Vinylalkylidenecyclopropanes from *gem*-Dichlorocyclopropanes by HCl Eliminations

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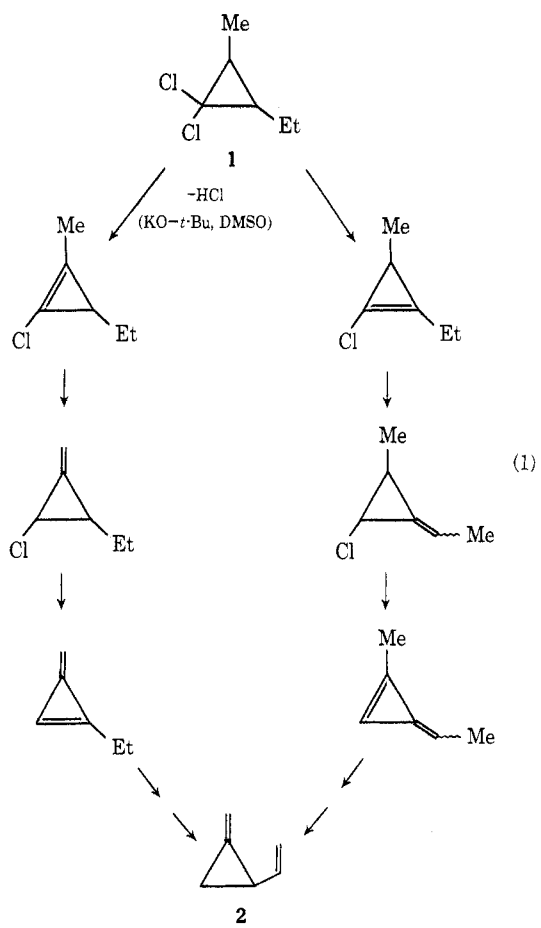
Vinylalkylidenecyclopropanes are produced by treating *gem*-dichlorocyclopropanes with potassium *tert*-butoxide in dimethyl sulfoxide (DMSO). Highly strained cyclopropenes and alkylidenecyclopropenes are probable intermediates. Prolonged exposure of vinylethylidenecyclopropane to the strongly basic medium resulted in further rearrangement to give *cis*- and *trans*-1,2-divinylcyclopropane. The cis isomer undergoes a spontaneous Cope rearrangement and bond migration to form 1,3-cycloheptadiene.

Alkali-induced elimination reactions of halo- and dihalocyclopropanes offer simple routes to certain cyclopropenes.[2] More typically, isomerization products[3] or nucleophilic addition adducts[4] are observed, particularly if the base is a strong nucleophile or the cyclopropene is highly strained. This suggested that appropriately substituted dihalocyclopropanes would be suitable precursors for previously unknown vinylalkylidenecyclopropanes. This paper presents more complete data for several systems which demonstrate the generality of this reaction.[5]

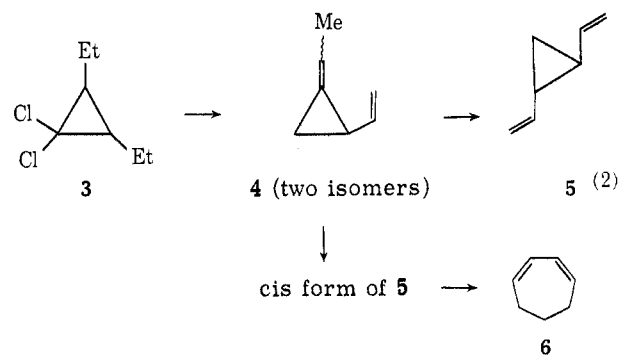
The simplest example is the formation of vinylmethylenecyclopropane (**2**) from 1,1-dichloro-2-ethyl-3-methylcyclopropane (**1**).[5] The reaction proceeds efficiently using potassium *tert*-butoxide in dimethyl sulfoxide (DMSO).



(1)

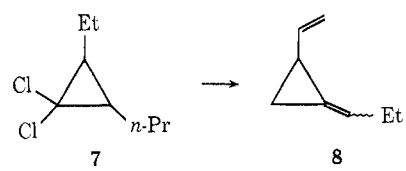
The conversion of **1** to **2** is interpreted as proceeding by the two closely related paths shown in eq 1, which avoid high-energy intermediate cyclopropenyl anions.[6] These paths rationalize the absence of 1-ethynyl-2-methylcyclopropane, which might have arisen if there had been consecutive HCl eliminations toward the ethyl substituent. Both paths proceed through relatively stable allylic anions except for the initial HCl elimination. As anticipated, attempts to detect intermediate methylenecyclopropenes between **1** and **2** were unsuccessful.

