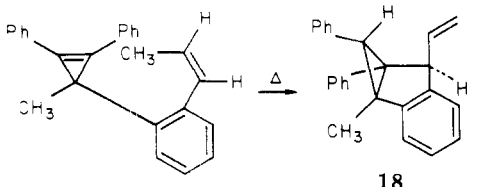
Ring inversion of diradical **16** to **17** followed by radical coupling gives rise to the endo-substituted benzotricycloheptene **14**. The preferential formation of diradical **15** is probably related to the fact that the nonbonded interactions between the methyl and phenyl groups are minimized in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

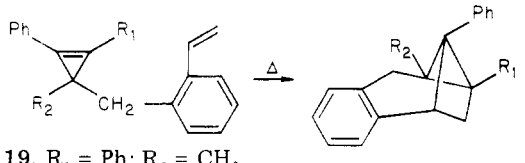
In marked contrast to the results obtained with cyclopropene **11**, thermolysis of **12** gave rise to 1-methyl-5,6-diphenyl-4-*endo*-vinyl-2,3-benzobicyclo[3.1.0]hexene (**18**) in quantitative yield. The NMR spectrum of **18**



12 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.

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.

(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.

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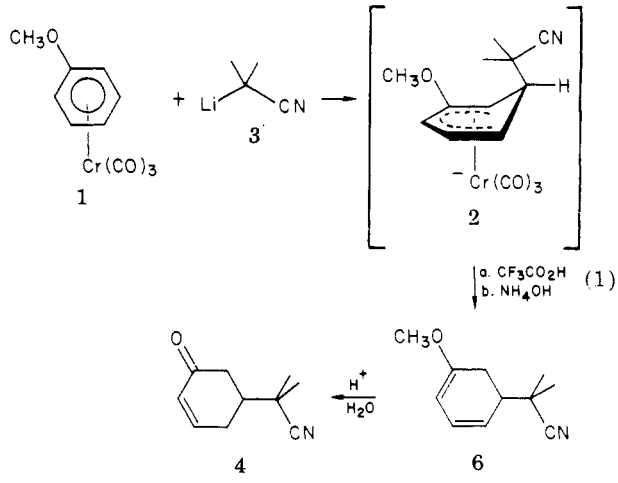
Formation of 3-Substituted Cyclohexenones by Nucleophilic Addition to Anisole-Chromium Complexes

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

(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.

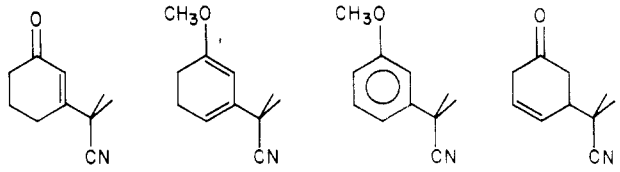
(6) Complex **1** was prepared in 95% yield by heating chromium hexacarbonyl with excess anisole in dioxane at reflux for 40–50 h. For earlier procedures and characterization, see: B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).

0022-3263/79/1944-3275$01.00/0

addition of trifluoroacetic acid (30 mmol, 1 h/−78 °C) produced a solution of unstable chromium complexes. The solution was poured into 50 mL of concentrated aqueous ammonium hydroxide, filtered, and shaken with ether. The ether solution was concentrated in vacuo and the residue was treated with a mixture of THF and 5 N aqueous hydrochloric acid (equal volume) at 100 °C for 20 h. The product was extracted into ether, and from the ether solution was isolated a colorless liquid which solidified after evaporative distillation. Recrystallization from ether gave 5-(2-cyano-2-propyl)-2-cyclohexenone (**4**): mp 54.5–55 °C; 1.13 g; 70% yield.[8]

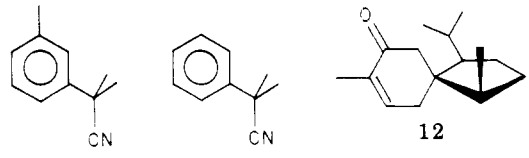
However, the product structure depends upon how long the intermediates are allowed to stir after treatment with trifluoroacetic acid. If the mixture is stirred for 8 h at 25 °C, then added to ammonium hydroxide and processed as before, the product mixture (88%) consists of **4** (11%) and 3-(2-cyano-2-propyl)-2-cyclohexanone (**5**, 77%).[9]

