

the generalizations¹¹ as to cyclolization of hydroxyacyl lactams may not apply to the amino analogs.

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

GEORGE I. GLOVER¹²
HENRY RAPOPORT¹³

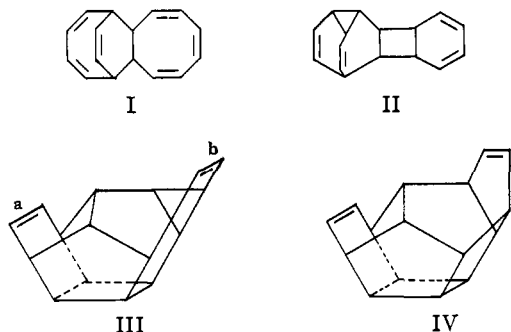
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Dimerization of Cyclooctatetraene. I. Structure of the "Three Double Bond" Dimer

Sir:

The data presented in this communication show that the so-called "three double bond" dimer of cyclooctatetraene actually contains only two double bonds and that the mistaken assignment of the number of double bonds was undoubtedly due to the presence of a cyclopropane ring. Structure III is assigned to the dimer on the basis of the following spectral and chemical data.

Four major dimeric products have been isolated from the thermal dimerization of cyclooctatetraene. Dimerization at temperatures below 100^o1,2 leads to the formation of the two dimers, I and II. Reports indicate that compound I is a precursor to II.^{1,2} At temperatures above 100^o two new products are obtained from the dimerization³⁻⁵; one has two double bonds and was shown to have structure IV by three-dimensional X-ray analysis,⁴ and the other has three double bonds.³ The structures I, II, and IV appear established.^{1,2,4} No definitive evidence has been presented for the structure of the so-called "three double bond" dimer. It absorbs three moles of hydrogen when the dimer is reduced in the presence of a palladium-charcoal catalyst, the third mole being taken up more slowly than the first two.



The dimer was prepared⁸ as a solid compound melting at 41^o (lit. m.p. 41.5^o).³ The infrared absorption spectrum was identical with that reported by Lord and Walker,⁶ and is in agreement with structure III. Two characteristic absorptions appear in the carbon-carbon double bond region (1615 and 1675 cm.⁻¹). The absorption at 1615 cm.⁻¹ is very similar in position (1606 cm.⁻¹) and intensity to one of the absorptions in the spectrum of the known dimer, IV. The double bond causing the absorption at 1615 cm.⁻¹ is labeled a in structure III. Upon inspection of either III or IV one can see that this double bond (a) is in a bicyclo-

[2.2.2]octene-2 ring system which shows carbon-carbon double bond absorption at 1614 cm.⁻¹ in its infrared absorption spectrum.⁶ The other absorption, at 1675 cm.⁻¹, is remarkably high and must involve the frequency-raising effect of large-angle strain. Such an effect would be expected for structure III since the double bond labeled b is located in a bicyclo[5.1.0]-octene-2 ring system, which shows double bond absorption at 1650 cm.⁻¹.⁷ Another feature of the spectrum of the dimer which is in agreement with structure III is the presence of absorption bands characteristic of a cyclopropane ring at 3035, 1035, and 867 cm.⁻¹.⁸

Comparison of the ultraviolet absorption spectra of the dimers III and IV is instructive. The former shows a maximum absorption at 232 m μ (ϵ 2935) and the latter shows only end absorption beyond 224 m μ . Only end absorption would be expected for compound IV since it contains two isolated carbon-carbon double bonds. However, the λ_{\max} at 232 m μ in the spectrum of III is significant. The ability of a cyclopropane ring to enter into conjugation with a neighboring unsaturated system is known,⁹ and Goodman and Eastman¹⁰ have recently shown that the steric relationship between the cyclopropane and the olefin has little consequence spectroscopically. The interaction of a cyclopropane group with an olefin is slightly less than that obtained for conjugated olefins. For example, the conjugated cyclic olefin, 1,3-cycloheptadiene, shows a λ_{\max} at 248 m μ ¹¹ (ϵ 741) while bicyclo[5.1.0]-octene-2 shows its λ_{\max} at 237 m μ (ϵ 560).⁷ Thus, the maximum absorption at 232 m μ in the spectrum of III is in good accord with the chromophore comprised of the double bond b and the cyclopropane ring in two bicyclo[5.1.0]octene-2 ring systems.

