Synthesis and Thermal Rearrangement of 7-(1,2-Butadienyl)bicyclo[2.2.1]hept-2-ene [7-(3-Methylallenyl)norbornene]

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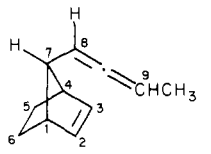
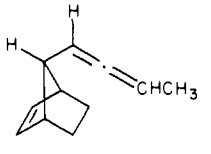
Abstract: A mixture of *syn*- and *anti*-7-(1,2-butadienyl)bicyclo[2.2.1]hept-2-ene [**1a** (30%) and **1b** (70%)] has been synthesized through a Grignard reaction employing *syn*-7-bromonorbornene and 3-bromo-1-butyne. Gas-phase pyrolysis of the mixture at 275 °C for 24 h gives 1-ethylindan (**7**) as the single isolable product in 28% yield. This result is interpreted in terms of an initial concerted $[{}_{\sigma}2_s + {}_{\pi}2_s + ({}_{\pi}2_s + {}_{\pi}2_a)]$ rearrangement of **1a** to 1-ethylidene-3a,4,5,7a-tetrahydroindene (**5**), which through a series of not less than five allowed [1,5] hydrogen shifts may give 1-ethylindan.

Recently,[2] two-component cycloaddition reactions involving an allene as at least one component have been interpreted in terms of a six-electron concerted $[{}_{\pi}2_s + ({}_{\pi}2_s + {}_{\pi}2_s)]$ process. Second-order PMO calculations applied to this transition-state model were compared with those applied to the $({}_{\pi}2_s + {}_{\pi}2_a)$ alternative model, and only the six-electron process correctly predicted experimentally observable regio- and stereoselectivities in many cases. Given the uncertainties associated with firmly defining the transition-state geometries actually involved with such intermolecular processes, we decided to study an allenyl system of limited conformational mobility which through an intramolecular valence isomerization might be expected to utilize its allenyl moiety in either a $({}_{\pi}2_s + {}_{\pi}2_s)$ or $({}_{\pi}2_s + {}_{\pi}2_a)$ manner.

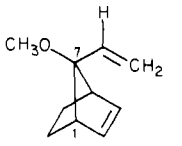
The substrate we chose to construct was 7-(1,2-butadienyl)-bicyclo[2.2.1]hept-2-ene, prepared as a mixture of epimers **1a** (syn) and **1b** (anti). Results of experimental work on similar systems[3] (e.g., **2**) indicate that thermal reorganization of the 1,5-diene



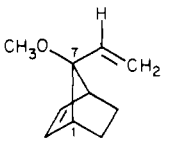
1a



1b

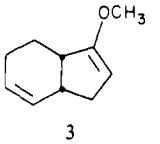


2a



2b

moiety in **1a** by an ordinary six-electron $({}_{\sigma}2_s + {}_{\pi}2_s + {}_{\pi}2_s)$ Cope rearrangement might be sterically retarded. Separate gas-phase pyrolyses of *syn*-7-ethenyl-*anti*-methoxybicyclo[2.2.1]hept-2-ene (**2a**) and its epimer **2b** at 250 °C (at which temperature the epimers did not interconvert) each gave a mixture of 1-methoxy-3a,6,7,7a-tetrahydroindene (**3**) and 2-methoxybicyclo-[3.2.2]nona-2,6-diene (**4**).[3b]



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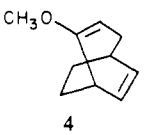

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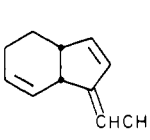
Competition experiments showed that **2a** and **2b** differed only slightly in pyrolysis rate, and the rearrangements were interpreted[3b] in terms of a diradical process initiated by cleavage of the 1,7 bond in **2**. Presumably severe framework distortions would be necessary to maintain sufficient overlap in the transition states for concerted **2a** → **3** and **2a** → **4** processes. However, in the case of **1a**, any steric inhibition for concerted thermal rearrangement might be circumvented by the presence of the "extra" π system in the allenyl component. Thus **1a** might be expected to readily rearrange by an eight-electron augmented $[{}_{\sigma}2_s + {}_{\pi}2_s + ({}_{\pi}2_s + {}_{\pi}2_a)]$ concerted Cope process to 1-ethylidene-3a,4,5,7a-tetrahydroindene (**5**) or possibly by a similarly augmented six-electron concerted [1,3] sigmatropic rearrangement $([{}_{\sigma}2_s + ({}_{\pi}2_s + {}_{\pi}2_s)])$ to 1-ethylidenebicyclo[3.2.2]nona-2,5-diene (**6**).



