Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.53. Found: C, 73.66; H, 8.04; N, 8.55.

The residue from the continuous ether extraction was made acid to congo red with dilute hydrochloric acid and the volume was doubled by the addition of water. The precipitated solid was filtered, dried, transferred to a Soxhlet extractor, and extracted with chloroform for 7 days. Evaporation of the chloroform gave a white solid which was dissolved in absolute ethyl alcohol, treated with Norit, filtered, and cooled to give 2.1 g (50%) of VII: mp 259–260° dec, ir (KBr), 8.75 μ (isoquinoline).

Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76. Found: C, 63.52; H, 6.49; N, 6.66.

VIII from VII.—Compound VII was decarboxylated at 264° *via* the procedure of Hart and Freeman.[7] Recrystallization from ethanol gave 0.6 g (73.6%) of white needles of VIII, mp 236–237°. The melting point was undepressed on admixture with the hydrolytic product (*vide supra*).

Registry No.—I, 107-91-5; II, 874-23-7; IVb, 17012-30-5; V, 109-77-3; VI, 17012-31-6; VII, 17012-32-7; VIII, 17012-33-8.

Acknowledgment.—We are indebted to Dr. E. C. Friedrich[11] for some of the nmr spectra and to Mr. R. H. DuBois for certain of the infrared spectra.

---

[11] Department of Chemistry, University of California at Davis, Davis, Calif.

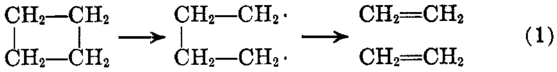
An Unusual Cyclobutane Pyrolysis

CLAYTON H. HEATHCOCK[1] AND BRUCE E. RATCLIFFE

Department of Chemistry, University of California at Berkeley, Berkeley, California 94720

Received April 23, 1968

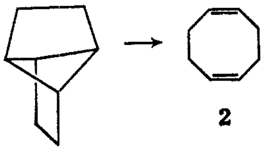
The thermal decomposition of cyclobutane to ethylene[2] is believed to involve the intermediacy of the tetramethylene diradical, which undergoes β scission to yield products (eq 1).[3] Numerous sub-



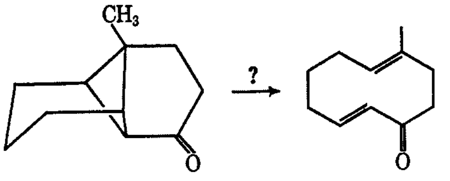
$$\begin{array}{c} CH_2{-}CH_2 \\ | \quad\;\; | \\ CH_2{-}CH_2 \end{array} \longrightarrow \begin{array}{c} CH_2{-}CH_2\cdot \\ | \qquad\quad \\ CH_2{-}CH_2\cdot \end{array} \longrightarrow \begin{array}{c} CH_2{=}CH_2 \\ CH_2{=}CH_2 \end{array} \qquad (1)$$

stituted cyclobutanes have been pyrolyzed and almost all undergo the reaction outlined in eq 1, the few exceptions being vinyl and 1,2-divinylcyclobutanes, which rearrange to cyclohexenes and cyclooctadienes, respectively.[3]

Srinivasan and Levi[4] found that tricyclo[3.3.0.0^{2,6}]-octane (1) undergoes thermal decomposition in the expected manner to yield 1,5-cyclooctadine (2). In connection with another study, we desired a method for preparing 8-methyl-2,7-cyclodecadien-1-one (4). One possibility appeared to be pyrolysis of the readily available tricyclic ketone 3.[5]



1 **2**



3 **4**

When compound **3** was heated at 360° in a sealed Pyrex vessel, two isomeric products were formed in varying amounts (Table I). The major product was identified as the octalone **5**, by comparison with an authentic sample.[5] The minor product was shown to be a cyclohexanone or cycloheptanone (ν_{max} 1700 cm^{-1}) containing a terminal methylene group (ν_{max} 890 cm^{-1}). Due to the extreme difficulty in isolating this minor product in a pure state, its structure was not further investigated.

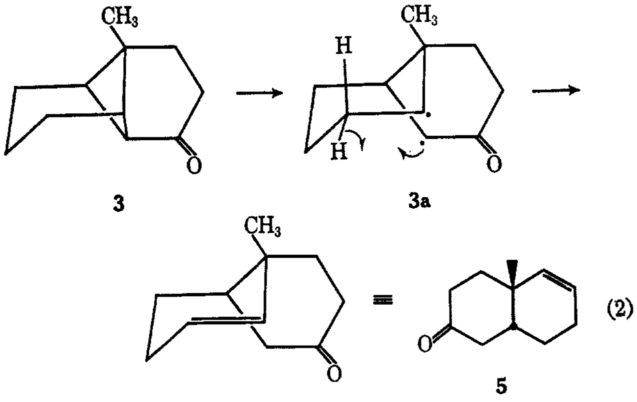
TABLE I

PYROLYSIS OF 1-METHYLTRICYCLO[4.4.0.0^{2,7}]DECAN-8-ONE

Run	Amount of 3, mg	Reaction mixture analysis, % 3	5	Other product
1	527.5	70.0	24.2	5.6
2	523.4	69.2	24.4	6.3
3	538.9	70.0	23.1	6.8
4	517.1	65.9	27.2	6.8
5	527.9	66.2	25.7	8.0
6	534.0	66.6	25.6	7.8
7	547.6	68.0	24.3	8.1
8	553.2	67.9	24.4	7.7[a]

[a] Analysis by internal standard showed 24.6% of nonvolatile products.

