$J_{BX}$ = 5.4 Hz, $-CH_BOCO-$), 4.55 (m, 1, $J_{AB}$ = 11.1 Hz, $J_{AX}$ = 2.6 Hz, $-CH_AOCO-$).

*Anal.* Calcd for $C_{16}H_{12}O_3$: C, 76.17; H, 4.80; O, 19.03. Found: C, 76.33; H, 4.84; O, 19.05.

**7-Aza-3,4-benzo-7-benzyl-2-oxa-5-phenylbicyclo[3.3.0]octan-6-one (9).**—A sample of the mixed bromo esters **7a** and **7b** (1.8 g of an oil obtained from the mixed dibromides **6**) was treated with benzylamine (10 ml) and heated on the steam bath for 16 hr. Excess amine was removed by distillation (<100°) under reduced pressure. The residue was treated with dry ether and the insoluble benzylamine hydrobromide (0.8 g, mp 220–223°) was removed by filtration. The filtrate was washed with dilute HCl and water and solid product (0.45 g, mp 165–167°) was recovered from the concentrated extract. One recrystallization from ethanol afforded pure lactam **9**: mp 167–168°; ir ($CHCl_3$) 1635 $cm^{-1}$ (lactam C=O); nmr $\delta$ 7.1 (m, 14, ArH), 5.16 (m, 1, $J_{AX}$ = 4.6 Hz, $J_{BX}$ = 7.6 Hz, $-OCH_X-$), 4.77 (d, 1, $J_{CD}$ = 14.5 Hz, $C_6H_5CH_CN-$), 4.37 (d, 1, $J_{CD}$ = 14.5 Hz, $C_6H_5CH_DN-$), 3.71 (m, 1, $J_{AB}$ = 12 Hz, $J_{BX}$ = 7.6 Hz, ring-$CH_B$-N-), 3.52 (m, 1, $J_{AB}$ = 12 Hz, $J_{AX}$ = 4.6 Hz, ring-$CH_A$-N-).

*Anal.* Calcd for $C_{23}H_{19}NO_2$: C, 80.91; H, 5.61; N, 4.11; O, 9.37. Found: C, 80.74; H, 5.60; N, 4.29; O, 9.50.

When a sample of the pure *trans*-bromo ester **7a**, mp 102–103°, was submitted to the foregoing procedure, none of the lactam **9** was detectable (ir) in the product. Instead, a liquid amino ester was produced from which a crude solid hydrochloride could be derived. However, this salt resisted all attempts at purification for more precise characterization.

**Registry No.**—**6a**, 25236-51-5; **6b**, 25236-52-6; **7a**, 25282-55-7; **7b**, 25236-53-7; **8**, 25236-54-8; **9**, 25236-55-9; **12**, 25236-56-0.

**Acknowledgments.**—We are indebted to Mrs. Evelyn Baker for the tlc tests of purity, to Mrs. Ruth Stanaszek for the nmr spectra, to Dr. Milton Levenberg for calculations of some of the theoretical nmr spectra, to Mr. Victor Rauschel for the microanalyses, and to Mr. Wm. Washburn for the infrared spectra.

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## Concerning the "Conjugation" of Cyclopropyl with an Adjacent Activated Olefinic Group. An Electrochemical Approach

