To this solution, 100 mL of an aqueous solution of $NaBH_4$ (1.9 g, 0.050 mol) and EHDMABr (0.0006 mol) was added and stirred vigorously for 1 h under a N_2 atmosphere. The organic layer was separated and treated with 20 mL of 6 N HCl, and then washed thoroughly with distilled water. The solution was dried over anhydrous $MgSO_4$, the solvent was then evaporated, and a pale yellow solid (2.36 g) was obtained. The solid was recrystallized from absolute ethanol and it was found that the product corresponded to the 2,4-dinitrotoluene (no melting point depression, IR, identified, 1.66 g, yield 60%).

Acknowledgment. We thank Dr. E. E. Gilbert for his helpful suggestions.

Registry No. 2,4,6-Trinitrotoluene, 118-96-7; 2,3,4-trinitrotoluene, 602-29-9; 2,4,5-trinitrotoluene, 610-25-3; sodium borohydride, 16940-66-2; 2,4-dinitrotoluene, 121-14-2.

Facile Synthesis of β-Thioxo Esters from β-Enamino Esters

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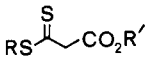
An integral part of our synthetic approach to 2-thioalkyl-substituted penems[1] required the use of β-thioxo esters, and in particular 1,1-dithiomalonates **1**. The



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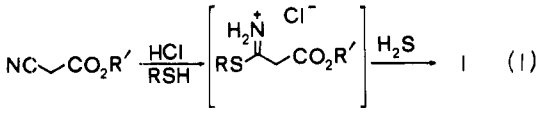
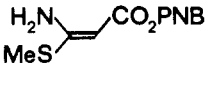
synthesis of such compounds and related substances has been accomplished by utilization of the classical modified Pinner reaction (eq 1), as exemplified by Scheithauer and



(1)

2

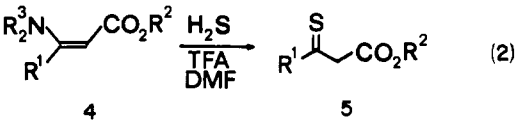
Mayer.[2] In addition, this method has been utilized as an approach to the synthesis of dithio esters in general.[3] However, we have found that application of this procedure, for our purposes, in which Pinner intermediate **2**, derived from *p*-nitrobenzyl cyanoacetate and methyl mercaptan (R = CH_3, R′ = $CH_2C_6H_4$-*p*-NO_2 ≡ PNB), when exposed to hydrogen sulfide for 10 min under the usual conditions[2] (dry pyridine, room temperature) gave after 2 h only a 7% yield of the desired dithioate **1** and a 60% yield of the neutralization product of **2**, β-enamino ester **3**.[4] As a result



3

of this finding, we have developed a simple, efficient modification of this method which: (a) provides useful yields of these thiocarbonyl compounds in relatively short reaction times; (b) circumvents the prolonged administration of the highly toxic hydrogen sulfide gas; and (c) offers an alternative method for the synthesis of other β-thioxo esters.

In general, it was found that β-enamino esters **4** (R^1 = alkyl, aryl, thioalkyl) were readily transformed into the corresponding thiocarbonyl compounds **5** (eq 2) when



(2)

4 **5**

treated with trifluoroacetic acid (TFA) in dry DMF at ambient temperature or below followed by the introduction of gaseous hydrogen sulfide for relatively short times (1–30 min). Typically, the β-thioalkyl-substituted enamines **4** (R^1 = SR) required both longer reaction times and greater amounts of H_2S for good conversions to dithiomalonates, as compared to the extremely rapid reactions of the corresponding β-alkyl- and aryl-substituted enamines, as illustrated by the examples in Table I.

Although it is apparent that these simple modifications constitute a circuitous thiolytic Pinner reaction for the synthesis of 1,1-dithiomalonates, several criticalities are noteworthy which reflect the potential advantages of the procedure. For example, with entry 3 in the table, it was demonstrated, after an extensive developmental effort, that the corresponding Pinner adduct **2** (eq 1) could be *directly* converted to the dithio ester **5** in high yield (80%). However, when this set of optimum conditions was applied to the analogous transformation for entry 4, none of the corresponding dithioate was detected. In contrast then, the results depicted in the table for these entries clearly demonstrate the reliability and efficiency of the method. Aside from the fact that the majority of the β-enamino ester precursors of dithiomalonates were conveniently synthesized by neutralization of intermediate **2** with dry pyridine, it should be noted that in certain cases this common intermediate may not be available, thus rendering the direct production of **1** impossible. Entry 2 illustrates such a case since exposure of (9-anthryl)methyl cyanoacetate and methyl mercaptan to gaseous HCl in dry benzene or dioxane instantaneously produced 9-(chloromethyl)anthracene and cyanoacetic acid quantitatively. Since the requisite β-enamino ester for this entry can be made by an alternative means, this procedure then offers a successful solution to the synthesis of dithiomalonates possessing functionalities that may be incompatible with the Pinner process.