1,1-Dichloro-2,3-diethylcyclopropane (**3**) allows isomerization of the initial product, vinylethylidenecyclopropene (**4**), to divinylcyclopropanes. However, it was



(2)

possible to isolate **4** (syn-anti mixture) in 80–90% yield after 30 min at 25°. After 2.3 hr, the yields were 34% **4**, 5% **5**, and 14% **6**. These results are all in accord with reports that *trans*-1,2-divinylcyclopropane (**5**) is stable at 25° while *cis*-**5** spontaneously undergoes a Cope rearrangement at −40°.[7] The immediate product of the Cope rearrangement would be 1,4-cycloheptadiene, but this would isomerize to the 1,3 isomer (**6**) under basic conditions, as was observed. Dichloride **7** gave



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(2) S. W. Tobey and R. West, *Tetrahedron Lett.*, 1180 (1963); P. D. Gardner, B. A. Loving, and T. C. Shields, *Chem. Commun.*, 556 (1967).

(3) J. A. Carbon, W. B. Martin, and L. R. Swett, *J. Amer. Chem. Soc.*, **80**, 1002 (1958); C. L. Osborn, T. C. Shields, B. A. Shoulders, J. F. Krause, H. V. Cortez, and P. D. Gardner, *ibid.*, **87**, 3158 (1965).

(4) K. B. Wiberg, R. K. Barnes, and J. Albin, *ibid.*, **79**, 4994 (1957); T. C. Shields, B. A. Shoulders, J. F. Krause, C. L. Osborn, and P. D. Gardner, *ibid.*, **87**, 3026 (1965).

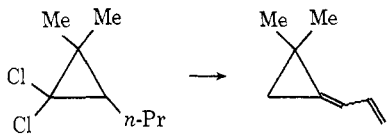
(5) For preliminary results see T. C. Shields, W. E. Billups, and A. R. Lepley, *ibid.*, **90**, 4749 (1968); T. C. Shields and W. E. Billups, *Chem. Ind. (London)*, 619 (1969).

(6) R. Breslow, "Organic Reaction Mechanisms," W. A. Benjamin, New York, N. Y., 1966, p 26.

(7) E. Vogel, K. H. Ott, and K. Gajek, *Justus Liebigs Ann. Chem.*, **644**, 172 (1961); E. Vogel and R. Erb, *Angew. Chem., Int. Ed. Engl.*, **1**, 53 (1962); W. v. E. Doering and W. R. Roth, *ibid.*, **2**, 115 (1963).

a single major product identified as vinylpropylidenecyclopropane (**8**).

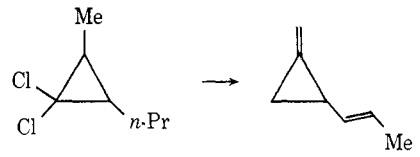
1,1-Dichloro-2,2-dimethyl-3-propylcyclopropane (**9**) forces both HCl eliminations to take place in the same



9 **10**

direction. The product was now a diene (**10**), 1-allylidene-2,2-dimethylcyclopropane (syn–anti mixture), and was isolated in 60% yield.

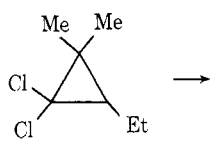
1,1-Dichloro-2-methyl-3-propylcyclopropane (**11**) introduces the opportunity for producing a conjugated



11 **12**

diene. However, 1-methylene-2-propenylcyclopropane (**12**) was produced in strict analogy to the formation of **1**.

1,1-Dichloro-2,2-dimethyl-3-ethylcyclopropane (**13**) introduces a constraint in that products of the type



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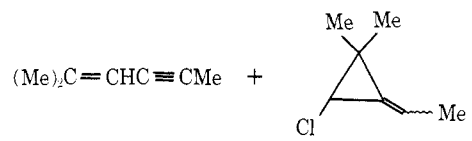
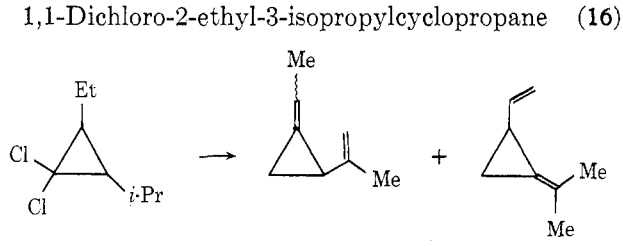


