n^{25}D 1.4603, n^{20}D 1.4621. This product, on gas–liquid partition chromatographic analysis,[15] showed a single peak of the same retention time as the isomeric mixture of methyl 3- and 4-methyl-3-cyclohexene-1-carboxylates, b.p. 91–93° at 20 mm. (lit.[6] b.p. 85–86° at 15 mm.), n^{25}D 1.4610, n^{20}D 1.4630 (lit. n^{25}D 1.4606,[6] n^{20}D 1.4655[16]), prepared by thermal condensation at 130–140° for 24 hr. On alkaline hydrolysis the product of the present experiment yielded, after repeated recrystallization from hexane,[6] 4-methyl-3-cyclohexene-1-carboxylic acid, m.p. 99.2–100.2° (lit.[6] m.p. 98.5–99° uncor.). A mixture melting point determination with an authentic sample[6] showed no depression.

Butadiene and Methyl Methacrylate (Expt. 13).—From 30.3 g. (303 mmoles) of methyl methacrylate in a similar way as in expt. 2 was obtained 26.7 g. (57.5%) of methyl 1-methyl-3-cyclohexene-1-carboxylate, b.p. 76–78° (20 mm.), n^{25}D 1.4565, n^{20}D 1.4600 (lit. b.p. 64–65° at 10 mm.,[17] n^{25}D 1.4568,[17] n^{20}D 1.4600[18]). Alkaline hydrolysis yielded 1-methyl-3-cyclohexene-1-carboxylic acid, m.p. 77–79° (from ligroin) (lit.[17] m.p. 78–79°).

2,3-Dimethylbutadiene and Methyl Acrylate (Expt. 14).—2,3-Dimethylbutadiene, 15.1 g. (184 mmoles), in 30 ml. of benzene was added in 5 min. to a solution prepared from 15.9 g. (185 mmoles) of methyl acrylate, 2.5 g. (19 mmoles) of aluminum chloride, and 280 ml. of benzene. The resulting mixture was stirred for 5 hr. at 20°, worked up in the usual way, and yielded on distillation 22.9 g. (74%) of methyl 3,4-dimethyl-3-cyclohexene-1-carboxylate, b.p. 104–106° (20 mm.), n^{25}D 1.4678.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.5; H, 9.6. Found: C, 71.4; H, 9.5.

A colorless viscous oil, 1.9 g., remained in the flask. Alkaline hydrolysis of the ester, with 30% aqueous sodium hydroxide on a boiling water bath, gave 3,4-dimethyl-3-cyclohexene-1-carboxylic acid, m.p. 80–82° (from hexane) (lit.[19] m.p. 83°).

Butadiene and Acrylic Acid (Expt. 16).—Butadiene, 5.4 l. (0.24 mole), was bubbled into a solution of 2.7 g. (14 mmoles) of titanium tetrachloride in 90 ml. of benzene at 20°. To this solution was added 5.1 g. (71 mmoles) of acrylic acid in 10 ml. of benzene in 5 min. at 20°, when the mixture turned to dark red. After stirring 1 hr. the mixture was decomposed with 30 ml. of water, and the benzene solution was washed with water, dried with anhydrous sodium sulfate, and distilled to yield 2.8 g. of a distillate, b.p. 75–128° at 19 mm. Gas–liquid partition chromatographic analysis using a 2.6-m. Silicone DC-550 column showed that it contained approximately 1.5 g. of 3-cyclohexene-1-carboxylic acid, yield 17%.