The complex n.m.r. spectrum of III shows several revealing characteristics. The vinyl proton region shows a complex multiplet (τ 4.2) which corresponds to four protons. For such an observation to indicate more than the presence of two double bonds migration of hydrogen at some stage of the dimerization would be necessary. Such migration seems unlikely in view of the fact that no such rearrangements are necessary to explain the formation of any of the known dimers I, II, and IV, and it will be pointed out later that III is an intermediate in the formation of IV and that II is a very likely precursor to III by an intramolecular Diels-Alder reaction. Another characteristic of the n.m.r. spectrum which is definitive of structure III is the presence of a complex absorption pattern of at least 13 lines corresponding to three protons centered at abnormally high field (τ 9.1). Absorption in this region of the spectrum can be due only to methyl group protons or cyclopropane protons.¹² The possibility of

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(9) For leading references see: M. T. Rogers and J. D. Roberts, *J. Am. Chem. Soc.*, **68**, 843 (1946); R. H. Eastman and S. K. Freeman, *ibid.*, **77**, 6642 (1955); R. S. Mohrbacher and N. H. Cromwell, *ibid.*, **79**, 401 (1957); G. W. Cannon, A. A. Santilli, and P. Shenian, *ibid.*, **81**, 1660 (1959); R. Fuchs, C. A. Kaplan, J. J. Bloomfield, and L. F. Hatch, *J. Org. Chem.*, **27**, 733 (1962).

(10) A. L. Goodman and R. H. Eastman, *J. Am. Chem. Soc.*, **86**, 908 (1964).

(11) E. Pesch and S. L. Friess, *ibid.*, **72**, 5756 (1950).

(12) Methine protons in cyclopropane rings absorb in this region of the spectrum as evidenced by several model compounds. For example, see spectra 273 and 693 in "High Resolution NMR Catalog," Vol. I and II, Varian Associates, Palo Alto, Calif.

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(3) W. O. Jones, *J. Chem. Soc.*, 2036 (1953).

(4) S. C. Nyburg and J. Hilton, *Acta Cryst.*, **12**, 116 (1959).

(5) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Ann.*, **560**, 1 (1948).

(6) R. C. Lord and R. W. Walker, *J. Am. Chem. Soc.*, **76**, 2518 (1954).

a methyl group is readily eliminated on the basis of the complexity of this pattern, while a complex absorption pattern would be expected in this region if the dimer contained a cyclopropane group containing three methine protons as in structure III. No absorption appears in this region of the n.m.r. spectrum of the known dimer, IV. Confirmation of the presence of two double bonds and a cyclopropane ring in III is obtained from the n.m.r. spectrum of the reduced dimer (after three moles of hydrogen have been consumed). The n.m.r. spectrum of this compound shows no absorption in the vinyl proton region or in the cyclopropane region.

Lord and Walker⁶ found that the ratio of compound III to IV produced in the dimerization of cyclooctatetraene depended upon the temperature at which the dimerization was run. If the dimerization was carried out above 200° or if III was heated for some time at such temperatures, IV was obtained. These observations were confirmed. The ease of this conversion of III to IV, which does not appear to be reversible, implies that the two dimers are not greatly dissimilar, and that the structure proposed for the unknown dimer, III, should enable one to understand the change to the other. These requirements are met by structure III. The double bond b and the cyclopropane ring comprise a vinylcyclopropane moiety. Vinylcyclopropane is known to rearrange to cyclopentene at high temperatures.¹³ Thermal rearrangement of the vinylcyclopropane moiety in III to a cyclopentene moiety would give the known dimer IV.¹⁴

The possibility of the dimer, II, being a precursor to III seems reasonable on the basis of an intramolecular Diels-Alder reaction. There are two possible stereochemical configurations for compound II, the *cis* isomer (*cis*-cyclobutane protons) and the *trans* isomer (*trans*-cyclobutane protons). Only in the *cis* compound would the geometry be favorable for an intramolecular Diels-Alder cyclization. Attempts to cyclize an authentic sample of II¹⁵ under a variety of conditions has given only polymers. This inability of intramolecular Diels-Alder cyclization is a good indication that the dimer, II (obtained at low temperatures), has the *trans* configuration. Further studies on the stereochemistry of II, as well as the sequence of reactions leading to the dimers of cyclooctatetraene, are currently being investigated.