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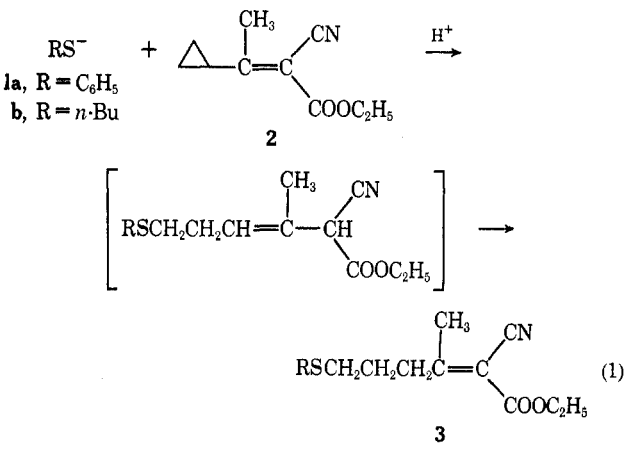
The possibility of conjugation between a cyclopropyl group and a carbon double bond has gained much attention.[1] While the data from uv spectroscopy indicated an affirmative answer for the excited state,[2] the interpretation of the results of hydrogenating such systems catalytically[3] or by sodium in liquid ammonia[4] is ambiguous. The report[1] that mercaptide ion (**1**) reacted with ethyl 2-cyano-3-cyclopropyl-2-butenoate (**2**) to yield a product (**3**) resulting from a formal 1,6 addition was rationalized as resulting from nucleophilic attack upon a conjugated system including the cyclopropyl group. Attempts to use a variety of secondary amines as nucleophiles failed.

(1) J. M. Stewart and D. R. Olsen, *J. Org. Chem.*, **33**, 4534 (1968), and references cited therein.

(2) M. J. Jorgenson and T. Leung, *J. Amer. Chem. Soc.*, **90**, 3769 (1968).

(3) E. F. Ullman, *ibid.*, **81**, 5386 (1959); M. T. Wuesthoff and B. Rickborn, *J. Org. Chem.*, **33**, 1311 (1968).

(4) H. M. Walborsky and J. B. Pierce, *ibid.*, **33**, 4102 (1968).




(1)

Since it is well known that extension of the conjugation of activated olefins[5] leads to a substantial anodic shift in the reduction potential of the olefins[6] and since reductive coupling in such a system is largely through the $\omega$ position,[5] it would be interesting to compare the behavior of **2** and its 3-*n*-propyl (**4**) analog,[7] ethyl 2-cyano-3-methyl-2-hexenoate, under electrolytic conditions and to assess by this means the contribution of the cyclopropyl group to conjugation. While **4**, because of steric conditions, would not be expected to undergo reductive coupling at the 3 position, **2** could reductively couple if opening of the cyclopropyl ring made available an unhindered position.

Polarographic studies (Table I) showed that the cyclopropyl group, even when adjacent to an electron-withdrawing group (**6**, **7**) is not electroreducible. The substances $RC(CH_3)=C(CN)COOC_2H_5$ were, as expected, reducible; however, changing R from ethyl (**5**) to *n*-propyl (**4**) to cyclopropyl (**2**) had virtually no effect upon the half-wave potential. This shows that only the activated olefinic group is involved in the reduction.

Compounds **2**, **4**, and **5** showed only one reduction wave in anhydrous DMF or in 10% aqueous DMF.[8] That this was a one-electron wave was demonstrated unequivocally for **4** which is capable at most of undergoing a two-electron reduction under these conditions: addition of phenol, a more effective proton donor than water, to the polarographic solution virtually doubled the wave height. The same result was then also observed with **2**. The ability of the first reduction species, an anion radical, to escape protonation by water in many cases is not a new phenomenon (*cf.* ref 10). The failure to obtain a second reduction wave for **2** and **4** as well as the complete irreversibility of the reduction of even **4** in DMF (exhibited in cyclic voltammetry at the fastest practical sweep rates, 20 V/sec) remain unexplained.[11] They indicate an extremely rapid follow-

(5) M. M. Baizer and J. D. Anderson, *J. Electrochem. Soc.*, **111**, 226 (1964).

(6) Compare, *e.g.*, the half-wave potentials (V. *vs.* saturated calomel electrode) of the following pairs: acrylonitrile, −1.9, 1-cyano-1,3-butadiene, −1.5; ethyl acrylate, −1.8, ethyl sorbate, ~−1.5; benzalfluorene, −1.67, cinnamylidenefluorene, −1.46.