The probable mode of formation of **5** is outlined in eq 2. The intramolecular diversion of the postulated diradical **3a** lends additional credence to the probable intermediacy of tetramethylene diradicals in cyclobutane pyrolyses.[3] The reason for the different modes of reaction of tricyclic compounds **1** and **3** is not clear.



3 **3a** **5**

Experimental Section

Pyrolysis of 1-Methyltricyclo[4.4.0.0^{2,7}]decan-8-one (3).—Approximately 500 mg of ketone 3[5] was sealed at 1 mm in a 20-ml Pyrex vessel. The tube was heated at 360° for 2 hr, cooled, and opened. Analysis of the reaction mixture by capillary vpc (150

---

[1] Fellow of the Alfred P. Sloan Foundation.

[2] (a) G. T. Genaux and W. D. Walters, *J. Amer. Chem. Soc.*, **73**, 4497 (1951); (b) F. Kern and W. D. Walters, *Proc. Nat. Acad. Sci. U. S.*, **39**, 937 (1952); (c) F. Kern and W. D. Walters, *J. Amer. Chem. Soc.*, **75**, 6196 (1953).

[3] H. M. Frey, "Gas Phase Pyrolyses of Some Small Ring Hydrocarbons," in Advances in Physical Organic Chemistry, Vol. 4, V. Gold, Ed., Academic Press, New York, N. Y., 1966.

[4] R. Srinivasan and A. A. Levi, *J. Amer. Chem. Soc.*, **86**, 3756 (1964).

[5] C. H. Heathcock, R. A. Badger, and J. W. Patterson, Jr., *ibid.*, **89**, 4135 (1967).

ft × 0.01 in. SF-96) revealed the presence of unreacted **3**, octalone **5**, and a second product. The results from various runs are summarized in Table I. From one run, compound **5** was isolated by preparative vpc (10 ft × 0.25 in. Carbowax 20M) and identified by infrared and nmr spectra.[5]

Registry No.—Cyclobutane, 287-23-0; **3**, 17159-66-9.

Acknowledgments.—This investigation was supported by Public Health Service Research Grant No. AI-07765-01 from the National Institute of Allergy and Infectious Diseases.

Reaction of Dichlorocarbene with Enol Ethers. IX. Ethoxycycloheptadiene[1]

WILLIAM E. PARHAM, FRED M. PARHAM, JOSEPH F. DOOLEY, AND MARCUS K. MEILAHN

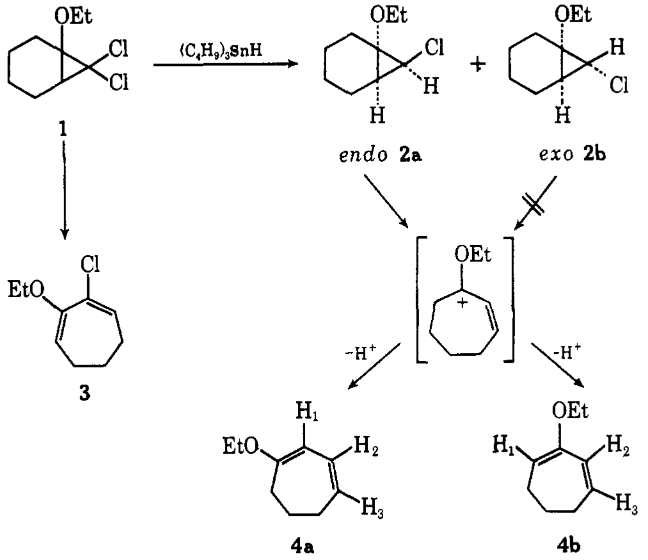
School of Chemistry of the University of Minnesota, Minneapolis, Minnesota 55455

Received March 31, 1968

Ring expansion of monohalocyclopropanes derived from cyclic enol ethers appeared, by analogy with the chemical behavior of the corresponding dihalo derivatives,[2] to be an attractive synthetic route to cyclic diene ethers and cyclic unsaturated ketones. This paper describes the synthesis of 1-ethoxy-1,3-cycloheptadiene (**4a**) and certain derivatives of this system.