Intermediate 1,3-cyclohexadienes **6** and **7** have been isolated. For example, under the conditions in eq 1 (CF_3CO_2H, −78 °C, 1 h), compound **6** was isolated after the ammonia treatment in 98% yield,[10] uncontaminated with **7**. After the longer reaction period with trifluoroacetic acid (25 °C/7.5 h), the ammonia treatment gave rise to a mixture of **6** and **7** (1:8) in a yield of 99% [after short-path distillation, 90 °C (0.01 torr)].[11] The mixture of **6** and **7** was aromatized by heating with 2,3-dichloro-5,6-dicyanoquinone (benzene, reflux, 1 h) to produce a single product, **8**, in 97% yield [short-path distillation, 80 °C (0.01 torr)].[13] The enol ether **6** was also hydrolyzed under carefully controlled conditions (THF/5% aqueous HCl, 1:1 by volume, 25 °C, 15 h) to give the β,γ-unsaturated ketone **9** in 77% yield.[14]



5 **7** **8** **9**

Alternative isolation procedures after treatment of **2** with trifluoroacetic acid produced different products. For example, after addition of trifluoroacetic acid (5 molar equiv) to a solution of **2** at −78 °C in THF, the mixture was warmed to 25 °C over 1 h and iodine (6 molar equiv of I_2) was added. After 15 h/25 °C, the excess iodine was removed with aqueous sodium sulfite, and the usual ether/aqueous extraction procedure provided a crude product which was purified by short-path distillation to give 3-(2-cyano-2-propyl)phenol (**10**, ca. 50% yield) as the only product.[15] A similar solution of the product(s) from **2** and trifluoroacetic acid (0 °C/0.5 h) was mixed with a solution of ceric ammonium nitrate (0.48 M, 4.2 molar equiv) in 1.1 N aqueous nitric acid and stirred at 25 °C/7 h. The mixture was partitioned between ether and water, and the product, isolated as before, was 2-methyl-2-phenylpropionitrile (**11**), 55% yield.[13]

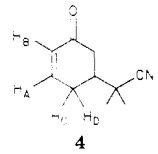


10 **11** **12**

An intramolecular example has been worked out (eq 2) which serves as a model sequence for a new approach to spirocyclic sesquiterpenes such as acorenone B (**12**).[16] Commercially available *m*-methoxycinnamic acid was converted in three conventional steps to 5-(3-methoxyphenyl)valeronitrile (**13**). Reaction of **13** (23 mmol) with chromium hexacarbonyl (70 mmol) in dioxane (40 mL, reflux, 48 h) produced the doubly coordinated complex **14**. The crude product in benzene was exposed to carbon monoxide (600 psi, 20 h, 25 °C) to give crude **15**. Purification by chromatography (Florisil, eluting with CH_2Cl_2) gave **15**: 5.3 g; 70% yield.[17] A solution of **15** (2.0 mmol) in THF was added to a solution of lithium diisopropylamide in THF at −78 °C under argon. After 1 h/−78 °C, trifluoroacetic acid (6 mmol) was added and the mixture was stirred for 1 h/−78 °C, then poured into 50 mL of

(7) The anion **3** was prepared by addition of 2-methylpropionitrile to a solution of lithium diisopropylamide (from *n*-butyllithium and *N,N*-diisopropylamine) in THF at −78 °C. The mixture was allowed stir at −78 °C for 1 h.

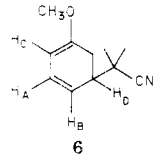
(8) Compound **4** showed: ^{1}H NMR ($CDCl_3$) δ 7.05 (ddd, 1 H, H, $J_{AB} \simeq 10$ Hz, $J_{AC} \simeq 5$ Hz, $J_{AD} \simeq 3$ Hz), 6.10 (dt, 1 H, H_B, $J_{AB} \simeq 10$ Hz, $J_{BC} = J_{BD} \simeq 1$ Hz), 2.0–2.8 (m, 5 H, $-CH_2-$ and >CH–), 1.40 (s, 6 H, CH_3); IR ($CHCl_3$) 2240 (w), 1680 (s) cm^{-1}. Anal. for $C_{10}H_{13}NO$: C, H, N.