(7) The uv maximum of **2** ($\lambda_{max}^{CH_3CN}$ 257 m$\mu$, log $\epsilon$ 3.99) showed an auxochromic shift with respect to **3** ($\lambda_{max}^{CH_3CN}$ m$\mu$, log $\epsilon$ 3.87) of +25 $\Delta\lambda$; this is similar to the results with other cyclopropyl olefinic esters.[2]

(8) A similar one-wave reduction was obtained for ethyl 2-cyanosorbate.[9]

(9) J. P. Petrovich, M. M. Baizer, and M. R. Ort, *J. Electrochem. Soc.*, **116**, 743 (1969).

(10) J. Simonet and M. Morenas, *C. R. Acad. Sci., Ser. C*, **269**, 42 (1969).

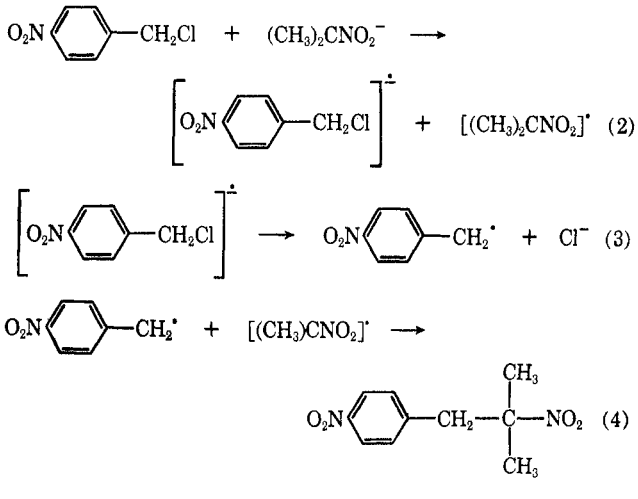
(11) Under these conditions diethyl fumarate showed completely reversible anion radical formation.

up reaction of the anion radicals, perhaps fragmentation or reaction with solvent or disproportionation; the elucidation of these phenomena is not critical to the argument presented below.

Macroelectrolysis of **4** (Table II) under conditions which have successfully yielded reductively coupled products from a variety of activated olefins[12] yielded the saturated derivative, ethyl 2-cyano-3-methyl hexanoate (**8**) but no hydro dimer. About 25% of **4** was simultaneously cleaved hydrolytically to methyl *n*-propyl ketone (**9**) and cyanoacetic ester (**10**) in a reversal of the method of synthesis. Macroelectrolysis of **2** (Table III) with partial conversion yielded **9**, **8**, **4**, and the products of hydrolytic cleavage **6** and **10**; there was no hydrodimer. Since **6** is not electroreducible, **9** must have arisen by reduction of **2** followed by hydrolysis. The formation of **4** as the major product is interesting. Heterogeneous catalytic hydrogenation with Raney nickel[13] and homogeneous catalysis using Wilkinson's catalyst[14] have been used successfully to reduce selectively the double bond of vinylcyclopropanes. The electrochemical method appears to offer a means of cleaving and reducing the cyclopropyl group and leaving the double bond intact.

The absence of an anodic shift in the polarographic reduction of **2** compared to **4** and the failure of **2** to yield any hydrodimer on electroreduction suggest that the reported reaction (eq 1) of mercaptide with **2**, which we have verified, may not be the result of a nucleophilic reaction but rather a conjugate electron-transfer–radical combination reaction. It is becoming increasingly recognized that this type of sequence obtains in many cases which formally appear to be nucleophilic reactions.[15]

In a reaction (eq 2–4) elucidated by Kerber, *et al.*,[16]



there is an electron-transfer step (eq 2), an intervening chemical reaction (eq 3) and finally a radical combination (eq 4). The 2-nitropropane radical gave a partially resolved esr spectrum but no dimer presumably because it and the *p*-nitrobenzyl radical are present in the same solvent cage and interact according to eq 4.

If the process of eq 1 proceeds by a similar route, the electron-transfer step would yield mercaptide radical and the anion radical of **2**. Cyclic voltammetry indicated that the latter was extremely unstable; macroelectrolyses showed that it does not dimerize. Obtaining a resolved spectrum for this anion radical was therefore, hopeless, but an esr signal (*vide infra*) for mercaptide radical was observed in the course of the reaction.