Finally entries 5–7 demonstrate the generality of the method for the *facile* synthesis of β-thioxo esters, in which the primary advantages over existing, popular methods[5] are as previously stated. It should be noted that although eq 2 depicts these entries **5** in a thioketo form, they in fact exist exclusively as the *cis*-enethiol tautomer.[6] In this

(1) DiNinno, F.; Linek, E. V.; Christensen, B. G. *J. Am. Chem. Soc.*, **1979**, *101*, 2210.

(2) Scheithauer, S.; Mayer, R. *Chem. Ber.* **1967**, *100*, 1413.

(3) See for example: Hoffmann, R.; Hartke, K. *Justus Liebigs Ann. Chem.* **1977**, 1743. Poupart, J.; Bruylants, A.; Crooy, P. *Synthesis.* **1972**, 622, and references cited therein.

(4) It should be noted that certain β-enamino esters have been converted to β-thioxo esters under these conditions: Bleisch, S.; Mayer, R. *Z. Chem.* **1964**, *4*, 146.

(5) See for example: (a) Duus, F. *J. Org. Chem.* **1977**, *42*, 3123. (b) Duus, F. *Tetrahedron.* **1974**, *30*, 3753. (c) Duus, F. *Ibid.* **1972**, *28*, 5923, and references cited therein.

(6) For an excellent discussion of this subject, see Duus, F. *Tetrahedron.* **1968**, *24*, 5323, and ref 5b and 5c.

(7) This β-enamino ester, mp 91–92 °C (Me_2CHOH–CH_2Cl_2), was prepared by a series of transformations in which (9-anthryl)methyl cyanoacetate (mp 144–145 °C, Me_2CHOH–CH_2Cl_2), prepared in 76% yield as described by Kornblum and Scott[8] from cyanoacetic acid and (9-anthryl)methyl chloride, was converted to the corresponding thioamide (64%, H_2S, Et_3N, EtOH, $CHCl_3$), mp 168 °C (Me_2CO–Me_2CHOH), and methylated (MeI, K_2CO_3, Me_2CO–MeCN (2:1), 100%).

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Table I. Thiolysis of β-Enaminoesters 4 to β-Thioxo Esters 5 (see eq 2)

entry	R_1	R_2	R_3	T, h	$T(H_2S)$, min	% yield[a]
1	SCH_3	PNB[b]	H	5.0	10	74
2	SCH_3	9-AM[b]	H[c]	2.5	10	64
3	$SCH_2CH_2NHCO_2PNB$	PNB	H	2.75	30	51
4	$SCH_2CH_2NHCO_2TCE$[b]	PNB	H	2.5	30	100
5	Ph	PNB	$(CH_2)_5$	0.25	3	76
6	p-OMePh	PNB	$(CH_2)_5$	0.25	1	98
7	CH_3	CH_3	$(CH_2)_4$[d]	0.3[e]	5	85[f]

[a] Isolated and unoptimized. [b] PNB = p-nitrobenzyl; 9-AM = 9-anthrylmethyl; TCE = trichloroethyl. [c] Reference 7. [d] Rao, R. B.; Singh, U. P.; Bhide, G. V. *Tetrahedron Lett.*, **1967**, 719. [e] At −25 to 0 °C. [f] Reference 5c.

regard, however, entries 1–4 were found to exist in the former state.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded in $CHCl_3$ solution on a Perkin-Elmer 727B infrared spectrophotometer and only selected absorptions are reported. The NMR spectra were recorded on either a Varian T-60 or SC-300 spectrometer in $CDCl_3$ solution with Me_4Si as an internal standard and chemical shifts are reported in parts per million (δ) relative to Me_4Si. Mass spectra were obtained on a LKB 9000 gas chromatograph–mass spectrometer at 70 eV and only the parent and/or significant ions are given.

All glassware was oven dried at 120 °C overnight prior to use. DMF was distilled from CaH_2 under nitrogen and removed with a dry syringe for reaction. All reactions were conducted under a positive atmosphere of nitrogen with the aid of a Firestone Valve (Ace Glass). Plate layer chromatography (PLC) was performed on either Analtech silica gel GF 20 × 20 cm or 20 × 40 cm plates. Column chromatography (CC) was conducted with Baker silica gel 60–200 mesh.

The data pertinent to the new compounds 4 and 5 in Table I are given below at the end of each general procedure by entry number, followed by the method of purification, yield, physical characteristics, and spectroscopic properties.