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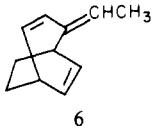

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Results and Discussion

We prepared allene **1** from the Grignard reagent[4] of *syn*-7-bromobicyclo[2.2.1]hept-2-ene (*syn*-7-bromonorbornene).[5] 3-Bromo-1-butyne[6] was added over a 1-h period to a 20% excess of the Grignard reagent in ether and under nitrogen at -45 to -60 °C. From this mixture, **1** was isolated in 25% yield by preparative VPC as the **1a**/**1b** epimeric mixture.[7]

The IR spectrum of **1** in CCl_4 had the diagnostic C=C=C stretching vibration at 1950 cm^{-1}. The high-resolution mass spectrum had its molecular ion (M) peak at m/e 146.110 ($C_{11}H_{14}$; calcd m/e 146.110) and in addition exhibited prominent peaks at m/e (relative intensity) 131 (88), 117 (92), and 91 (100). These fragments correspond to even-electron ions with formulas $C_{10}H_{11}$ (M − CH_3), C_9H_9 (M − ethene and H·), and C_7H_7 (M − neutral allenyl unit and H_2). The ^1H NMR spectrum of **1** (see Experimental Section) showed it to be 30% syn (**1a**) and 70% anti (**1b**).[8,9] The coupling constants $J_{7,8}$ = 3 Hz and $J_{8,9}$ = 5 Hz were uncovered through homonuclear decoupling. When the methyl resonance was irradiated, the H-9 resonance collapsed to a doublet and the

(1) To whom correspondence should be addressed at Lewis and Clark College.

(2) See Pasto, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 37, and references therein.

(3) (a) Berson, J. A.; Jones, M., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 5017, 5019. (b) Berson, J. A.; Walsh, E. J., Jr. *Ibid.* **1968**, *90*, 4732. (c) Berson, J. A.; Miyashi, T.; Jones, G., II *Ibid.* **1974**, *96*, 3468.

(4) Sauers, R. R. *Chem. Ind. (London)* **1960**, 176.

(5) Kwart, H.; Kaplan, L. *J. Am. Chem. Soc.* **1954**, *76*, 4072.

(6) Sondheimer, F.; Ben-Efraim, D. A. *J. Am. Chem. Soc.* **1963**, *85*, 52.

(7) The mechanism for this type of reaction has recently been scrutinized: Pasto, D. J.; Shults, R. H.; McGrath, J. A.; Waterhouse, A. *J. Org. Chem.* **1978**, *43*, 1382.

(8) By comparison, carbonation of the Grignard reagent of *syn*-7-bromonorbornene gives a 1:2 mixture of *syn*- to *anti*-7-carboxynorbornenes.[4]

(9) Assignments based on those established for compounds similar to **2**.[3c] The resonances of the allenyl moiety are remarkably unaffected by its syn or anti position, presumably because preferred conformations keep it far from the bicyclic ring.

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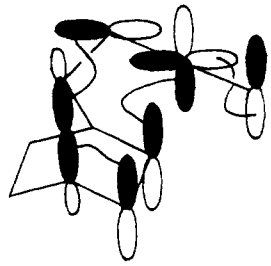


Figure 1. $[{}_{\sigma}^{2}{}_{s} + {}_{\pi}2_{s} + ({}_{\pi}2_{s} + {}_{\pi}2_{a})]$.

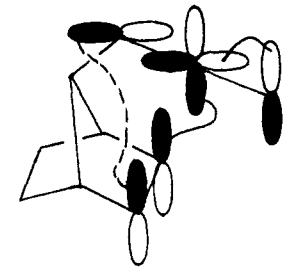
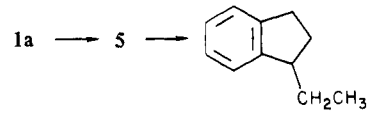


Figure 2. $[{}_{\pi}2_{s} + ({}_{\pi}2_{s} + {}_{\pi}2_{s})]$.