4

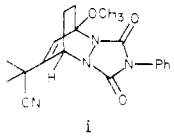
(9) The isomers **4** and **5** were separated by preparative GLC. Compound **5** showed: ^{1}H NMR ($CDCl_3$) δ 6.20 (t, 1 H, vinyl H, J = 2 Hz), 1.8–2.6 (m, 6 H, $-CH_2-$), 1.55 (s, 6 H, CH_3); IR ($CHCl_3$) 2250 (w), 1680 (s), 1025 (m) cm^{-1}. Anal. for $C_{10}H_{13}NO$: C, H, N.

(10) Compound **6** showed: ^{1}H NMR ($CDCl_3$) δ 6.02 (ddd, 1 H, H_a, J_{AD} = 2 Hz, J_{AC} = 6 Hz, J_{AB} = 10 Hz), 5.29 (dd, 1 H, H_b, J_{BD} = 4 Hz, J_{AB} = 10 Hz), 4.90 (d, 1 H, H_c, J_{AC} = 6 Hz), 3.55 (s, 3 H, $-OCH_3$), 2.2–2.7 (m, 3 H, $-CH_2-$, >CH–), 1.34 (s, 6 H, $-CH_3$); mass spectrum *m/e* 177 (parent).



6

(11) Compound **7** was not obtained completely free of **6**. Subtracting signals due to **6** (5% impurity), ^{1}H NMR data for **7** ($CDCl_3$): δ 5.50 (br s, 1 H, vinyl H), 4.95 (br s, 1 H, vinyl H), 3.60 (s, 3 H, $-OCH_3$), 2.20 (m, 4 H, $-CH_2-$), 1.50 (s, 3 H, $-CH_3$). Reaction with *N*-phenyl-1,2,4-triazoline-3,5-dione[12] gave a Diels–Alder adduct tentatively assigned structure **i** based on the integrated intensity of ^{1}H NMR signals at δ 3.75 (s, 3 H, $-OCH_3$), 5.02 (br s, 1 H, bridgehead H), 6.42 (d, 1 H, J = 2 Hz, vinyl H, w coupling).



i

(12) J. C. Stickler and W. H. Pirkle, *J. Org. Chem.*, **31**, 3444 (1966).

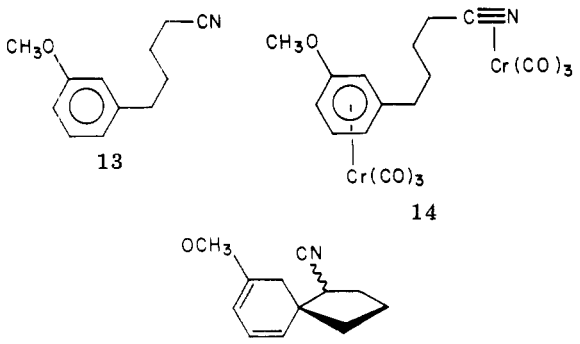
(13) This compound was prepared and fully characterized by Mr. Glenn Clark, Ph.D. Thesis, Cornell University, Ithaca, New York, 1977.

(14) ^{1}H NMR ($CDCl_3$) δ 6.03 (br s, 2 H, vinyl H), 2.95 (br s, 2 H, O=CH_2C=), 2.65 (br s, 2 H, $-CH_2$C=O), 2.4–2.6 (m, 1 H, $-CH$C=), 1.38 (s, 6 H, $-CH_3$); IR (neat) 2960 (m), 2220 (w), 1705 (s), 1680 (m), 1460 (m), 1380 (m), 650 (m) cm^{-1}; mass spectral molecular weight, *m/e* 163.

(15) ^{1}H NMR δ 6.6–7.3 (m, 5 H, aryl H, and phenol OH), 1.20 (s, 6 H, $-CH_3$); IR (neat) 3400 (m), 2960 (m), 1600 (m), 720 (m), 690 (m) cm^{-1}; mass spectral molecular weight, *m/e* 161; calcd for $C_{10}H_{11}ON$, 161.