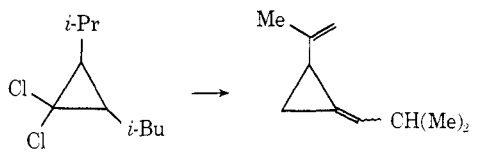
14 **15**

formed previously are not possible. The formation of 2,2-dimethylethynylcyclopropane was still avoided. Instead a complex mixture of products whose composition was dependent upon reaction time was produced; however, at an early stage of the reaction 2-methyl-2-hexen-4-yne (**14**) was shown to be the major product. A second product, provisionally identified as 1-chloro-2,2-dimethyl-3-ethylidenecyclopropane (**15**), was also detected.

1,1-Dichloro-2-ethyl-3-isopropylcyclopropane (**16**)



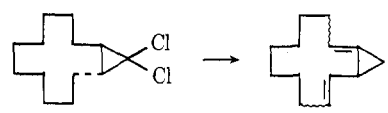
16 **17** **18**



19 **20**

and 1,1-dichloro-2-isobutyl-3-isopropylcyclopropane (**19**) are representative of more highly branched dichlorocyclopropanes. The former gave a mixture of **17** and **18** (3.5:1), whereas **19** gave **20** (>95%).

The elimination–isomerization reaction sequence also occurs readily when dichlorocarbene adducts of some cyclic olefins are treated with KO-*t*-Bu–DMSO. Thus, 13,13-dichlorobicyclo[10.1.0]tridecane (**21**) gave **22** in 94% yield.



21 **22**

Experimental Section

General.—Nmr spectra were obtained at 60 Mc with TMS internal standard, and signal positions are reported in δ units. Infrared spectra were recorded using Beckman IR-5-A and IR-8 spectrometers. Ultraviolet spectra were obtained in cyclohexane solvent with a Cary Model 14 spectrophotometer.

Materials.—Dimethyl sulfoxide (Crown Zellerbach or Aldrich) was dried over calcium hydride. 2-Pentene (Phillips Petroleum Co.) and other olefins (Chemical Samples Co.) were used without further purification. Potassium *tert*-butoxide was K and K, Alfa Inorganics, or MSA Corp. material. Dichlorocyclopropanes were prepared by the method of Skell and Garner.[8]

Vinylmethylenecyclopropane (**2**).—The preparation of this compound from **1** is representative of the other preparations outlined. Potassium *tert*-butoxide (84 g, 0.75 mol) was added to 400 ml of dimethyl sulfoxide in a creased flask fitted with stirrer and condenser. 1,1 Dichloro-2-ethyl-3-methylcyclopropane (**1**) (38 g, 0.25 mol) was added dropwise at 25° under nitrogen (external cooling). After 2 hr, product was isolated in 62% yield (determined by gc) by addition to ice–water, pentane extraction, drying, and removal of pentane at 25°. The thermal instability of **2** necessitated purification by preparative glpc (10 ft × 0.5 in. column, Varian FFAP packing operated at 45°). Both injection port and detector were kept below 100° to minimize rearrangement to 3-methylenecyclopentene.[5]

Anal. Calcd for C_6H_8: C, 89.9; H, 10.1; mol wt, 80. Found: C, 89.6; H, 10.3; mol wt, 80 (mass spectrum, **2** probably isomerized in the heated inlet).

Spectra follow: ir (film) 5.71, 5.80, 6.12, 7.11, 8.41, 8.90, 9.22, 9.75, 10.15, 10.6, 11.2 (broad), 11.6, and 12.06 μ; nmr (CCl_4) δ 1.0 (m) and 1.46 (m, 1 H each, cyclopropyl $-CH_2-$), 2.0 (m, 1 H, cyclopropyl), 5.45 (m, $=CH_2$), and 4.7–5.8 (m, vinyl).

Vinylethylidenecyclopropane (**4**).—Addition of 1,1-dichloro-2,3-diethylcyclopropane (**3**) to KO-*t*-Bu–DMSO produced a mixture of *syn*- and *anti*-**4** (~1:1)[9] in 80–90% yield after 30 min at 25°. After 2.3 hr **4**, **5**, and **6** were produced in yields of 34, 5, and 14%. The products were isolated by preparative glpc using columns packed with Varian FFAP or propylene carbonate[9] packing.