Reaction between Butadiene and Acrylonitrile (Expt. 18).—To a stirred suspension of 61 g. (457 mmoles) of aluminum chloride and 300 ml. of benzene was added 26.6 g. (502 mmoles) of acrylonitrile in 100 ml. of benzene at 60°. Aluminum chloride dissolved and a large amount of dark red precipitates was formed. Butadiene (0.9 mol.) was bubbled into the mixture in a period of 4 hr. and the reaction mixture was worked up as usual and distilled to yield (i) 2.3 g. of a forerun, b.p. <80° (20 mm.); (ii) 46.0 g. (86%) of 3-cyclohexene-1-carbonitrile, b.p. 80–87° (20 mm.); (iii) 24.7 g. of higher boiling materials, b.p. 90–155° (3 mm.); and (iv) 80 g. of viscous dark red residue. Fraction ii had n^{20}D 1.4742 (lit. b.p. 83° at 20 mm.,[14] n^{20}D 1.4736,[14] n^{20}D 1.4758[20]), and the gas chromatographic retention time and infrared spectrum were identical with those of the authentic sample[14] of 3-cyclohexene-1-carbonitrile. Fraction iii gave on vacuum distillation a center cut, b.p. 102–107° (1 mm.), a mixture of isomeric diphenylbutanes.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.4; H, 8.6; mol. wt., 210. Found: C, 91.7; H, 8.6; mol. wt., 201 (freezing point depression of benzene).

On gas–liquid partition chromatographic analysis using a 2.6-m. PEG-6000 column it gave three peaks, one of which coincided with that of 1,2-diphenylbutane. The infrared spectrum was similar to a superposition of the spectra of 1,1-diphenylbutane[21] and 1,2-diphenylbutane.[8]

---

(15) Columns (2.6-m.) of PEG-600, Silicone DC-550, TCP, and DOP (Shimadzu Seisakusho Ltd., Kyoto) were ineffective in attempted separations of the isomers.

(16) I. N. Nazarov, Yu. A. Titov, and A. I. Kuznetsova, *Dokl. Akad. Nauk SSSR*, **124**, 586 (1959); *Chem. Abstr.*, **53**, 11268 (1959).

(17) J. D. Roberts, A. K. Jeydel, and R. Armstrong, *J. Am. Chem. Soc.*, **71**, 3248 (1949).

(18) H. E. Hennis, *Ind. Eng. Chem., Process Design Develop.*, **1**, 71 (1962).

(19) J. Monnin, *Helv. Chim. Acta*, **41**, 2112 (1958).

(20) A. P. Terent'ev, A. N. Kost, and S. M. Gurvich, *Vestn. Mosk. Univ., Ser. Fiz.-Mat. Estestv. Nauk, No. VIII*, **6**, No. 12, 79 (1951); *Chem. Abstr.*, **47**, 6877 (1953).

(21) "Sadtler Standard Infrared Spectra," Midget Ed., Sadtler Research Laboratories, Philadelphia, Pa., 1959, Spectrum No. 9980.

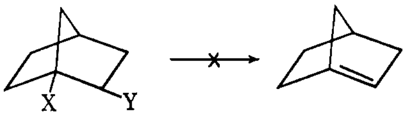
Bredt Rule Interdictions of Cyclopropane Rearrangements. The Vinylnortricyclenes[1]

JEROME A. BERSON AND M. ROBERT WILLCOTT[2]

Department of Chemistry, University of Wisconsin, Madison, Wisconsin

Received March 29, 1965

The Bredt rule[3–5] recognizes the extreme torsion imposed on a hypothetical double bond at the bridgehead of a small bicyclic system. If the "olefinic" carbons in such an environment use sp²-hybrid orbitals for σ-bond formation, the p-orbitals to be used for π-bond formation are nearly orthogonal.[6] The geometry corresponds roughly to that of the transition state for thermal *cis–trans* olefin interconversion and consequently, if its electronic state is singlet, it lies some 60–65 kcal./mole above a hypothetical strainless species.[7] The much discussed[8] possibility that intersystem crossing to a triplet state might lower the energy of the twisted species provides a conceivable way of making this form more accessible, but no violations of the Bredt rule by such a device have ever been reported. In any case, even if the transition state enthalpy for "olefin" formation is lowered by intersystem crossing, the full effect will not be felt in the rate. Because of the change of multiplicity, the benefit is purchased at the expense of a severe drop in the pre-exponential term.[8] Thus, the net result would be that anti-Bredt species (*e.g.*, II) would be kinetically inaccessible by way of conventional olefin-forming reactions, for example, by vicinal elimination from a 1,2-disubstituted norbornane (I).