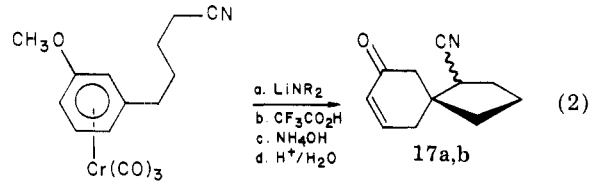
(16) For recent successful synthesis and leading references, see: (a) J. F. Ruppert, M. A. Avery, and J. D. White, *J. Chem. Soc., Chem. Commun.*, 978 (1976); (b) B. M. Trost, M. Hiroi, and N. Holy, *J. Am. Chem. Soc.*, **97**, 5873 (1975); (c) H. Wolf and M. Kolleck, *Chem. Ber.*, **109**, 2805 (1976); (d) W. Oppolzer and K. K. Mahalanabis, and K. Battig, *Helv. Chim. Acta*, **60**, 2388 (1977); (e) W. Rascher and H. Wolf, *Tetrahedron*, **33**, 575 (1977); (f) M. Pesaro and J-P. Bachmann, *J. Chem. Soc., Chem. Commun.*, 203 (1978); (g) G. L. Lange, W. J. Orrom, and D. J. Wallace, *Tetrahedron Lett.*, 4479 (1979).

(17) ^{1}H NMR δ 4.69–5.70 (m, 4 H, coordinated aryl H), 3.70 (s, 3 H, $-OCH_3$), 2.10–2.70 (m, 4 H, $-CH_2$Ar and $-CH_2$CN), 1.50–2.10 (m, 4 H, $-CH_2-$); IR ($CHCl_3$) 2290 (s), 1960 (s), and 1800 (s) cm^{-1}; mp ~25 °C; mass spectral molecular weight, calcd for $C_{15}H_{15}O_4NCr$, 325.0406; found, 325.0394.



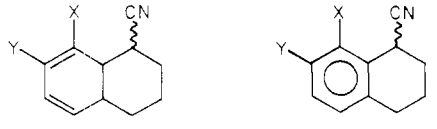
13 14 16a,b

concentrated aqueous ammonium hydroxide. After extraction procedures as before, short-path distillation (90 °C (0.01 torr)] afforded a liquid shown to be a mixture of **16a** and **16b** (278 mg, 70% yield together),[18] separable by analytical GLC. Treatment of the mixture **16** with a solution of aqueous hydrochloric acid (5 M) and THF (equivolume) at reflux for 24 h gave, after the usual isolation procedures, a mixture of diastereoisomeric spirocyclohexenones (**17a,b**; 96% yield) which were separable by preparative GLC.[19]



15 17a,b (2)

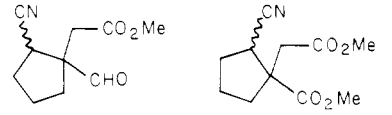
The analysis of the ^{1}H NMR spectral data for **16** is consistent with the proposed structures, especially using correlations with **4**. However, the fused ring isomers (e.g., **18** and **19**) are not easily ruled out using these data and



18, X = OCH_3; Y = H **20**, X = OCH_3; Y = H
19, X = H; Y = OCH_3 **21**, X = H; Y = OCH_3

are reasonable alternatives considering that: (1) cyclization of parent example of **15** (where $-OCH_3$ is $-H$) leads exclusively to ortho attack to give the fused ring (tetralin) system[20] and (2) treatment of **16** with DDQ (benzene, reflux) produced a mixture of 8-methoxy- and 7-methoxy-1-cyanotetralin (**20** and **21**).[21] This latter observation is consistent with structures **18** and **19**, and requires a spiro-to-fused ring rearrangement in order to be accommodated by structures **16**.

To verify structures **16**, the mixture was treated with ozone to produce **22**; the aldehyde unit was oxidized (Ag_2O) and esterified to form **23**. The diester **23** was prepared



22 23

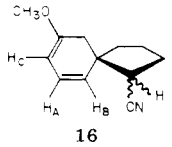
for comparison by alkylation of 2-(carbomethoxy)cyclopentanone with methyl 2-bromoacetate, followed by reaction of the ketone unit with tosylmethyl isocyanide.[23] The products **23** were identical (GLC retention time, ^{1}H NMR) with a mixture of diastereomeric cyano diesters from degradation of **16**.