H-8 resonance to a doublet of doublets. Also when the H-8 and H-9 resonances were simultaneously irradiated, the methyl resonance collapsed to a singlet and the H-7 resonance simplified to a broad singlet.

Samples of **1** for pyrolysis were placed in Carius tubes, deoxygenated by repeated cycles of evacuation and filling with helium, sealed at 10^{-2} torr, and heated in a molten salt bath. Samples were recovered as ether solutions and analyzed by VPC. Only the peak corresponding to allene **1** was detected for samples heated below 250 °C for less than 3 h; however, a single prominent new peak was observed for a sample heated at 275 °C for 5 h. In a preparative scale run on 0.6 g of **1**, which was heated at 275 °C for 24 h, 0.17 g of the new compound was collected by VPC, and no residual peak for **1** or any other peak was detected.

The high-resolution mass spectrum of this compound showed it to be a $C_{11}H_{14}$ rearrangement product (calcd *m/e* 146.110; found 146.110); hence 28% of **1** had rearranged in the preparative scale run, or about the percentage of **1a** in the **1a/1b** mixture. The IR (neat) spectrum of this $C_{11}H_{14}$ compound showed an ortho-disubstituted benzene moiety and it was tentatively identified as 1-ethylindan (**7**). This assignment was confirmed by comparing



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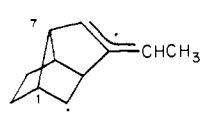
the IR and ^{1}H NMR spectra of the rearrangement product with those spectra recorded for a sample of authentic 1-ethylindan we prepared from 1-indanone.[10]

As **7** shares a common ring system with isomer **5**, it is likely that **5** is an intermediate in the formation of **7** from **1**. A series of not less than five allowed [1,5] hydrogen shifts may transform **5** into **7**. We currently favor a $[{}_{\sigma}2_{s} + {}_{\pi}2_{s} + ({}_{\pi}2_{s} + {}_{\pi}2_{a})]$ augmented Cope process (see Figure 1) for an alleged **1a** → **5** process.[11] This is supported by the failure of **1** to also rearrange to **6**[12] as might be expected for an ordinary diradical mechanism, given the fact that **2** rearranges to both **3** and **4**. Although the temperature required for rearrangement of **1a** (250–275 °C) may seem excessive for a concerted process, it is helpful to note that Berson[13] has found that the corresponding *syn*-7-ethenylnorbornene is stable at 250 °C, and at 320 °C it decomposes without rearrangement. One contributing factor to the high-temperature requirement for the rearrangement may be the low incidence of the required conformation shown in Figure 1, as supported by the ^{1}H NMR results.[9]

An interesting alternative mechanistic formulation for **1a** → **5** would involve an initial allowed $[{}_{\pi}2_{s} + ({}_{\pi}2_{s} + {}_{\pi}2_{s})]$ geometrically foiled six-electron [2 + 2] cycloaddition process to give **8** in a stereoselective manner (see Figure 2).[2,14] Diradical **8** would then collapse to **5** by cleavage of the 1,7 bond. Further distinctions among possible pathways for the overall **1** → **7** transformation must await pyrolytic studies planned for **5** and a 1-methyl-substituted allene **1a**, which have yet to be completely synthesized.



Experimental Section

^{1}H NMR spectra were obtained at 60 MHz on a Varian Model EM-360L spectrometer. All chemical shifts are reported in ppm (δ) relative to internal Me_4Si. IR spectra were recorded on either a Beckman IR-8 or IR-10 spectrophotometer. High-resolution mass spectra were recorded at 70 eV on a CEC 21-110 mass spectrometer. Preparative vapor-phase chromatography (VPC) was performed, with helium as the carrier gas (flow rate = 40 mL/min), on a Varian Model 1520 chromatograph using a $^3/_8$ in. × 10 ft column of 23% Carbowax 20M on 60/80 Chromosorb W-NAW. Liquid N_2 was used to condense the samples in collectors protected from moisture with $CaSO_4$. The microanalysis was performed by R. Wielesek at the University of Oregon, Eugene, OR. The ether used in the Grignard reaction was dried over CaH_2 and distilled immediately prior to its use. A positive pressure of N_2 was maintained throughout the preparation and reaction of the Grignard of 7-bromonorbornene.