I II

---

[1] We are grateful for grants from the Army Research Office (Durham) and the Camille and Henry Dreyfus Foundation which provided partial support of this work.

[2] National Institutes of Health Postdoctoral Fellow, 1964–1965.

[3] J. Bredt, *Ann.*, **437**, 1 (1924).

[4] For a review, see F. S. Fawcett, *Chem. Rev.*, **47**, 219 (1950).

[5] *Cf.* E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 298.

[6] (a) If the σ-bond is made from sp³-hybrid orbitals, the situation is not nearly so bad, since the residual sp³-orbitals are not orthogonal. To the extent that overlap and bond strength are porportional, these can form a bond about two-thirds as strong as an ordinary π-bond, as can be estimated from standard tables of overlap integrals[6b] and reasonable estimates of molecular geometry. (b) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

[7] (a) J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, *ibid.*, **23**, 315 (1955); (b) B. S. Rabinovitch and K. W. Michel, *J. Am. Chem. Soc.*, **81**, 5065 (1959).

[8] For reviews, see B. F. Gowenlock, *Quart. Rev.* (London), **14**, 133 (1960); R. B. Cundall, *Progr. Reaction Kinetics*, **2**, 167 (1964).

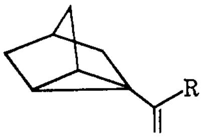
It is nevertheless conceivable that a vicinal diradical (of unspecified multiplicity) might be formed, at least as a transient intermediate. The present paper reports unsuccessful attempts to demonstrate this.

The thermal cleavage of cyclopropanes leads to 1,3-diradicals[9,10]; these species recyclize with loss of stereochemical integrity or else transfer hydrogen intramolecularly to form olefin. The cleavage is facilitated kinetically by attachment of a vinyl group (as in III), but the resulting diradical species IV now escapes essentially irreversibly to a cyclopentene (V).[11–14]

III IV Va V

The closure of the cyclopentene ring is accompanied in simple cases by formation of a π-bond, which can be represented conceptually *as if* a separate step Va → V were involved. In the stepwise mechanism,[14] the π-bond-forming process (Va → V) does not provide appreciable kinetic driving force for the σ-bond-breaking process (III → IV). Disregarding any difference in electronic repulsion energies that may exist, we can estimate crudely that the cyclization step IV → Va is exothermic (by about 20 kcal./mole[17]), since a diradical containing a π-bond and four σ-bonds is transformed to a diradical containing five σ-bonds. Consequently, once the diradical IV is formed, there is no obvious prohibition to its cyclization, even if forming the final π-bond (Va → V) is prohibited by the Bredt rule. This permits the hope that the chemistry of "1,2-diradicals" might be examined.

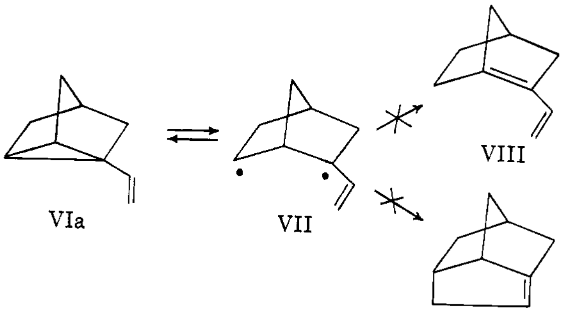
The required type of vinylcyclopropane system is incorporated in 1-vinylnortricyclenes VIa–c. 1-Acetylnortricyclene[18] is the precursor for the synthesis of 1-vinylnortricyclene (VIa) by way of the corresponding secondary alcohol, which previously had been prepared by Hart and Martin.[18] The Chugaev pyrolysis of methyl 1-nortricyclyethyl xanthate gives a 50% yield of 1-vinylnortricyclene (VIa). 1-Methyl-1-(1-nortricyclyl)ethylene (VIb) and 1-phenyl-1-(1-nortricyclyl)ethylene (VIc) are obtained by addition of the appropriate Grignard reagent to 1-acetylnortricyclene and dehydration of the resulting tertiary alcohol.