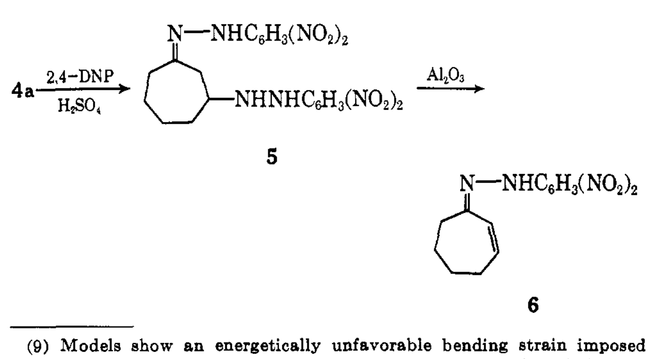
Reduction of 1-ethoxy-7,7-dichlorobicyclo[4.1.0]heptane (**1**) with tri-*n*-butyltin hydride[3] gave a mixture of *endo*- and *exo*-1-ethoxy-7-chloro[4.1.0]heptane which was separated in 35 and 6% yield, respectively, by fractional distillation. The configurations of the isomeric chlorocyclopropanes were assigned on the basis of their nmr spectra. Compound **2a** showed a doublet for the cyclopropyl hydrogen centered at 3.13 ppm with $J = 9.0$ Hz; **2b** exhibited a doublet at 2.59 ppm with $J = 4.4$ Hz. In cyclopropane systems *cis* coupling constants are known to be larger than *trans* coupling constants,[4] and the values observed are in close agreement with those reported[3] for *endo*- and *exo*-chloronorcaranes (*endo*, triplet, 3.14 ppm, $J = 7.5$ Hz; *exo*, triplet, 2.56 ppm, $J = 3.7$ Hz).

Ring expansion of halocyclopropanes are thought to occur by ionization of the carbon-chlorine bond,[5,6] with concerted ring opening, in which the substituents *trans* to the leaving group rotate outward.[7,8] Application of the Woodward-Hoffman selection rules[7] to **2** suggested that **2a** should undergo ring expansion much more readily[9] than **2b**, and this order of reactivity was confirmed experimentally.



Reaction of **2a** with refluxing pyridine gave ethoxycycloheptadiene (**4**) in 56% yield, while **2b**, under identical conditions, gave only recovered starting material. Ring expansion of **2a** might be expected to give either of two dienes (**4a** and/or **4b**). The nmr spectrum of the product **4** showed a single sharp quartet for the ethoxy methylene protons and vpc analysis showed a single peak. The absorption in the vinyl proton region was complex and consisted of two multiplets centered at 4.72 ppm (wt 1) and 5.40 ppm (wt 2). The most shielded vinyl proton in **4a** and **4b** must be H_1 owing to the conjugation with the ethoxy group. Decoupling of the vinyl proton at 4.72 ppm from the allylic protons simplified the pattern to a sharp doublet ($J = 8.5$ Hz) which is only compatible with **4a**, and the assignment of the structure is made on this basis. It is of interest to note that the only product reported by treatment of **1**, under identical conditions, was 2-ethoxy-3-chloro-1,3-cycloheptadiene (**3**) which was isolated in 83% yield.[2b]

Reaction of **4a** with 2,4-dinitrophenylhydrazine reagent[10] gave a diadduct (mp 170–171°) with composition in agreement with that calculated for **5**.[11] Chromatography of the product **5** on alumina gave in high



---

(1) This work was supported by Grants GP-3357 and GP-6169X from the National Science Foundation.

(2) (a) W. E. Parham, R. W. Soeder, and R. M. Dodson, *J. Amer. Chem. Soc.*, **84**, 1755 (1962); (b) W. E. Parham, R. W. Soeder, J. R. Throckmorton, K. Kuncl, and R. M. Dodson, *ibid.*, **87**, 321 (1965); (c) W. E. Parham and R. J. Sperley, *J. Org. Chem.*, **32**, 926 (1967).

(3) D. Seyferth, H. Yamozaki, and D. L. Alleston, *ibid.*, **28**, 703 (1963).

(4) (a) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); (b) V. Schöllkopf and G. J. Lehmann, *Tetrahedron Lett.*, 165 (1962); (c) G. L. Closs, R. A. Moss, and J. J. Coyle, *J. Amer. Chem. Soc.*, **84**, 4985 (1962).

(5) (a) W. E. Parham, H. E. Reiff, and P. Swartzentruber, *ibid.*, **78**, 1437 (1956); (b) P. S. Skell and S. R. Sandler, *ibid.*, **80**, 2024 (1958); (c) W. E. Parham and R. J. Sperley, *J. Org. Chem.*, **32**, 924 (1967).

(6) W. E. Parham and E. Schweizer, *Org. Reactions*, **13**, 55 (1963).

(7) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

(8) (a) C. H. DePuy, L. G. Swack, J. W. Hauser, and W. Wiedimann, *ibid.*, **87**, 4006 (1965); (b) S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *ibid.*, **87**, 4007 (1965).

(9) Models show an energetically unfavorable bending strain imposed on the carbon skeleton in the transition state for such a reaction of **2b**.

(10) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p 219.

(11) A diadduct presumably formed from 2-cycloheptenone has been reported to melt at 170 and 164°. *Cf.* (a) R. Jacquier and R. Fraisse, *Bull. Soc. Chim. Fr.*, 108 (1957); (b) J. E. Hodgkins and R. J. Flores, *J. Org. Chem.*, **28**, 3356 (1963).