3-Bromo-1-butyne. A 24.5-g portion of the crude product prepared from 3-butyn-2-ol (Columbia Organic Chemicals) by the method of Sondheimer and Ben-Efraim[6] was chromatographed on 100 g of activated alumina (MCB, 80–200 mesh) with 300 mL of pentane. The pentane solution was concentrated by distillation through a Vigreux column. The pure product (5.08 g) was obtained by preparative VPC (150 °C, retention time = 10 min): ^{1}H NMR (neat) δ 1.90 (d, 3 H, J = 7 Hz), 2.65 (d, 1 H, J = 3 Hz), 4.60 (dd, 1 H).

7-(1,2-Butadienyl)bicyclo[2.2.1]hept-2-ene (1). A 100-mL three-neck flask was charged with 1.16 g (47.7 mmol) of magnesium turnings and fitted with a septum, a reflux condenser, a 50-mL pressure-equalizing dropping funnel, and a stir bar. The apparatus was flame-dried under a dry N_2 atmosphere; when cool to the touch, 10 mL of ether and 2 drops of 1,2-dibromoethane as initiator were added to the flask, and a solution of 7.93 g (45.8 mmol) of *syn*-7-bromonorbornene[5] in 25 mL of ether was placed in the dropping funnel. The solution of the bromide was added dropwise over a 2-h period to the contents of the flask with stirring. After the ether had stopped boiling, the mixture was heated gently at reflux for an additional 2.5 h and then cooled to −60 °C.

A solution of 5.08 g (38.2 mmol) of 3-bromo-1-butyne in 15 mL of ether was added dropwise through the funnel to the Grignard reagent over a 1-h period with stirring at −60 to −45 °C. The resulting mixture, containing solid $MgBr_2$, was allowed to warm to room temperature and stirred overnight. To the two layers which resulted (the solid had disappeared) was cautiously added 20 mL of water through the septum. When the exothermic reaction had subsided, the layers were separated and the aqueous layer was extracted several times with ether. The combined ether extracts were washed several times with water and the dried ($MgSO_4$) and filtered ether solution was concentrated by distillation. Approximately 1.4 g (25%) of the **1a/1b** mixture was obtained from the ether solution by preparative VPC (160 °C, retention time = 21.5 min). Smaller amounts of norbornene and 3-bromo-1-butyne in the ether concentrate were identified by their shorter retention times. Only very small amounts of yet unidentified components, also with shorter retention times, were present. A single component with longer retention time was isolated and tentatively identified by its ^{1}H NMR spectrum as dinorbornene. An analytical sample (52 mg) was obtained by reinjecting 103 mg of the allene (**1**) collected above; it suffered no rearrangement or decomposition at the injector (175 °C) or on the column (160 °C): IR (CCl_4) 3060, 2960, 2950, 2925, 2875, 1950, 1455, 1440, 1365, 1325, 1265, 1115, 1085, 1030, 976, 905, 870, 830, 708, 675 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.9 (m, 2, H-5 endo), 1.6 (m, 2, H-5 exo), 1.63 (d × d, 3, $J_{9,Me}$

(10) Khalaf, A. A.; Roberts, R. M. *J. Org. Chem.* **1966**, *31*, 89.
(11) This supposes that all of **1b** is lost to severe pyrolytic decomposition.
(12) However, **6** might be selectively destroyed by, or formed reversibly in, the pyrolysis of **1**.
(13) Berson, J. A., Yale University, personal communication, 1975.
(14) Baldwin, J. E.; Roy, U. Y. *J. Chem. Soc. D* **1969**, 1225.