VIa, R = H
b, R = CH_3
c, R = C_6H_5

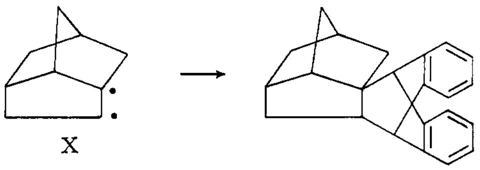
1-Vinylnortricyclene (VIa) is recovered essentially unchanged from gas phase pyrolyses. Faint discoloration occurs after prolonged heating above 350°, but decomposition is extremely slow. Even at 475°, 90% recovery of starting material is achieved after 25 min. Under still harsher conditions, extensive nonspecific degradation occurs.

The contrast between this behavior and that of ordinary vinylcyclopropanes is striking. For example, 1-methyl-1-vinylcyclopropane[17] would have a half-life of about 1 sec. at 460°. Even an unactivated cyclopropane would have passed through one or two half-lives for 1,3-diradical formation under these conditions. Evidently the diradical VII must be formed, but, finding that the normal exits (hydrogen transfer to VIII and cyclization to IX) are blocked, can only retreat to starting material. In fact, the cleavage–recyclization VIa → VII is a reaction which, in our opinion, surely occurs but which there is no way of detecting. It is a "no-reaction" reaction.



VIa VII VIII IX

From the argument already given, it seems likely that cyclization of the diradical VII to X, a variant of the anti-Bredt olefin IX with a feeble or nonexistent π-bond, might well occur. This species should be a powerful dienophile, but no evidence of adduct (*e.g.*, XI) formation is found when pyrolyses of VIa are carried out in the presence of such diene-trapping agents as benzene or anthracene.



X XI

Although an appropriately situated phenyl group might stabilize the cyclized diradical enough to permit it sufficient time for intersystem crossing to a triplet state, 1-phenyl-1-(1-nortricyclyl)ethylene (VIc) shows

---

[9] B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

[10] S. W. Benson, *ibid.*, **34**, 521 (1961).

[11] M. Flowers and H. M. Frey, *J. Chem. Soc.*, 3547 (1961).

[12] H. M. Frey and D. C. Marshall, *ibid.*, 3981 (1962).

[13] C. G. Overberger and A. E. Borchert, *J. Am. Chem. Soc.*, **82**, 1007, 4897 (1960).

[14] There is some controversy on whether the steps III → IV and IV → V are stepwise as shown or concerted. The activation energies for vinylcyclopropane rearrangements cluster about 50 kcal./mole,[11,12,15] while many ordinary cyclopropane cleavages require activation energies about 14 kcal./mole higher. The increment agrees well with the allylic resonance energy estimated on other grounds and is interpreted in terms of a stepwise mechanism in which the transition state receives the full benefit of this resonance.[16] On the other hand, the pre-exponential terms are one or two orders of magnitude smaller for the vinylcyclopropane rearrangements than for the cleavages, which is interpreted[15] as favoring the concerted mechanism. However, this could also be reasonably attributed in the stepwise mechanism to a steric requirement for the vinyl group to achieve proper orbital alignment for allylic resonance.

[15] R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 959, 4188 (1964).

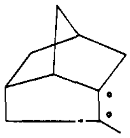
[16] K. W. Egger, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 5420 (1964).

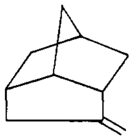
[17] T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworth and Co. (Publishers), Ltd., London, 1958, p. 273.

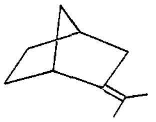
[18] H. Hart and R. A. Martin, *J. Org. Chem.*, **24**, 1276 (1959).

no triplet electron spin resonance signal when irradiated with ultraviolet light in a fluorocarbon matrix.[19]

The cyclized diradical (XII) from 1-methyl-1-(1-nortricyclyl)ethylene (VIb) might be expected to transfer hydrogen by a 1,3-shift[20] and produce a stable product (XIII). In the event, however, pyrolysis at 430° gives isopropylidenenorbornane (XIV) as the major component of the product mixture. This substance is a formal hydrogenation product of the starting material VIb, and at present we can only speculate on the mechanism of its formation.


