4** (R_1 = CH_3; R_2 = CH_3; R_3 = $(CH_2)_4$), 1524-17-6; **5** (R_1 = SCH_3; R_2 = PNB), 70388-95-3; **5** (R_1 = SCH_3; R_2 = 9-AM), 71001-44-0; **5** (R_1 = $SCH_2CH_2NHCO_2PNB$; R_2 = PNB), 71001-45-1; **5** (R_1 = $SCH_2CH_2NHCO_2TCE$; R_2 = PNB), 71001-46-2; **5** (R_1 = Ph; R_2 = PNB), 71001-47-3; **5** (R_1 = *p*-OMePh; R_2 = PNB), 71001-48-4; **5** (R_1 = CH_3; R_2 = CH_3), 36441-65-3; *p*-nitrobenzyl cyanoacetate, 71001-49-5; methanethiol, 74-93-1; *N*-(*p*-nitrobenzyloxycarbonyl)cysteamine, 65750-59-6; *N*-(trichloroethoxycarbonyl)cysteamine, 71001-50-8; cyanoacetic acid, 372-09-8; *p*-nitrobenzyl alcohol, 619-73-8; *p*-nitrobenzyl phenylpropiolate, 71001-51-9; *p*-nitrobenzyl *p*-methoxyphenylpropiolate, 71001-52-0; piperidine, 110-89-4; phenylpropiolic acid, 637-44-5; *p*-methoxyphenylacetylene, 768-60-5; *p*-nitrobenzyl chloroformate, 4457-32-3; 9-anthrylmethyl cyanoacetate, 71001-53-1; 9-anthrylmethyl chloride, 24463-19-2; cysteamine hydrochloride, 156-57-0; trichloroethyl chloroformate, 17341-93-4.

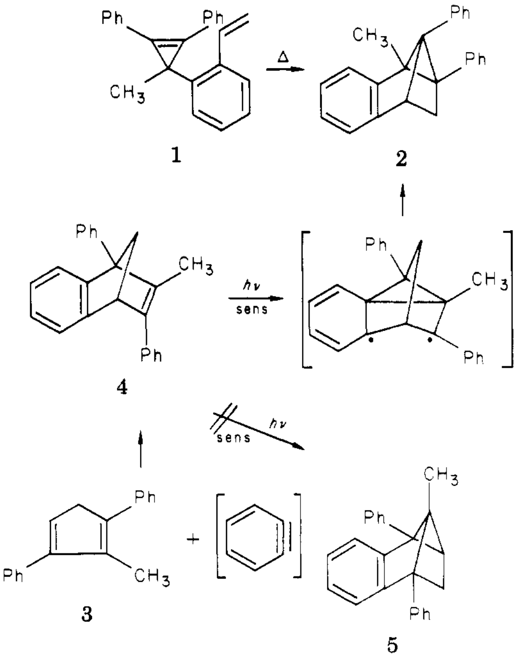
Communications

Synthesis of the Benzotricyclo[3.2.0.0^{2,7}]heptene Ring System via an Intramolecular (2 + 2) Cycloaddition Reaction

Summary: Thermolysis of 3-(*o*-vinylphenyl)-substituted diphenylmethylcyclopropenes results in an intramolecular (2 + 2) cycloaddition reaction and gives rise to benzotricyclo[3.2.0.0^{2,7}]heptenes in excellent yield.

Sir: The thermal (2 + 2) cycloaddition of untwisted ethylenes to form cyclobutanes is a rare phenomenon.[1-6] The constraints imposed upon such reactions by orbital symmetry factors[7] make them of more than usual mechanistic interest. We have previously reported that the thermolysis of 3-allyl-substituted cyclopropenes results in a novel intramolecular (2 + 2) cycloaddition.[8] This reaction is unique in that the other reported examples of thermal olefin cycloadditions either occur in compounds in which the double bond is subjected to severe torsional strain[9-11] or else involve reactants that bear substituents capable of stabilizing diradical or dipolar intermediates.[12-14] In cyclopropene, the torsional angle is close to zero and p–p overlap should not be significantly different from that of a normal olefin. Thus the propensity of the cyclopropene ring to undergo internal cycloaddition is primarily due to relief of angle bending rather than torsional strain. As an extension of our studies dealing with intramolecular cycloaddition reactions of cyclopropene derivatives, we have examined the thermal behavior of a series of 3-(*o*-vinylphenyl)-substituted cyclopropenes. We report here the results of these studies.