In the case of the anion radical of **2**, the intervening chemical reaction corresponding to eq 3 above is ring opening and protonation yielding $\cdot CH_2CH_2CH_2C(CH_3)=C(CN)COOC_2H_5$. Combination of this radical with mercaptide radical completes the sequence. No disulfide was found indicating that here too, the final reaction may have occurred in a solvent cage.

Further support for the above proposal was sought by examining the reaction of phenyl mercaptide with **4**. It was anticipated that since addition of mercaptide (anion or radical) to the 3 position of **4** was sterically disfavored, if phenyl mercaptide radical were formed as a result of an electron transfer to **4**, it would have ample opportunity to dimerize. This was indeed the case: when **4** was treated with benzenethiol and a small quantity of sodium ethoxide in refluxing ethanol for 6 hr with careful exclusion of air there was a fifteenfold increase in the quantity of diphenyl disulfide obtained from a blank run without **4**; vpc analysis indicated formation of a miniscule amount of a second product definitely not **8**. The electron-transfer step may be reversible (*cf.* ref 16): extension of the reaction period to 16 hr yielded only 4.8 times the amount of diphenyl disulfide formed in a blank run under identical conditions.

## Experimental Section

**Materials.**—Methyl cyclopropyl ketone **6** (Aldrich Chemical Co., Inc.) was used as received. Ethyl 2-cyano-3-cyclopropyl-2-butenoate **2**,[1] the analogous 3-ethyl **5** and 3-*n*-propyl derivatives **4**,[17] and ethyl 2-cyano-3-*n*-propylbutanoate **8** were prepared according to the literature.

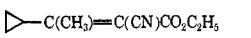
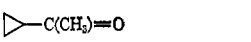
In our hands, the preparation of **2** always yielded more of the solid isomer (methyl/cyano *cis*[1]) than reported. Only the solid isomer was used in this work. Cyclopropyl cyanide **7** was prepared from 4-bromo- rather than 4-chlorobutyronitrile by essentially a literature procedure.[18] Attempts to reduce only the double bond of **2** by palladium–charcoal in ethanol, Raney nickel,[13] or diimide[19] failed. The DMF used in polarographic solutions was purified as described;[9] when used in macroelectrolyses the final purification through a molecular sieve was omitted. Tetra-*n*-butylammonium iodide (polarographic grade, Southwestern Analytical Chemicals) was used as received. Tetra-*n*-heptylammonium iodide (Eastman Organic Chemicals) was recrystallized from ethyl acetate. Tetraethylammonium *p*-toluenesulforate (Aldrich Chemical Co., Inc.) was recrystallized from acetone.

**Equipment.**—The polarograph was a Sargent Model XXI. The dropping mercury electrode constants were $m$ = 1.08 mg/sec, $t$ = 6.2 sec, $m^{2/3}t^{1/6}$ = 1.455. Standard polarographic H cells were used throughout. The polarograms were recorded against a saturated calomel electrode as the reference using 0.1 *M* supporting electrolyte in dimethylformamide as solvent. Cell resistances were around 1000 ohms and no correction was made for *ir* drop in the cell. The cells used for macroelectrolyses

(12) M. M. Baizer, J. D. Anderson, J. H. Wagenknecht, M. R. Ort, and J. P. Petrovich, *Electrochim. Acta*, **12**, 1377 (1967).
(13) M. T. Wuesthoff and B. Rickborn, *J. Org. Chem.*, **33**, 1311 (1968).
(14) C. H. Heathcock and S. R. Poulter, *Tetrahedron Lett.*, 2755 (1969).
(15) K. A. Bilevich and O. Yu. Okhlobystin, *Russ. Chem. Rev.*, **37**, 954 (1968); K. A. Bilevich, N. N. Pubnov, and O. Yu. Okhlobystin, *Tetrahedron Lett.*, 3465 (1968).
(16) R. C. Kerber, G. W. Urry, and N. Kornblum, *J. Amer. Chem. Soc.*, **87**, 4520 (1965). See also F. J. Smentowski, *ibid.*, **85**, 3036 (1963).
(17) A. C. Cope, C. M. Hofmann, C. Wyckoff, and E. Hardenbergh, *ibid.*, **63**, 3452 (1941).
(18) G. M. Lampman, D. A. Horne, and G. D. Hager, *J. Chem. Eng. Data*, **14**, 396 (1969).
(19) J. W. Hamersma and E. I. Snyder, *J. Org. Chem.*, **30**, 3985 (1965).