Acknowledgment.—The author wishes to express his appreciation to Dr. Karl Folkers for helpful suggestions throughout the course of this work.

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(14) The vinylcyclopropane moiety is within a bicyclo[5.1.0]octene-2 ring system which is known to rearrange thermally to 1,4-cyclooctadiene [W. von E. Doering and W. R. Roth, *Angew. Chem.*, **75**, 27 (1963)]. However, this type of rearrangement is impossible in III since it would give a compound with a bridgehead double bond.

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STANFORD RESEARCH INSTITUTE
MENLO PARK, CALIFORNIA

HAROLD W. MOORE

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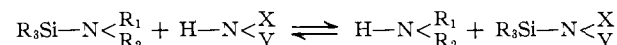
New Silyl Donors

Sir:

Silylation of amine, amide, and hydroxyl functions has become a valuable tool for separation and analysis

of compounds with a high degree of hydrogen bonding. Replacement of protons by silyl groups can lead to derivatives of considerably higher vapor pressure which after distillation or vapor phase chromatographic separation can readily be reconverted into the starting materials.

The silylamine-amine exchange reaction introduced by Larsson and Smith¹ has found extensive use in the preparation of silyl-substituted amines,² amides, lactams, carbamates, and ureas.³ Hexamethyldisilazane and other disilazanes also undergo this silyl-transfer reaction which has been used in preparing silyl derivatives of peptides,⁴ ureas,⁵ tetrazoles,⁶ and flavonoid compounds.⁷ Silylations with silylamines, silanedi- amines and -triamines, as well as disilazanes are based on a relatively slow exchange reaction between silyl donor and acceptor. The success of the procedure



depends on the removal of the lower boiling amine HNR_1R_2 , a process which usually requires several hours of heating at the reflux temperature of the mixture.

We have now found that N-silyl-substituted aromatic ureas and amides represent very powerful silyl donors. The equilibrium in solutions of these donors in mixtures with amines, amides, or hydroxyl compounds is established *within a few minutes at room temperature*, a time that is several orders of magnitude shorter than that required by "conventional" silyl donors. Furthermore, the position of equilibrium is such that nearly quantitative silylation of aliphatic or aromatic acceptors occurs within this period of time if disilyl-substituted amides like $CH_3C(Osime_3)=Nsime_3$ ⁸ are applied. Use of monosilyl-substituted donors like $C_6H_5N(Sime_3)-CO-NHC_6H_5$ leads to complete silylation of aliphatic acceptors while aromatic amines or amides require removal of one of the products from the equilibrium for complete silylation.

The difference in rate of silylation between "amine-type" and "amide-type" silyl donors is demonstrated by the following experiments.

Equimolar mixtures of N,N'-dimethylurea as silyl acceptor and (a) hexamethyldisilazane, (b) N-trimethylsilylpiperidine, (c) N-trimethylsilylaniline, and (d) N-trimethylsilyl-N,N'-diphenylurea⁵ in acetonitrile were prepared and the progress of the reaction was followed by vapor phase chromatography. The extent of N-trimethylsilyl-N,N'-dimethylurea formation after 75 hr. at room temperature was: (a) 0%; (b) 10%; (c) 3%. Mixture d, containing trimethylsilyl-diphenylurea as silyl donor, showed complete conversion to N-trimethylsilyldimethylurea after 1 min. at room temperature. Silylations with other amide-type donors were followed by proton magnetic resonance spectroscopy of the mixtures which confirmed the rapid rates of silylation.⁹

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