XII


XIII


XIV

Experimental Section[21]

1-Vinylnortricyclene (VIa).—1-Acetylnortricyclene was prepared as described[18] but was worked up by steam distillation of the acetylation mixture. The methylene chloride layer was separated and dried. After the solvent was removed by distillation, a trace of quinoline was added to the pot; distillation gave a 50% yield (based on nortricyclene) of acetylnortricyclene, b.p. 48° (2 mm.). The corresponding alcohol, prepared by lithium aluminum hydride reduction,[18] was converted to the xanthate.[22] The xanthate (15 g.) was heated to 180° in a distilling apparatus equipped with a Dry Ice cooled receiver and maintained at 100-mm. pressure. In 4 hr., 8.7 g. of material had collected in the receiver, from which 6 g. of vinylnortricyclene was obtained by preparative vapor chromatography (v.p.c.) on a 2.5 m. × 7 mm. 20% Carbowax 20M on 60–80-mesh Chromosorb P column at 110°.

Anal. Calcd. for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.82; H, 9.90.

The n.m.r. spectrum showed typical isolated vinyl group absorption, a two-proton, seven-line pattern between $\delta = 4.7$ and 5.1 p.p.m. and a one-proton, four-line pattern between 5.5 and 6.0 p.p.m. The C-4 proton absorbed at $\delta = 2.02$ p.p.m. The infrared spectrum showed bands at 885 and 1630 cm.$^{-1}$ (double bond) and the pair of bands at 785 and 855 cm.$^{-1}$ found[18] in many 1-substituted nortricyclenes.

1-Methyl-1-(1-nortricyclyl)ethylene (VIb).—The alcohol from 2.2 g. of 1-acetylnortricyclene and methylmagnesium iodide was distilled without deliberate addition of acid from a flask at 120° and 10 mm. The crude distillate exhibited no significant hydroxyl absorption in the infrared and was purified by preparative v.p.c. on a 2.5 m. × 7 mm. 15% tricyanoethoxypropane (TCEP) on 60–80-mesh Chromosorb P column at 110°, to give 1.1 g. of olefin (50%).

Anal. Calcd. for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.40; H, 10.69.

The n.m.r. spectrum showed absorptions at $\delta = 2.00$ (C-4 proton) and 4.51 p.p.m. (terminal methylene protons). The infrared spectrum showed bands at 785, 855, 870, and 1620 cm.$^{-1}$.

1-Phenyl-1-(1-nortricyclyl)ethylene (VIc) was prepared from the alcohol formed by the reaction of acetylnortricyclene and phenylmagnesium bromide. A portion of 2.65 g. of the alcohol was distilled from 500 mg. of potassium acid sulfate, b.p. 160–180 (1 mm.). Redistillation gave 880 mg. of material, b.p. 90–95° (0.4 mm.). Purification by v.p.c. on a 2 m. × 7 mm. 20% Carbowax 20M on 60–80-mesh Chromosorb P column at 180° gave VIc. The ultraviolet spectrum in ethanol showed λ_{max} 243 mμ (ϵ 8050).[23]

Anal. Calcd. for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.60; H, 8.22.

The n.m.r. and infrared spectra were again consistent with the assignments. The n.m.r. showed aromatic absorptions centered at 7.25 p.p.m. (five protons), a four-line AB pattern centered at 5.09 p.p.m., $J = 2.1$ c.p.s. (two protons), a single proton peak (C-4 bridgehead) at 2.05 p.p.m., and a complex upfield pattern between 1.3 and 1.5 p.p.m. (eight protons). The infrared spectrum showed bands at 785, 855, 890, and 1610 cm.$^{-1}$.