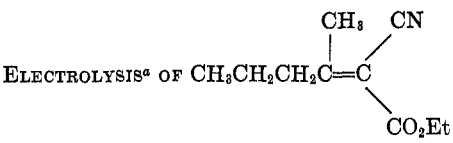
TABLE I

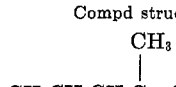
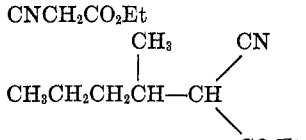
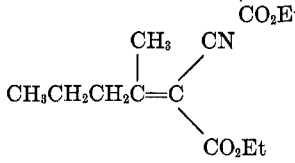
POLAROGRAPHIC DATA

| Compd No. | Structure | Anhydrous DMF $-E_{1/2}$[a] | Anhydrous DMF $Id$[b] | DMF with proton donor $-E_{1/2}$ | DMF with proton donor $Id$[b] |
|---|---|---|---|---|---|
| 2 |  | 1.72 | 1.35[c] | 1.68[d] | 1.07 |
| | | | | 1.71[e] | 2.73 |
| 4 | $CH_3CH_2CH_2C(CH_3)=C(CN)CO_2C_2H_5$ | 1.75 | 1.32 | 1.70[d] | 1.07 |
| | | | | 1.75[e] | 2.45 |
| 5 | $CH_3CH_2C(CH_3)=C(CN)CO_2C_2H_5$ | 1.74 | 1.36 | 1.70[d] | 1.08 |
| 6 |  | No wave | | | No wave[d] |
| 7 |  | No wave | | | No wave[d] |

[a] $E_{1/2}$ (V) *vs.* sce in dimethylformamide (DMF) with 0.1 *M* tetraheptylammonium iodide. [b] $Id$ = height wave (mm) × sensitivity ($\mu$a/mm)/concentration (mmol/l. × $m^{2/3}t^{1/6}$) (see Experimental Section); concentration of depolarizer ~1.5 × $10^{-3}$ *M*. [c] Substance produced "maximums". [d] With 10% $H_2O$. [e] With phenol in 0.1 *M* tetrabutylammonium iodide.

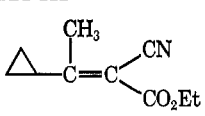
TABLE II

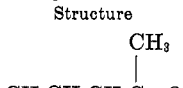
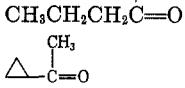
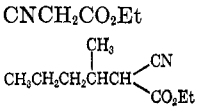
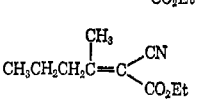
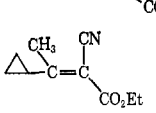
ELECTROLYSIS[a] OF 

| Catholyte: Depolarizer, mol | Salt, g | DMF, ml | $H_2O$, ml | HOAc, ml | Products recovered: Compd no. | Compd structure | mmol | A hr equiv |
|---|---|---|---|---|---|---|---|---|
| 0.100 | 10.0 | 50 | 5 | 1.0 | 9 |  | 26 | |
| | | | | | 10 | $CNCH_2CO_2Et$ | 23 | |
| | | | | | 8 |  | 21 | 1.12 |
| | | | | | 4 |  | 33.4 | |

[a] Conditions: mercury cathode, 23°, 0.5 A for 150 min.