Scheme I



Thermolysis of 1,2-diphenyl-3-methyl-3-(*o*-vinylphenyl)cyclopropene (**1**)[15] at 175 °C for 4 h gave a quantitative yield of benzotricycloheptene **2** (Scheme I): NMR ($CDCl_3$, 100 MHz) δ 1.40 (s, 3 H), 1.41 (d, 1 H, J = 9.0 Hz), 2.99 (dd, 1 H, J = 9.0 and 8.0 Hz), 3.69 (d, 1 H, J = 8.0 Hz), 7.42–7.03 (m, 14 H); ^{13}C NMR ($CDCl_3$, ppm) 12.4 (q), 38.1 (t), 42.5 (s), 44.3 (s), 45.9 (d), 68.3 (s), 120–129 (m), 136 (s), 139 (s), 144 (s), and 148 (s). The identity of structure **2** was based on its spectroscopic and analytical properties and was further confirmed by comparison with an independently synthesized sample. The reported sensitized photorearrangement of benzonorbornadienes to benzotricyclo[3.2.0.0^{2,7}]heptenes[16,17] suggested a similar approach for the synthesis of **2**. The preparation of

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(1) Meinwald, J.; Kapecki, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 6236.

(2) Nelson, S. F.; Gillespie, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 6237, 6238.

(3) Wittig, G.; Koenig, G.; Claus, K. *Justus Liebigs Ann. Chem.*, **1955**, *593*, 127.

(4) Mitchell, R. H.; Sondheimer, F. *Tetrahedron Lett.* **1968**, 2872.

(5) Roberts, J. D.; Sharts, C. M. *Org. React.* **1962**, 12, 1.

(6) Doering has recently shown that 2,5-diphenyl-1,5-heptadiene undergoes internal (2 + 2) thermal cycloaddition; see ref 43, Dewar, M. J. S.; Wade, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 4419.

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

(8) Padwa, A.; Blacklock, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 1321. *ibid*, **1979**, *101*, 3390.

(9) Kesse, R.; Krebs, E. D. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 262.

(10) (a) Burns, W.; McKervey, M. A. *J. Chem. Soc. Chem. Commun.* **1974**, 858. (b) Lenoir, D. *Tetrahedron Lett.* **1972**, 4049. (c) Gano, J. E; Eizenberg, L. *J. Am. Chem. Soc.* **1973**, *95*, 972.

(11) (a) Adams, B. L.; Kovacic, P. *J. Am. Chem. Soc.* **1973**, *95*, 8206. (b) Farcasiu, M.; Farcasiu, D.; Conlin, R. T.; Jones, M.; Schleyer, P. R. *J. Am. Chem. Soc.* **1973**, *95*, 8207.

(12) Shea, K. J.; Wise, S. *Tetrahedron Lett.* **1978**, 2283.

(13) Bartlett, P. D. *Science* **1968**, *159*, 833.

(14) Huisgen, R. *Acc.* Chem. *Res.* **1977**, *10*, 117.

(15) Cyclopropenes 1 and 6 were prepared from the reaction of diphenylmethylcyclopropenyl perchlorate with the Grignard reagent derived from *o*-bromostyrene followed by chromatographic separation. Satisfactory spectral and analytical data were obtained for each new compound.

(16) Edman, J. P. *J. Am. Chem. Soc.* **1966**, *88*, 3454. *Ibid.* **1969**, *91*, 7103.

(17) Tufariello, J. J.; Rowe, D. W. *J. Org. Chem.* **1971**, *36*, 2057.

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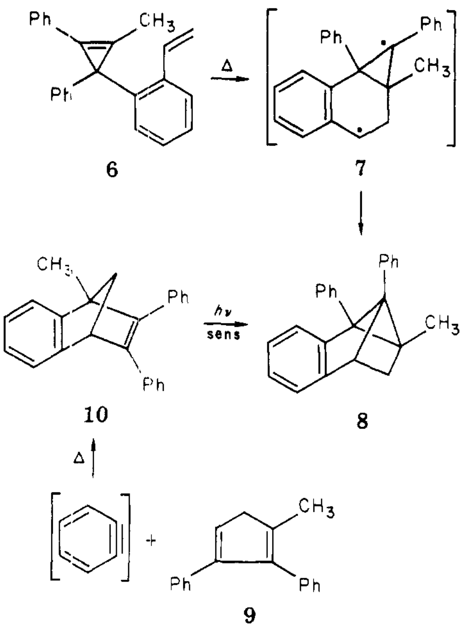
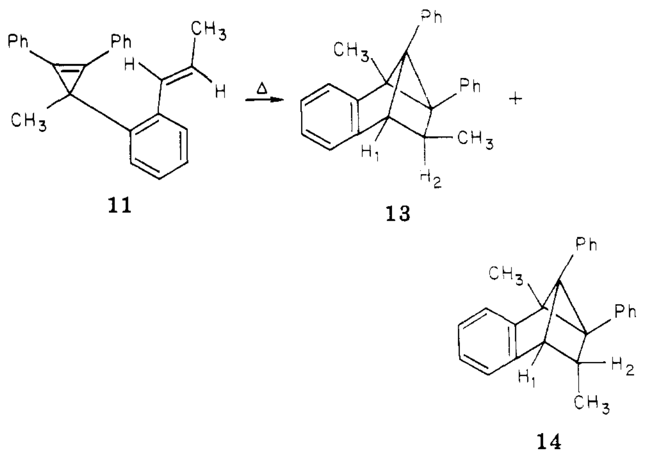
Scheme II