Pyrolyses, General Description.—The Pyrex tubes employed were washed with ammonium hydroxide, rinsed with distilled water, and dried before use. These were used to fashion 10 × 100 mm. tubes (volume of 10–15 ml.) that were pumped down to 10^{-5} mm. pressure for a few minutes. The vinyl compound (4 μl.) was introduced at atmospheric pressure; the tube was cooled to liquid nitrogen temperature, evacuated to 10^{-5} mm., and sealed. After heating in an air bath, the tubes were removed and one end was frozen in liquid nitrogen. They were opened and the contents were examined by infrared and v.p.c.

The identical procedure was employed for the large-scale runs but a 30 × 200 mm. tube (volume 150 ml.) was employed and sample sizes were 100–200 μl.

The results of pyrolyses of **1-vinylnortricyclene** under varying conditions were as follows: 275° for 5 hr. gave a water-white pyrolysate which was essentially unchanged starting material; 375° for 12 hr. gave a slightly yellow pyrolysate which was nevertheless essentially pure starting material; heating in the presence of an internal standard (*n*-heptane) at 475° for 24 min. gave a colorless pyrolysate, analysis of which with the TCEP column showed only 10% reaction; heating neat at 475° for 36 min. led to a brown mixture which showed 28 v.p.c. peaks. Attempts to trap a diradical by heating 1-vinylnortricyclene with benzene (1:100) at 325° for 22 hr., with anthracene (1:2) at 325° for 22 hr., and with iodine (1:2) at 325° for 20 min. were unsuccessful.

Pyrolysis of 200 μl. of **1-methyl-1-(1-nortricyclyl)ethylene** for 10 min. at 430° gave 130 μl. of pyrolysate. The v.p.c. showed two major peaks, one of which corresponded to starting material. A number of minor components were also present, no one of which comprised more than 5% of the total. Preparative v.p.c. on the TCEP column gave 42 μl. of starting material (identical infrared spectra) and 31 μl. (24%) of the second major component, a material with a slightly shorter retention time. This material showed a parent peak at *m/e* 136 ($C_{10}H_{16}$) in the mass spectrum and was shown by comparison of infrared and n.m.r. spectra to be isopropylidenenorbornane (XIV).

A mixture of 80 μl. of *p*-cymene and 20 μl. of the vinyl compound were heated for 12 min. at 430°. No significant change in the course of the reaction was observed, and in particular the amount of isopropylidenenorbornane in the reaction mixture was not enhanced.

2-Isopropylidenenorbornane (XIV).—The crude alcohol resulting from the reaction of isopropylmagnesium bromide with 4.4 g. of norcamphor was distilled from 1.5 g. of potassium acid sulfate at 180° and 90 mm. The semisolid distillate (3 g.) consisted of about 60% unchanged alcohol and 40% isopropylidenenorbornane. The latter was isolated as a colorless liquid by preparative v.p.c. on the TCEP column. The n.m.r. spectrum showed no vinyl hydrogens.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 87.85; H, 12.11.

This compound had been reported previously by Alder and Ache,[24] who described its ozonolysis to norbornanone and ace-

---

(19) By the technique of R. W. Murray, A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3214 (1962). We are greatly indebted to Dr. E. Wasserman of Bell Telephone Laboratories for these measurements.

(20) For a review, see A. Fish, *Quart. Rev.* (London), **18**, 243 (1964); *cf.* O. A. Reutov and T. N. Shatkina, *Tetrahedron*, **18**, 305 (1962).

(21) The infrared spectra were obtained on neat samples using a Beckman IR-8 spectrometer. The ultraviolet spectra were measured with a Cary Model 15 spectrophotometer. The n.m.r. spectra were taken in carbon tetrachloride solution with tetramethylsilane (TMS) as an internal reference using a Varian A-60 instrument. Chemical shifts are given in δ values, in parts per million downfield from TMS. Mass spectra were obtained using a Consolidated Engineering Co. Model 21-103 mass spectrometer. We are indebted to Mr. J. M. Gaidis for the mass spectra. Wilkens Engineering Co. Aerograph A-90 and Hy-Fi instruments were used for the gas chromatographic separations. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

(22) According to the general procedure described by O. R. Nace, *Org. Reactions*, **12**, 54 (1962).