General Procedures for the Preparation of β-Enamino Esters 4. A. Preparation of Entries 1, 3, and 4. A stirred solution of equimolar quantities of cyanoacetate[9] and mercaptan[11] in dry benzene (distilled from sodium) was treated with a vigorous stream of HCl gas at 25 °C for 1 h. The reaction mixture was stirred overnight and the resulting insoluble material was separated from the reaction solution by suction filtration through a filter stick and washed similarly with dry benzene. The benzene-moist precipitate was dissolved in dry pyridine (distilled from BaO) and stirred at 25 °C for 0.5 h, after which time it was partitioned between Et_2O and ice–H_2O. The organic phase was separated, washed with ice–H_2O (4×) and saturated NaCl (aqueous), dried ($MgSO_4$), filtered, and evaporated.

1: recrystallization; 60%; yellow solid, mp 95–96 °C (Et_2O–petroleum ether); IR 3636, 3322, 1664 cm^{-1}; NMR δ 2.4 (s, 3 H), 4.68 (s, 1 H), 5.17 (s, 2 H), 6.43 (br s, 2 H), 7.43 (d, J = 8 Hz, 2 H), and 8.13 (d, J = 8 Hz, 2 H); MS m/e 268 (M^+).

3: PLC (PhH–EtOAc (4:1)); 40%; yellow solid, mp 122–123 °C; IR 1710 and 1660 cm^{-1}; NMR δ 3.0 (m, 2 H), 3.4 (m, 2 H), 4.83 (s, 1 H), 5.17 (s, 4 H), 5.4 (br s, 1 H), 6.77 (br s, 2 H), 7.45 (d, J = 9 Hz, 4 H), and 8.13 (d, J = 9 Hz, 4 H); MS no m/e 476 (M^+), m/e 256, 220.

4: recrystallization; 73%; yellow solid, mp 95–96 °C (Me_2CHOH–Et_2O); IR 1715 and 1640 cm^{-1}; NMR δ 3.07 (m, 2 H), 3.57 (m, 2 H), 4.73 (s, 2 H), 4.9 (s, 1 H), 5.22 (s, 2 H), 5.4 (br s 1 H), 6.73 (br s, 2 H), 7.57 (d, J = 9 Hz, 2 H), and 8.23 (d, J = 9 Hz, 2 H); MS no m/e 473 (M^+), m/e 253, 220.

B. Preparation of Entries 5 and 6. Stoichiometric quantities of the arylpropiolic acid ester[12] and piperidine in benzene solution were stirred under reflux for 2.5 h.[14] The volatiles were removed under reduced pressure and the residue obtained was purified by recrystallization.

5: 66%; light yellow solid, mp 96–100 °C (absolute EtOH); IR 1680 cm^{-1}; NMR δ 1.6 (m, 6 H), 3.13 (m, 4 H), 5.0 (s, 3 H), 7.33 (m, 7 H), and 8.13 (d, J = 9 Hz, 2 H); MS m/e 366 (M^+), 230, 186.

6: 62%; yellow solid, mp 119 °C (Me_2CHOH); IR 1675 cm^{-1}; NMR δ 1.63 (m, 6 H), 3.17 (br m, 4 H), 3.8 (s, 3 H), 5.0 (s, 1 H), 5.07 (s, 2 H), 6.91 (d, J = 9 Hz, 2 H), 7.23 (d, J = 9 Hz, 2 H), 7.37 (d, J = 9 Hz, 2 H), and 8.2 (d, J = 9 Hz, 2 H); MS m/e 396 (M^+), 260, 216.

General Procedure for the Preparation of β-Thioxo Esters 5. To a stirred solution of β-enamino ester 4 (1 mmol) in 1 mL of dry DMF at ambient temperature or below was added dropwise 1.1 mmol of neat trifluoroacetic acid. After the addition was complete, H_2S (g) **(Caution: highly toxic, use only in a well-ventilated hood)** was bubbled through the solution with the aid of a filter stick at a vigorous rate and stirred as indicated in Table I. The reaction mixture was partitioned between Et_2O and ice–H_2O and the organic phase was separated, washed further with cold H_2O (3×) and saturated NaCl (aqueous) solution, dried ($MgSO_4$), filtered, evaporated, and purified.

1: CC ($CHCl_3$–petroleum ether (1:1)); orange-red oil; IR 1742, 1613, and 1522 cm^{-1}; NMR δ 2.67 (s, 3 H), 4.13 (s, 2 H), 5.23 (s, 2 H), 7.47 (d, J = 9 Hz, 2 H), and 8.17 (d, J = 9 Hz, 2 H); MS m/e 285 (M^+).

2: recrystallization; yellow-orange solid, mp 101–102.5 °C (Et_2O–hexane); IR 1733 cm^{-1}; NMR δ 2.52 (s, 3 H), 4.0 (s, 2 H), 6.15 (s, 2 H), 7.37–8.47 (m, 9 H); MS m/e 340 (M^+).