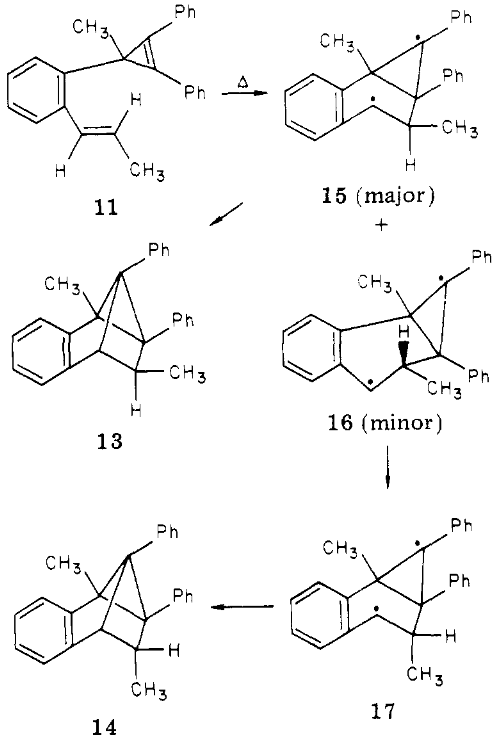
benzonorbornadiene **4** was achieved in high yield by treating 2-methyl-1,3-diphenyl-1,3-cyclopentadiene (**3**)[18] with benzyne. A dilute solution of **4** in benzene was photolyzed in the presence of acetophenone to give **2** as the exclusive photoproduct (98%). No signs of the isomeric benzotricyclic hydrocarbon **5** could be detected in the crude photolysate. The observed regiospecifity of the di-π-methane photorearrangement of **4** is expected on the basis of formation of the most stable diradical intermediate.[19]

The thermal chemistry of the closely related 1,3-diphenyl-2-methyl-3-(*o*-vinylphenyl)cyclopropene (**6**)[15] was also studied in order to probe the regiospecificity of the cycloaddition. Upon heating at 175 °C for 45 min, **6** is converted into a single product in quantitative yield (Scheme II). The structure of the cycloadduct [NMR ($CDCl_3$, 100 MHz) δ 1.41 (d, 1 H, $J = 9.0$ Hz), 1.61 (s, 3 H), 2.76 (dd, 1 H, $J = 9.0$ and 7.6 Hz), 3.78 (d, 1 H, $J = 7.6$ Hz), 7.29–6.63 (m, 14 H)] was established by comparison with an independently synthesized sample obtained from the sensitized photolysis of benzonorbornadiene **10**. The regioselectivity exhibited by cyclopropene **6** can be readily rationalized in terms of the formation of the most stable diradical intermediate (i.e. **7**).

Scheme III



Scheme IV



The question of possible stereochemical preference in the intramolecular (2 + 2) cycloaddition of these systems is of obvious interest, especially since the thermolysis of labeled 3-allyl-substituted cyclopropenes has been shown to occur with complete inversion of stereochemistry about the double bond.[8] The effect of substituents on the stereochemical course of the cycloaddition was probed using (*E*)- (**11**) and (*Z*)-1,2-diphenyl-3-methyl-3-(*o*-1-propenylphenyl)cyclopropene (**12**). These compounds were prepared by treating diphenylmethylcyclopropenyl perchlorate with the Grignard reagents derived from (*E*)- and (*Z*)-1-(*o*-bromophenyl)-1-propene. Heating cyclopropene **11** at 175 °C gave a nearly quantitative yield of two isomeric products in a ratio of 4.6:1 whose structures were assigned as *exo*- (**13**) and *endo*-benzotricycloheptene (**14**) (Scheme III). The stereochemistry of the cycloadducts was easily assigned on the basis of their characteristic 100-MHz NMR spectra [*exo*-**13**: δ 1.32 (s, 3 H), 1.33 (d, 3 H, $J = 6.0$ Hz), 1.63 (q, 1 H, $J = 6.0$ Hz), 3.09 (s, 1 H), 7.01–7.38 (m, 14 H). *endo*-**14**: δ 0.12 (d, 3 H, $J = 6.0$ Hz), 1.32 (s, 3 H), 2.92–3.22 (m, 1 H), 3.80 (d, 1 H, $J = 8.0$ Hz), and 7.05–7.40 (m, 14 H)]. The absence of coupling between H_1 and H_2 with benzotricyclic **13** fixes the C_2-methyl group in the exo position. This is to be expected since molecular models show that the dihedral angle for this set of protons is ~90°. Appropriate control experiments established that no cis–trans isomerization of either the starting materials or the products was operative under the reaction conditions.