(23) Compare α-cyclopropylstyrene, λ_{max} 243 mμ (ϵ 9700): S. Sarel and E. Breuer, *J. Am. Chem. Soc.*, **81**, 6522 (1959).

(24) K. Alder and H. Ache, *Chem. Ber.*, **95**, 503 (1962).

tone. Our sample (100 mg.), on ozonolysis followed by hydrogenation over 10% palladium on charcoal, gave these two ketones (identified by v.p.c. retention times and infrared spectra) in yields of 28 and 12%, respectively. The n.m.r. spectrum showed a single-proton peak at 2.8 p.p.m. (allylic bridgehead) and a broad single-proton peak at 2.25 p.p.m. (C-4 bridgehead); the upfield pattern was complex and featured strong absorptions at 1.62, 1.48, and 1.29 p.p.m.

One-Step Olefin-to-Allene Conversion

Karl G. Untch, Donald J. Martin,
and Nicholas T. Castellucci

Mellon Institute, Pittsburgh, Pennsylvania 15213

Received June 8, 1965

For other investigations, we prepared 1,2,6-cyclononatriene according to the general two-step method for synthesizing allenes,[1,2] *i.e.*, the addition of dibromocarbene (generated from bromoform) to the olefin[3] followed by reaction of the dibromocyclopropane derivative with an alkyllithium reagent. The reported overall conversion of 1,5-cyclooctadiene to 1,2,6-cyclononatriene by this method is 23% (based on olefin).[4] Skattebøl has since obtained *ca.* 45% yields of 1,2,6-cyclononatriene by this two-step sequence using 1 equiv. of olefin to 1 equiv. of bromoform.[5] Since the triene was to be our starting material, an improvement in the yield was desirable.

Prompted by the report of Skattebøl[2] that trimethylethylene and carbon tetrabromide in the presence of excess methyllithium gave a 50% yield of 2-methylpenta-2,3-diene (the two-step sequence gave 58% yield), we treated a fourfold excess of 1,5-cyclooctadiene with 1 equiv. of carbon tetrabromide and 2 equiv. of methyllithium in diethyl ether at *ca.* −65°. This one-step conversion gave *ca.* 70% of 1,2,6-cyclononatriene (based on carbon tetrabromide) in four experiments (Table I). When the same reaction was carried out using *n*-butyllithium in hexane, instead of methyllithium in ether, a 37% yield of 1,2,6-cyclononatriene was obtained.

TABLE I

OLEFIN-TO-ALLENE CONVERSIONS WITH CARBON TETRABROMIDE AND ALKYLLITHIUM (RLi)

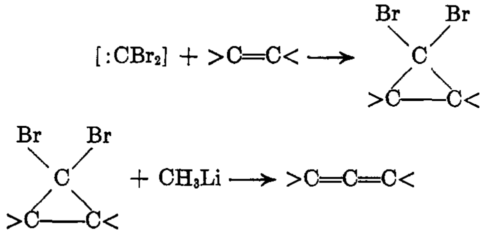
Olefin	R	Allene	Temp., °C.	Yield,[a] %
1,5-Cyclooctadiene	C_4H_9[b]	1,2,6-Cyclononatriene	*ca.* −65	36.8
1,5-Cyclooctadiene	CH_3[c]	1,2,6-Cyclononatriene	*ca.* −65	67.8
1,5-Cyclooctadiene	CH_3[c]	1,2,6-Cyclononatriene	*ca.* −65	71.2
1,5-Cyclooctadiene	CH_3[c]	1,2,6-Cyclononatriene	*ca.* −65	67.9
1,5-Cyclooctadiene	CH_3[c]	1,2,6-Cyclononatriene	*ca.* −65	64.4
cis-Cyclooctene	C_4H_9[b]	1,2-Cyclononadiene	0	*ca.* 30
cis-Cyclooctene	CH_3[c]	1,2-Cyclononadiene	*ca.* −65	73.7

[a] The yields are based on the amount of carbon tetrabromide used and were determined by g.l.p.c. (see Experimental Section). [b] In hexane. [c] In diethyl ether.