= 6.8 Hz, $J_{8,Me}$ = 3.6 Hz, CH_3), 2.2 (m, 1, H-7), 2.65 (anti epimer **1b**) 2.70 (syn epimer **1a**) (m, 2, H-1), 4.80 (q×d, 1, $J_{9,Me}$ = 6.8 Hz, $J_{8,9}$ = 5 Hz, H-9), 4.98 (d×q×d, 1, $J_{8,9}$ = 5 Hz, $J_{8,Me}$ = 3.6 Hz, $J_{7,8}$ = 3.0 Hz, H-8), and 5.87 (syn epimer **1a**), 6.03 (anti epimer **1b**)[9] (t, 2, $J_{1,2}$ = 2 Hz, H-2); mass spectrum *m/e* (rel intensity) 146 (28), 131 (88), 118 (25), 117 (92), 105 (45), 93 (45), 91 (100). High resolution mass spectrum: calcd for $C_{11}H_{14}$, 146.110; found, 146.110. Anal. ($C_{11}H_{14}$): C, H.

Pyrolysis of 7-(1,2-Butadienyl)bicyclo[2.2.1]hept-2-ene (1). Several pyrolyses of the epimeric mixture of allenes **1a** and **1b** were carried out as follows. Samples were placed in 20 × 250 mm Pyrex Carius tubes and deoxygenated by six or seven cycles of evacuation and filling with helium. The tubes were then sealed at 10^{-2} torr and placed in a potassium nitrate–sodium nitrite (1:1) bath maintained at various temperatures. To minimize wall effects, the tubes had been treated with concentrated aqueous HCl followed by 5% EDTA in concentrated ammonium hydroxide. They were then rinsed with copious amounts of water and dried at 200 °C.

Following pyrolysis, samples were recovered as ether solutions and analyzed by VPC (160 °C). For those samples heated below 250 °C for 3 h or less, only the peak corresponding to the **1a/1b** allene mixture (retention time = 21.5 min) could be detected. For samples heated at 275 °C for 5 h or more, a single new peak (retention time = 33.5 min) was observed. A preparative scale pyrolysis using 0.6 g of the **1a/1b** mixture was performed at 275 °C for 24 h. It yielded 0.17 g of the new compound by preparative VPC. The VPC trace showed no residual allene or the presence of any other product. The high-resolution mass spectrum of this compound had its molecular ion (M) peak at *m/e* 146.110 ($C_{11}H_{14}$; calcd *m/e* 146.110) and in addition exhibited prominent peaks at *m/e* (rel intensity, formula) 117 (100, C_9H_9), 115 (53, C_9H_7), and 91 (46, C_7H_7).[15]

1-Ethylindan was prepared by the method of Khalaf and Roberts,[10] and its IR and ^1H NMR spectra were found to be identical with those recorded for the rearrangement product obtained above: IR (neat) 3090, 3040, 2975, 2940, 2875, 1480, 1460, 1380, 1160, 1090, 1020, 930, 760, 750, 740 cm^{-1}; ^1H NMR (CCl_4) δ 1.0 (t, 3 H), 1.1–2.4 (m, 5 H), 2.9 (m, 2 H), 7.1 (s, 4 H).

Acknowledgment. We are grateful for the financial support provided by the Research Corporation and for grants to Reed College by the Andrew W. Mellon Foundation and the National Science Foundation, the latter through their Undergraduate Research Participation Program. We also thank the Olin Foundation for their generous gift of a Varian Associates EM-360L nuclear magnetic resonance spectrometer, as part of a major capital gift to Lewis and Clark College.

Registry No. 1a, 81141-97-1; **1b**, 81141-98-2; **7**, 4830-99-3; 3-bromo-1-butyne, 18668-72-9; *syn*-7-bromonorbornene, 20047-65-8.

(15) The peak at *m/e* 91 probably arises from an initial intramolecular rearrangement followed by loss of a neutral C_4H_7 radical component.