Identification of **4** rested on its spectra: ir (film) 6.12 (C=C) and 11.2 μ (methylenecyclopropane); nmr (CCl_4) δ 1.76 (m, 3 H, methyl), 0.65–2.20 (m, 3 H, cyclopropyl), 4.60–5.4 (m, 3 H, vinyl), and 5.70 (m, 1 H, olefinic). The nmr spectra of *syn*- and *anti*-**4** were virtually indistinguishable. The mass spectrum had a parent peak of 94, as calculated.

The ir and nmr spectra of **5** coincide with those of an authentic sample.[10] The nmr spectrum of **6** [δ 1.92 (m, 4 H, allylic), 2.31 (m, 4 H, $-CH_2CH_2-$), and 5.69 (m, 4 H, vinyl H)], is identical with that reported previously.[11]

Vinylpropylidenecyclopropane (**8**).—Treatment of 1,1-dichloro-2-ethyl-3-propylcyclopropane (**7**) with KO-*t*-Bu in DMSO for 30 min produced **8** in 70–80% yield: nmr multiplets at δ 1.02, 1.42, 2.12 (9 H), 4.65–5.6 (3 H, vinyl), and 5.7 (1 H, olefinic).

(8) P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, **78**, 3409 (1956).

(9) Syn and anti isomers separated on a 7-ft propylene carbonate column operated at room temperature. We thank Mr. Steven Vanderpool for assistance with this separation.

(10) We thank Professor E. Vogel for providing these spectra.

(11) R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 594 (1961).

1-Allylidene-2,2-dimethylcyclopropane (10).—This product formed in 60% yield from 1,1-dichloro-2,2-dimethyl-3-propylcyclopropane (9) after treatment with 3 equiv of base for 75 min at 25°; it was isolated by flash distillation.

Anal. Calcd for C_8H_{12}: C, 88.2; H, 11.2; mol wt, 108. Found: C, 88.5; H, 11.5, mol wt, 108 (mass spectrum).

Spectra follow: ir (film) 5.55, 6.19, 6.95 (broad), 7.27, 8.03, 8.89, 10.1 (very broad), and 11.15 μ (broad); nmr δ 0.98 (m, 2 H, cyclopropyl), 1.19 (s) and 1.23 (s, 6 H total, methyls), 4.85–5.5 (m, 2 H, $=CH_2$), and 6.0–6.8 (m, 2 H, $-CH=CH-$); λ_{max} 230 nm (ϵ 21,900). The nmr bands at δ 1.19 and 1.23 are interpreted as due to the *gem*-dimethyl on the syn and anti isomers. The area ratio of the δ 1.23 to 1.19 band was 1.2:1. It is not known which band corresponds to which isomer.

1-Methylene-2-propenylcyclopropane (12).—1,1-Dichloro-2-methyl-3-propylcyclopropane (11) afforded a major product in 40–50% yield when treated with a threefold excess of the base for 25 min at 25°. **12** was purified by preparative glpc, and showed strong infrared absorption at 10.22 μ, characteristic of methylenecyclopropanes. The nmr spectrum showed one proton signal at δ 0.98, 1.5, 2.2 (cyclopropyl), a methyl doublet at 1.74 (J = 6.5 cps), and an olefinic pattern extending from 4.6 to 5.7.

2-Methyl-2-hexen-4-yne (8).—1,1-Dichloro-2,2-dimethyl-3-propylcyclopropane (7) produced two products when treated with base for 25 min. The major product (57%) was isolated by preparative glpc and identified as **8** by its nmr spectrum:[12] signals at δ 1.92 (s, 3 H, $-C\equiv CCH_3$), 1.7 (m, 6 H, isopropylidene), and 5.48 (m, 1 H, olefinic). A second product, obtained in impure form, is provisionally identified as 1-chloro-2,2-dimethyl-3-ethylidenecyclopropane on the basis of an nmr singlet at δ 3.28 ($-CHCl-$) and by analogy to the formation of 1-chloro-2,2-dimethyl-3-methylenecyclopropane from 1,1-dichloro-2,2,3-trimethylcyclopropane.[13]

1-Ethylidene-2-isopropenylcyclopropane (17) **and 1-Isopropylidene-2-vinylcyclopropane** (18).—1,1-Dichloro-2-ethyl-3-isopropylcyclopropane (16) produced **17** (56%) and **18** (16%) when treated with base: nmr (**17**) δ 1.2 (cyclopropyl), 1.6 (3 H isopropenyl methyl), 1.8 (3 H, ethylidene methyl) overlapping a multiplet extending to 2.3 (cyclopropyl) 4.65 (2 H, methylene), and 5.8 (q, 1 H, olefinic); nmr (**18**) δ 0.6–2.3 (3 H, cyclopropyl), 1.78 (6 H, isopropylidene), 4.5–5.7 (3 H, vinyl).