3: CC (C_6H_6–EtOAc (4:1)); yellow solid, mp 82–83 °C; IR 3400, 1720 (sh), 1710, 1601, 1520 cm^{-1}; NMR δ 3.45 (m, 4 H), 4.08 (s, 2 H), 5.1 (br s, 1 H), 5.17 (s, 2 H), 5.27 (s, 2 H), 7.42 (d, J = 8 Hz, 4 H), and 8.12 (d, J = 8 Hz, 4 H); MS no m/e 493 (M^+), m/e 446, 256, 239, 209, 195, 165, 153, 136, 120.

4: CC ($CHCl_3$–C_6H_6–EtOAc (4:1:1)); yellow oil, IR 1725 cm^{-1}; NMR δ 3.1 (br s, 2 H), 3.5 (br s, 2 H), 4.82 (s, 2 H), 5.36 (s, 2 H), 5.65 (br s, 1 H), 7.7 (m, 2 H), and 8.3 (d, J = 9 Hz, 2 H); MS m/e 492, 490, 488 (M^+), 251, 218, 204.

5: recrystallization; white needles, mp 103–105 °C (EtOH); IR 1672 cm^{-1}; NMR δ 5.37 (s, 2 H), 6.23 (s, 1 H), 6.97 (s, 1 H), 7.55 (m, 7 H), 8.23 (d, J = 9 Hz, 2 H); MS m/e 315 (M^+).

6: recrystallization; white crystals, with purple tinge, mp 118–119 °C (Me_2CHOH–CH_2Cl_2); IR 1680 cm^{-1}; NMR δ 3.8 (s, 3 H), 5.3 (s, 2 H), 6.2 (s, 1 H), 6.8 (d, J = 8 Hz, 2 H), 7.2 (s, 1 H), 7.33 (apparent d, J = 9 Hz, 4 H), and 8.2 (d, J = 9 Hz. 2 H); MS m/e 345 (M^+).

Acknowledgment. We wish to express our appreciation to Dr. B. Arison, Mr. H. Flynn, and Mr. J. Smith for

(8) Kornblum, N.; Scott, A. *J. Am. Chem. Soc.* **1974**, *96*, 590.

(9) p-Nitrobenzyl cyanoacetate, mp 67–68 °C (Me_2CHOH) (lit. mp 68–69 °C) was prepared in 90% yield by esterification of cyanoacetic acid with p-nitrobenzyl alcohol in refluxing benzene with azeotropic H_2O removal via a Dean–Stark trap.

(10) Parker, C. O. *Tetrahedron.* **1962**, *17*, 109.

(11) N-(p-Nitrobenzyloxycarbonyl)cysteamine, mp 67–68 °C (Et_2O–petroleum ether), and N-(trichloroethyloxycarbonyl)cysteamine, bp 144–146 °C (2.0 mm), were prepared by acylation of cysteamine hydrochloride with the appropriate chloroformate in Et_2O–$NaHCO_3$–H_2O at 0 °C.

(12) p-Nitrobenzyl phenylpropiolate, mp 83–85 °C (EtOH), was prepared in 65% yield from phenylpropiolic acid and p-nitrobenzyl alcohol as indicated in ref 9. p-Nitrobenzyl p-methoxyphenylpropiolate, mp 100–101 °C (Me_2CHOH), was synthesized in 64% yield by acylation of the acetylide anion, generated from p-methoxyphenylacetylene[13] and BuLi in THF at −78 °C, with p-nitrobenzyl chloroformate.

(13) Iwai, I.; Yura, Y. *Chem. Abstr.* **1961**, *55*, 4400e.

(14) Bestmann, H. J.; Geismann, C. *Justus Liebigs Ann. Chem.* **1977**, 282, and references cited therein.

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.

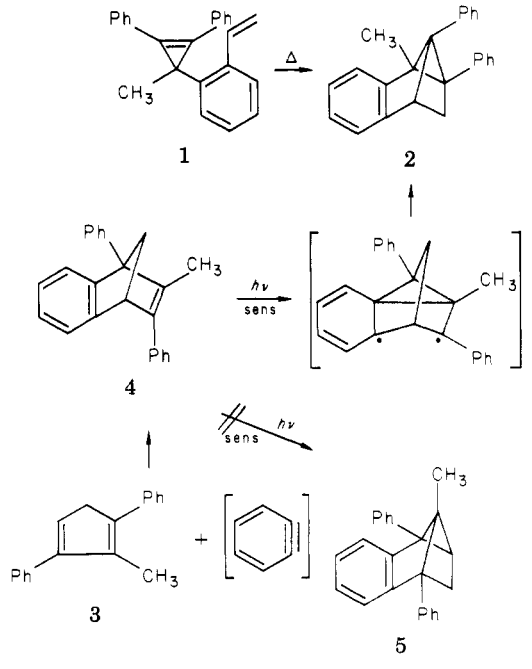
Communications

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 oribital 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

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