Cyclooctene, under the same conditions (fourfold excess, carbon tetrabromide and methyllithium), gave a 74% yield of 1,2-cyclononadiene. When cyclooctene was treated with carbon tetrabromide and *n*-butyllithium in hexane at 0°, *ca.* a 30% yield of 1,2-cyclononadiene resulted. The amounts of cyclic allene obtained in these two latter cases are not readily comparable to those reported for the two-step sequence separately by Moore and Ward[1] (55%) and by Skattebøl[2] (60%) for cyclooctene, since their yields are based on olefin used, whereas here the yields are based on the amount of carbon tetrabromide used.

This modification of the general allene synthesis combines the two-step sequence into one as shown in eq. 1 and 2. The marked decrease in the yield of 1,2,6-cyclononatriene when *n*-butyllithium was used could be due to either part (1 or 2) of the transformation, to both, or to a separate side reaction. In those cases where Moore and Ward,[1] and Skattebøl[2] treated a dibromocyclopropane derivative with both *n*-butyllithium and methyllithium, the yields of the corresponding allene show that methyllithium provides the better result.

$$>C{=}C< + CBr_4 + CH_3Li \longrightarrow$$



(1)

(2)

In conclusion, the ease with which the reaction can be carried out makes this modification preferable, whether the yield of allene obtained by the one-step conversion is higher than the two-step sequence or not.

Experimental Section

1,2,6-Cyclononatriene.—To a stirred mixture of 54.0 g. (0.50 mole) of 1,5-cyclooctadiene and 41.5 g. (0.125 mole) of carbon tetrabromide (under a nitrogen atmosphere), cooled to *ca.* −65°, were added 74.0 ml. (0.125 mole) of methyllithium in diethyl ether (Foote Mineral Co.) during a 45-min. period. The stirred mixture was kept between −65 and −68° for an additional 30 min., then 80.5 ml. (0.135 mole) of the ethereal methyllithium solution was added during a 30-min. period. The reaction mixture was further stirred for 30 min. at −68° and allowed to come to 0°, and the water was added. The ethereal layer was separated, washed with water until neutral, and dried over sodium sulfate. The bulk of the ether was removed by distillation and the concentrated ethereal solution was analyzed by g.l.p.c.

The yields (based on carbon tetrabromide) of 1,2,6-cyclononatriene for four such experiments were obtained by isothermal (100°) g.l.p.c. analyses using a 6 ft. × 0.25 in. column containing 10% Apiezon L on 80–90-mesh Anakrom ABS in conjunction with an F & M Scientific Corp., Model 500 chromatograph. The planimetered peak areas corresponding to 1,5-cyclooctadiene and 1,2,6-cyclononatriene (identical retention times with pure samples) gave the ratio of starting material to product. Fractional distillation of the reaction mixtures gave 1,2,6-cyclononatriene (*ca.* 80% of that present, determined by g.l.p.c. analysis), b.p. 65–66° (16 mm.), $n^{19.8}D$ 1.5234, infrared and n.m.r. spectra identical with those of a sample prepared according to Skattebøl.[2] The above procedure for the preparation using *n*-butyllithium in hexane (Foote Mineral Co.) was followed.

1,2-Cyclononadiene.—The above procedure was followed using 55.0 g. (0.50 mole) of cyclooctene, 41.5 g. (0.125 mole) of carbon tetrabromide, and 154.5 ml. (0.260 mole) of methyllithium in ether. The fractionally distilled allene, b.p. 77–79° (*ca.* 30 mm.),

---

[1] W. R. Moore and H. R. Ward, *J. Org. Chem.*, **27**, 4179 (1962).

[2] L. Skattebøl, *Tetrahedron Letters*, 167 (1961); *Acta Chem. Scand.*, **17**, 1683 (1963).

[3] W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **76**, 6162 (1954), and subsequent papers.

[4] This yield can easily be raised by using the olefin in excess, but it is clear that Dr. Skattebøl was interested in preparing the bisdibromocyclopropane derivative of 1,5-cyclooctadiene as well, which he converted into cyclodeca-1,2,6,7-tetraene.

[5] Private communication.