1-Isobutylidene-2-isopropenylcyclopropane (20) was produced in 48% yield from 1,1-dichloro-2-isobutenyl-3-isopropylcyclopropane: nmr δ 1.05 (6 H, isopropyl methyls), 0.8–2.2 (3 H, cyclopropyl), 1.58 (3 H, isopropenyl methyl), 2.5 (1 H, isopropyl), 4.65 (2 H, methylene), and 5.72 (1 H, olefinic).

Bicyclo[10.1.0]trideca-1,10-diene (22).—Addition of 13,13-dichlorobicyclo[10.1.0]tridecane (21) to KO-*t*-Bu–DMSO provided **22** in 94% yield: nmr δ ~1.1, 1.4, 1.15 (~17 H), 4.74–6.1 (3 H); ir (film) prominent absorptions at 6.17, 6.87, 7.0, 7.6, 10.2, and 13.9 μ.

Registry No.—**2**, 19995-92-7; **4**, 22703-93-1; **10**, 19985-76-3.

Acknowledgment.—W. E. B. gratefully acknowledges the Research Corporation for partial support of this work.

(12) I. A. Favorskaya, E. M. Auvinene, and Y. P. Artsybasheva, *Zh. Obshch. Khim.*, **28**, 1785 (1958); *Chem. Abstr.*, **52**, 1097*i* (1958).

(13) T. C. Shields and W. E. Billups, *Chem. Ind. (London)*, 1999 (1967).

The Vinyl Anion. II

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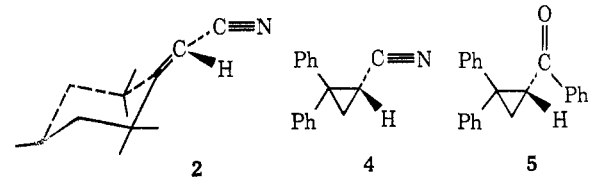
The exchange and racemization reactions of 2,2,4,6,6-pentamethylcyclohexylideneacetophenone (1) with sodium methoxide in methanol have been investigated. The ketone 1 exhibits only a moderate degree of retention of optical activity (30% at 50°), k_e/k_r = 1.43. This contrasts with the high degree of retention (>99% at 50°) observed with the corresponding 2,2,4,6,6-pentamethylcyclohexylideneacetonitrile (2). On the basis of primary hydrogen–deuterium and deuterium–tritium isotope effects, it is suggested that in both the base-catalyzed exchange and racemization reactions of 1 the rate-determining step is proton abstraction. Both (−)-1 and its precursor (−)-2,2,4,6,6-pentamethylcyclohexylideneacetic acid [(−)-3] have been tentatively assigned the *R* configuration on the basis of their Cotton effects.

Recently this laboratory reported that the vinyl anion obtained by reaction of 2,2,4,6,6-pentamethylcyclohexylideneacetonitrile (2) with sodium methoxide in methanol was capable of maintaining its configuration (>99% retention at 50°). Moreover, based on the small kinetic isotope effect for the hydrogen isotope exchange reactions of 2, it was proposed that proton abstraction was *not rate determining* in either the exchange or racemization reactions.[2]

These observations paralleled analogous data obtained in the investigation of the configurational stability of the cyclopropyl anion similarly derived from 1-cyano-2,2-diphenylcyclopropane (4) which indicated >99% retention at 50–75°.[3] In contrast to the behavior exhibited by the anion derived from **2** and **4**, however, the cyclopropyl anion generated from 1-benzoyl-2,2-diphenylcyclopropane (5) by base-catalyzed proton abstraction showed only moderate retention of optical activity (~27% retention at 75°). Further, the normal kinetic isotope effects observed in the isotope exchange reactions of **5** suggested that proton abstraction was rate limiting in both the exchange and racemization reactions.[4] This article presents our data on the rates of the sodium methoxide catalyzed exchange and racemization reactions of 2,2,4,6,6-pentamethylcyclohexylideneacetophenone (1).



2 4 5

Results and Discussion

Synthesis.—The synthesis of racemic 2,2,4,6,6-pentamethylcyclohexylideneacetophenone is outlined in

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(2) H. M. Walborsky and L. M. Turner, *J. Amer. Chem. Soc.*, **94**, 2273 (1972).

(3) H. M. Walborsky and J. M. Motes, *ibid.*, **92**, 2445 (1970).

(4) J. M. Motes and H. M. Walborsky, *ibid.*, **92**, 3697 (1970).