We are currently undertaking tests of the scope of this new method of synthesis of 3-substituted cyclohexenones, including applications in the area of spirocyclic sesquiterpenes.[24]

Registry No. 1, 12116-44-8; **2**, 71076-33-0; **3**, 55440-70-5; **4**, 71060-35-0; **5**, 71060-36-1; **6**, 71060-37-2; **7**, 71060-38-3; **8**, 17653-93-9; **9**, 71060-39-4; **10**, 71060-40-7; **11**, 1195-98-8; **12**, 21653-33-8; **13**, 62248-72-0; **14**, 71076-34-1; **15**, 62259-89-6; *trans*-**16**, 71060-41-8; *cis*-**16**, 71060-42-9; *cis*-**17**, 71060-43-0; *trans*-**17**, 71060-44-1; **18**, 71060-45-2; **19**, 71060-46-3; **20**, 62248-74-2; **21**, 62248-73-1; **22**, 71060-47-4; **23**, 71060-48-5; *m*-methoxycinnamic acid, 6099-04-3; 2-(carbomethoxy)cyclopentanone, 10472-24-9; methyl 2-bromoacetate, 96-32-2; 2-methylpropionitrile, 78-82-0; 3-(*m*-methoxyphenyl)-1-propanol, 7252-82-6; 3-(*m*-methoxyphenyl)-1-iodopropane, 57822-33-0; chromium hexacarbonyl, 13007-92-6; 2-(carbomethoxy)-2-(carboethoxymethyl)cyclopentanone, 41301-65-9.

Supplementary Material Available: Full experimental details (10 pages). Ordering information is given on any current masthead page.

(18) The diastereoisomers **16** were not separated. The region δ 4.7–6.3 (vinyl H) in the ^{1}H NMR spectrum was particularly revealing.



16

H_A: overlapping doublet of doublets, centered at δ 6.00 and 5.86; J_{AB} = 9.0 Hz, J_{AC} = 6.0 Hz. H_B: overlapping doublets centered at δ 5.10 and 5.38; J_{AB} = 9.0 Hz, $J_{BC} \simeq 0$. H_C: overlapping doublets (broadened) centered at δ 4.96 and 4.92; J_{AC} = 6.0 Hz.

(19) Eluted first (OV-17, 190 °C) was **17a**: ^{1}H NMR ($CDCl_3$) δ 6.8–7.1 (m, 1 H, vinyl H), 6.1 (dt, 1 H, vinyl H), 1.6–2.7 (m, 11 H); IR ($CHCl_3$) 2250 (m), 1680 (s) cm^{-1}; mass spectral molecular weight, 175.0971; calcd for $C_{11}H_{13}NO$, 175.0946. Eluted second was **17b**: ^{1}H NMR ($CDCl_3$) δ 6.8–7.0 (m, 1 H, vinyl H), 6.1 (br d, 1 H, vinyl H), 1.6–2.8 (m, 11 H); IR ($CHCl_3$) 2250 (m), 1625 (s) cm^{-1}; mass spectral molecular weight, 175.0968; calcd for $C_{11}H_{13}NO$, 175.0946.

(20) M. F. Semmelhack, Y. Thebtaranonth, and L. Keller, *J. Am. Chem. Soc.*, **99**, 959 (1977).

(21) Compounds **20** and **21** showed ^{1}H NMR, IR, and mass spectral data consistent with the assigned structures. They were conclusively identified by oxidative decyanation[22] and comparison of the resulting 8-methoxy- and 7-methoxy-1-tetralones with commercial samples (GLC retention time, ^{1}H NMR data).

(22) S. J. Selikson and D. S. Watt, *J. Org. Chem.*, **40**, 267 (1975).

(23) O. H. Oldenziel and A. M. VanLeusen, *Tetrahedron Lett.*, 1357 (1973).

(24) We are please to acknowledge financial support of our research program by the National Science Foundation, the National Institutes of Health, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. Mass spectra were obtained at the Cornell Mass Spectrometry Facility under the direction of Dr. Tim Wachs, to whom we are grateful.

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(26) Recipient of a postdoctoral research fellowship from the National Science Foundation.

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Received November 15, 1978

Synthesis of Cyclopropanes via the Addition of Organometallics to 3-Substituted-1-alkenyl Sulfones

Summary: 3-Bromo-1-(phenylsulfonyl)-1-propene reacts with allylic, propargyl, aryl, and benzyl Grignard reagents to give *trans*-2-substituted-cyclopropyl phenyl sulfones in yields up to 80%.

Sir: The stabilization of carbanionic centers by adjacent sulfur groups is the basis of many valuable transformations