A Critical Test of the Theory of Stereoelectronic Control

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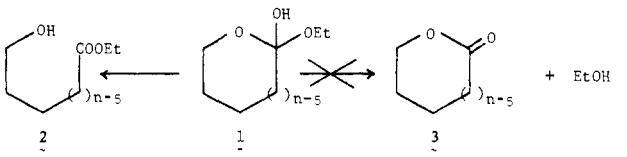
Contribution from the Department of Chemistry, D-006, University of California, San Diego, La Jolla, California 92093. *Received August 27, 1981*

Abstract: According to Deslongchamps' theory of stereoelectronic control, preferential cleavage of a tetrahedral intermediate occurs when there are two lone pairs antiperiplanar to the leaving group. However, it is concluded that the experimental evidence is ambiguous, because it requires an unreasonable assumption regarding rates of ring inversion and because there is a simpler explanation for the observations. Nevertheless, the theory is a plausible one, deserving unambiguous evidence to support it. The hydrolysis of cyclic amidines (**4**), via the hemiorthoamide (**5**), can provide a suitable test. It is observed that 2-amino-1-pyrroline (**4**, *n* = 5) and "2-iminopiperidine" (**4**, *n* = 6) hydrolyze in base solely to the amino amide (**6**), which is converted under the reaction conditions to the thermodynamically more stable lactam (**7**). This result is the first unambiguous evidence for stereoelectronic control, and it also shows that cleavage of the intermediate (**5**) is fast compared to nitrogen inversion.

Introduction

According to Deslongchamps'[1] theory of stereoelectronic control, preferential cleavage of a tetrahedral intermediate occurs when there are two lone pairs antiperiplanar to the leaving group. This is certainly a plausible theory, since anti elimination is generally preferred,[2] and since involvement of *both* lone pairs is required to produce the resonance stabilization of the ester or amide product. Indeed, MO calculations[3] support the theory. The experimental evidence is contained in a notable series of papers by Deslongchamps[1] and his co-workers. The key result is the "unexpected" observation[4] that a cyclic hemiorthoester (**1**, *n* = 5, 6), produced by two independent routes, cleaves only to the hydroxy ester (**2**), rather than the lactone (**3**).



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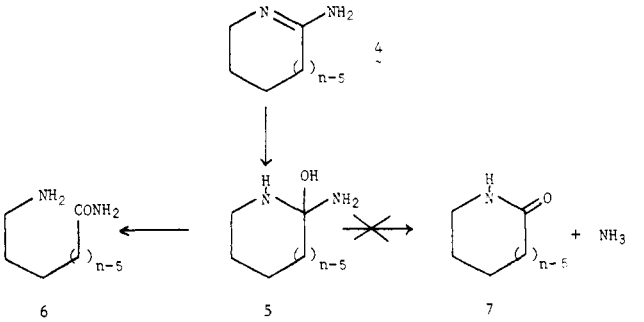
Nevertheless, for reasons presented below, this evidence is ambiguous. In contrast, for reasons presented below, the hydrolysis of cyclic amidines (**4**, *n* = 5, 6) can provide unambiguous evidence



for the theory of stereoelectronic control. According to this theory, plus a supposition regarding nitrogen inversion, a cyclic hemiorthoamide (**5**, *n* = 5, 6) should cleave only to the amino amide (**6**), rather than the lactam (**7**). Despite several previous reports of a high yield of lactam (**7**, *n* = 5,[5a,b] 6[5c]) from amidine hydrolysis, we now report that the kinetic product from **4** (*n* = 5, 6) is indeed the amino amide.

(1) (a) Deslongchamps, P. *Tetrahedron* **1975**, *31*, 2463. (b) Deslongchamps, P. *Heterocycles* **1977**, *7*, 1271, and references cited.

(2) Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper & Row: New York, **1981**; pp 548–554.

(3) Lehn, J.-M.; Wipff, G. *J. Am. Chem. Soc.* **1980**, *102*, 1347.

(4) (a) Deslongchamps, P.; Atlani, P.; Frêhel, D.; Malaval, A.; Moreau, C. *Can. J. Chem.* **1974**, *52*, 3651. (b) Deslongchamps, P.; Chênevert, R.; Taillefer, R. J.; Moreau, C.; Saunders, J. K. *Ibid.* **1975**, *53*, 1601.

(5) (a) Moriconi, E. J.; Cevasco, A. A. *J. Org. Chem.* **1968**, *33*, 2109. (b) Schaafsma, S. E.; Geerts, L. H. German Offen. Patent 2542397, 1967; *Chem. Abstr.* **1976**, *85*, 32833v. (c) Grave, T. B. *J. Am. Chem. Soc.* **1924**, *46*, 1460.

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