TABLE III

ELECTROLYSIS[a] OF 

| Catholyte: Depolarizer, mol | Salt, g | DMF, ml | $H_2O$, ml | HOAc, ml | Products recovered: Compd No. | Compd Structure | mmol | A hr equiv |
|---|---|---|---|---|---|---|---|---|
| 0.100 | 10.0 | 50 | 5 | 1.0 | 9 |  | 4.2 | 0.225 |
| | | | | | 6 |  | 9.7 | |
| | | | | | 10 | $CNCH_2CO_2Et$ | 13.9 | |
| | | | | | 8 |  | 1.39 | 0.149 |
| | | | | | 4 |  | 6.80 | 0.365 |
| | | | | | 2 |  | 61.5 | |

[a] Conditions: mercury cathode, 23°, 0.8 A for 225 min.

with mercury cathodes were the one previously described[20] and also a scaled-down version cathode area 38.4 cm², catholyte volume ~75 ml. The vpc analyses were performed on a Varian Series 1200, Hi-Fi III gas chromatograph (single column, single flame ionization detector). The two columns used were both 6-ft, 1/8 in. diameter stainless steel packed respectively with 10% Carbowax 20M on 80–100 mesh Chromosorb W (NAW) and 3% SE-30 on 100–200 mesh Varaport 30.

The esr spectra were obtained using a Varian V-4502 spectrometer equipped with a 12 in. magnet. The modulation frequency was 100 kHz. The Varian rapid scan cavity was used in conjunction with the Varian rapid scan unit and the C-1024 time averaging computer. The microwave frequency under experimental conditions was measured with a Hewlett-Packard X350A wavemeter and was 9.544 GHz. The sweeps were calibrated using a basic aqueous solution of potassium peroxylamine disulfonate ($g$ = 2.0055, $a$ = 13 G) and were found to be satisfactorily linear.

**Procedures.**—The macroelectrolyses were carried out under the conditions summarized in Tables II and III. The mercury was then separated from the catholyte and the latter diluted with water and thoroughly extracted with methylene chloride. The extracts were washed and dried over anhydrous magnesium sulfate. The analyses were performed as follows. The excess methylene chloride was carefully removed from the products using a rotary evaporator and a vacuum pump (10 mm), keeping the water bath at room temperature. When most of the $CH_2Cl_2$ had been removed, the temperature of the water bath was increased to 50° and the vacuum increased to 5 mm. The low boiling products were collected in two Dry Ice–acetone traps in series.

The above distillate typically contained the ketones and methylene chloride. These products were analyzed neat at 70° using 10% Carbowax 20M.

The residue from the above stripping, which contained the bulk of the products, was analyzed (20% in acetone) using 10% Carbowax 20M, programmed from 120 to 220° at 10° min⁻¹. Relative retention times and relative response factors were calculated using diethyl malonate as an internal standard. Components were qualitatively determined by subsequent injection of authentic samples prepared independently.