The most significant finding here is that the (2 + 2) cycloaddition proceeds with predominant retention (82%) of stereochemistry about the π bond. This result indicates that although stereochemistry is partly lost during the cycloaddition reaction, complete randomization of the label is not occurring. Different stereochemistries in the benzotricycloheptene formed would occur from the two biradical configurations **15** and **16**, as shown in Scheme IV.

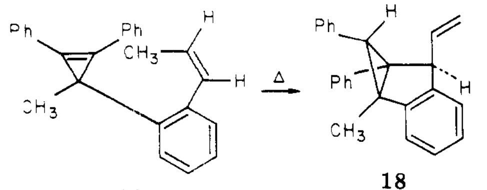
---

[18] Padwa, A.; Blacklock, T. J.; Getman, D.; Hatanaka, N.; Loza, R. *J. Org. Chem.* **1978**, *43*, 1481.

[19] Hixson, S. S.; Marrano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531.

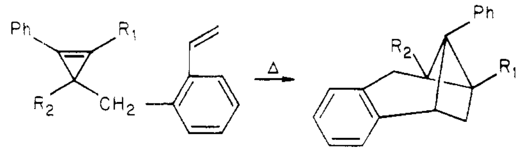
Ring inversion of diradical **16** to **17** followed by radical coupling gives rise to the endo-substituted benzotricycloheptene **14**. The preferential formation of diradical **15** is probably related to the fact that the nonbonded interactions between the methyl and phenyl groups are minimized in the initial bonding step.

In marked contrast to the results obtained with cyclopropene **11**, thermolysis of **12** gave rise to 1-methyl-5,6-diphenyl-4-*endo*-vinyl-2,3-benzobicyclo[3.1.0]hexene (**18**) in quantitative yield. The NMR spectrum of **18** consists of singlets at δ 1.56 (3 H) and 2.02 (1 H), doublets at 4.07 (1 H, J = 7.0 Hz), 4.96 (1 H, dd, J = 16.7 and 1.5 Hz), 5.12 (1 H, dd, J = 10.0 and 1.5 Hz), and 6.03 (1 H, ddd, J = 16.7, 10.0, and 7.0 Hz) and a multiplet between 6.51 and 7.28 (14 H). We suggest that **18** most reasonably arises from **12** by a concerted ene reaction. The geometry necessary for this type of reaction is easily achieved with the Z-substituted cyclopropene **12**. Although bimolecular ene reactions of cyclopropenes are well known,[20] the above case constitutes the first example of an intramolecular version of this reaction.



12 **18**

Finally, it should be noted that the thermolysis of the homologous cyclopropenes **19** and **20** afforded cycloadducts **21** and **22** in high yield.



19, R_1 = Ph; R_2 = CH_3
20, R_1 = CH_3; R_2 = Ph

21, R_1 = Ph; R_2 = CH_3
22, R_1 = CH_3; R_2 = Ph

The results obtained with the above systems may be most simply interpreted on the basis of an unusually easy bond formation between the double bond and the cyclopropene ring to produce a diradical intermediate which collapses to the observed cycloadduct. The driving force for these reactions is undoubtedly associated with the considerable relief of bond angle strain of the cyclopropene ring. The facility with which the cycloadditions occur makes this type of approach particularly attractive for the synthesis of some unusual tricyclic ring compounds.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation.

Registry No. **1**, 70913-08-5; **2**, 70913-09-6; **3**, 62937-87-5; **4**, 70913-10-9; **6**, 70913-11-0; **10**, 70913-12-1; **11**, 70913-13-2; **12**, 70913-14-3; **13**, 70913-15-4; **14**, 70981-12-3; **18**, 70913-16-5; **19**, 70913-17-6; **20**, 70913-18-7; **21**, 70913-19-8; **22**, 70913-20-1; benzyne, 462-80-6; (E)-1-(*o*-bromophenyl)-1-propene, 70968-46-6; (Z)-1-(*o*-bromophenyl)-1-propene, 70913-21-2.