For determining the esr spectra, separate solutions of 1.65 g of **1** (with R = $C_6H_5$) in 5 ml of ethanol (with 0.025 g of sodium) and of 2.25 g of **2** in 20 ml of ethanol were mixed under exclusion of oxygen. The sample tubes were sealed under nitrogen and heated for a few minutes at 50–70° before they were transferred to the esr cavity at room temperature. A well-resolved five-line spectrum was detected under the proper modulation conditions (optimum conditions about 0.75 peak to peak modulation). The spectra were very weak and required many hours of data accumulation. Typically, accumulation of 900 scans over 8 hr gave a signal to noise ratio of about 12. The intensity ratios of the peaks varied with the modulation amplitude, pointing to the fact that the peaks were of different widths and shapes and contained unresolved features; at 0.75 G peak to peak modulation the ratio was 1:1.6:2.6:1. Because of the weakness of the signals it was not possible to resolve additional structure by lowering the modulation amplitude. The same five-line spectrum (although much weaker) was also obtained when **2** was excluded, but oxygen was allowed to come into contact with the solution. This observation, together with the explanations that follow, lead us to attribute the spectrum to the phenylmercaptyl radical. The $g$ factor was found to be 2.030. This value is close to the isotropic $g$ value of 2.040 attributed by Zandstra and Michaelsen[21] to phenylmercaptyl radical produced during the pyrolysis of diphenyldisulfide. This assignment has been criticized by Schmidt[22] who found a much smaller $g$ factor (isotropic $g$ = 2.007) for the supposed phenylmercaptyl radical produced by uv irradiation of diphenyl disulfide. It should be noticed that in both references the radicals were observed in a frozen matrix, and that therefore no hyperfine structure was detected that could support the assignments. On the other hand, the hyperfine structure of phenoxyl radical has been resolved by Stone and Waters[23] who reported the following hyperfine constants: $a_{2,6}$ = 6.65 G, $a_4$ = 10.1 G, $a_{3,5}$ = 1.8 G. Our spectrum can be interpreted in terms of hyperfine constants $a_{2,6}$ = 2.7 G, $a_4$ = 5.4 G, $a_{3,5}$ = 1.0 G. The splitting with the 3,5 hydrogens was too small to be resolved, but from the observed linewidth an upper limit of about 1 G was estimated for $a_{3,5}$. Compared to the phenoxy radical, the much smaller hyperfine constants observed in our case are consistent with the fact that in mercaptyl radicals the spin density is concentrated on the sulfur atom most of the time.[21]

(20) M. M. Baizer, *J. Electrochem. Soc.*, **111**, 215 (1964).
(21) P. J. Zandstra and J. D. Michaelsen, *J. Chem. Phys.*, **39**, 933 (1963).
(22) U. Schmidt, *Organosulfur Chem.*, 75 (1967).
(23) T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 213 (1964).

**Registry No.**—**2**, 17407-28-2; **4**, 25528-05-6; **5**, 25528-06-7.

## The Cyclization of Epoxy Olefins. VIII. Attempted π Routes to Bridged Bicyclic Systems[1]

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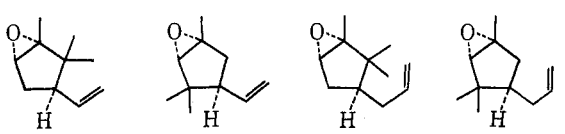
*Department of Chemistry, Emory University, Atlanta, Georgia 30322*

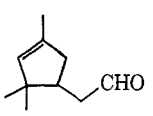
*Received January 20, 1970*

In a previous report[3] on work in the area of epoxide cyclizations we described attempts to form the bornane skeleton by closure of **1**. These experiments led only to noncyclic rearrangement products. As suggested previously,[3,4] the transition state for cyclization of compounds like **1** appears to allow for little overlap between the orbitals of the double bond and the ring carbon atom. In addition, one of the rearrangement reactions of **1** has as a strong driving force the relief of the crowding of groups on three adjacent positions of a cyclopentane ring. In order to investigate these factors we chose to examine the reactivities of three related epoxy olefins **2**, **3**, and **4**.



**1** **2** **3** **4**

In structure **2** the propensity of the α-campholene system for rearrangement[5] has been eliminated since this compound no longer features 1, 2, 3 ring substitution. In addition, opening of the epoxide ring of **2** in either a cyclization or a ketone forming reaction should occur at the tertiary center which in this case is insulated from the *gem*-dimethyl group. With **3** the steric difficulties encountered with **1** in bringing an olefinic carbon and a ring carbon within bonding distance should be diminished. Compound **4** in turn embodies both structural variations discussed for **2** and **3**.



**5**

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(2) Coca Cola Research Fellow, 1963–1965.
(3) D. J. Goldsmith and C. J. Cheer, *J. Org. Chem.*, **30**, 2264 (1965).
(4) L. J. Dolby and R. H. Iwamoto, *ibid.*, **30**, 2420 (1965).
(5) (a) F. Tieman, *Chem. Ber.*, **29**, 3006 (1896); (b) E. R. Buchman and H. Sargent, *J. Org. Chem.*, **7**, 140 (1942).