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(20) (a) Breslow, R.; Dowd, P. *J. Am. Chem. Soc.* **1963**, *85*, 2729. (b) Dowd, P.; Gold, A. *Tetrahedron Lett.* **1969**, 85. (c) Weigert, F. J.; Baird, R. L.; Shapley, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 6630.

(21) Direct correspondence to this author at the Department of Chemistry, Emory University, Atlanta, Georgia, 30322.

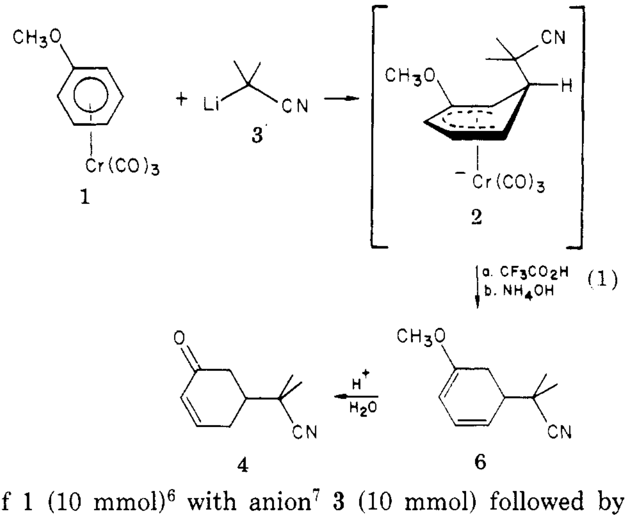
Formation of 3-Substituted Cyclohexenones by Nucleophilic Addition to Anisole-Chromium Complexes

Summary: The addition of cyano-stabilized anions to π-anisolechromium tricarbonyl leads to intermediates which are treated with acid to produce 1-methoxy-1,3-cyclohexadiene derivatives.

Sir: Substituted cyclohexenones are important intermediates in organic synthesis, often prepared by condensation reactions of carbonyl compounds. Substituted aryl ether derivatives lead to cyclohexenones through a two-step Birch reduction/hydrolysis sequence, where the position of the olefinic unit begins in a β,γ-position, and may become conjugated during the hydrolysis.[1] Recently, a three-step procedure of Birch reduction/alkylation/hydrolysis has been developed for conversion of *o*-methoxybenzoic acid derivatives into 2-alkyl-2-cyclohexenones, where the new carbon substituent begins as an electrophile.[2] Here we report a new method, involving addition of carbon nucleophiles to anisole derivatives, with subsequent protonation and hydrolysis to produce 3-substituted 2- and 5-cyclohexenones.

The method is based on two observations which we have reported in preliminary form: that carbon nucleophiles will attack π-anisolechromium tricarbonyl (**1**) selectively at the meta position,[3] and that η^5-cyclohexadienyl complexes of chromium (i.e., simple analogues of **2** lacking the methoxy group) can be protonated and freed from the chromium to give 1-substituted cyclohexa-1,3-dienes.[4,5] We assume that anion addition to the anisole ligand in **1** gives rise to η^5-(6-alkyl-2-methoxycyclohexadienyl)tricarbonylchromium (i.e., **2**), but no attempt has been made to observe these intermediates. Most of our basic work on the method reported here has been carried out with 2-lithio-2-methylpropionitrile (**3**), because it adds efficiently to **1** and is >95% selective for meta substitution.

A prototype process is illustrated in eq 1. Treatment of **1** (10 mmol)[6] with anion[7] **3** (10 mmol) followed by



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(1) Cf., A. J. Birch, *Q. Rev., Chem. Soc.*, **4**, 69 (1950).

(2) For examples and leading references, see: D. F. Taber, *J. Org. Chem.*, **41**, 2849 (1976).

(3) M. F. Semmelhack and G. Clark, *J. Am. Chem. Soc.*, **99**, 1675 (1977).

(4) M. F. Semmelhack, H. T. Hall, Jr., and M. Yoshifuji, *J. Am. Chem. Soc.*, **98**, 6387 (1976).

(5) M. F. Semmelhack, H. T. Hall, Jr., R. Farina, M. Yoshifuji, G. Clark, T. Bargar, K. Hirotsu, and J. Clardy, submitted for publication.

(6) Complex **1** was prepared in 95% yield by heating chromium hexacarbonyl with excess anisole in dioxane at reflux for 40–50 h. For earlier procedures and characterization, see: B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).

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