driodic acid was refluxed for 36 hours and then hydrolyzed by adding 35 ml. of 30% aqueous potassium hydroxide and refluxing for 12 hours in the dark under nitrogen. The reaction mixture was extracted with ether, the aqueous layer separated, acidified with 2 N hydrochloric acid and extracted with chloroform. The chloroform solution, after washing to neutrality with water and drying over sodium sulfate, was concentrated and distilled *in vacuo* yielding 1.84 g. (80%) of 6,8-dithioloctanoic acid (VI), b.p. 180° (bath temperature) (1.5 mm.), n^{22}D 1.5225; infrared spectrum 1285, 1235 (OH-carboxyl), 1710 (CO-carboxyl) cm.$^{-1}$.

Anal. Calcd. for $C_8H_{16}O_2S_2$: C, 46.12; H, 7.74. Found: C, 46.37; H, 7.74.

6-Thioctic Acid (DL-α-Lipoic Acid) (VII).—1.01 g. of dithiol-acid (VI) were dissolved in 2.3 ml. of 2 N sodium hydroxide, diluted with 17 ml. of water containing 3.5 mg. of iron trichloride hexahydrate, yielding a dark red solution, through which a slow stream of oxygen was bubbled for 10 hours. The resulting pale yellow solution was washed with chloroform. The aqueous layer, acidified with 2 N hydro-

chloric acid, was extracted with chloroform and this was washed to neutrality and evaporated to dryness. The yellow oily residue crystallized upon trituration with petroleum ether (boiling range 40–60°). After one crystallization from petroleum ether, 0.8 g. of pure 6-thioctic acid (DL-α-lipoic acid) (VII) (80%) was obtained, m.p. 61–62°; ultraviolet spectrum λ_{max}^{EtOH} 333 mμ (ε 147); infrared spectrum bands at 1285, 1235 (OH-carboxyl), 1700 (CO-carboxyl) cm.$^{-1}$.

Anal. Calcd. for $C_8H_{14}O_2S_2$: C, 46.57; H, 6.68; S, 31.13. Found: C, 46.66; H, 6.90; S, 31.20.

S-Benzylisothiuronium salt, m.p. 153–154°[18] (from absolute methanol). *Anal.* Calcd. for $C_{16}H_{24}N_2O_2S_3$: C, 51.61; H, 6.45; N, 7.53; S, 25.79. Found: C, 51.53; H, 6.73; N, 7.56; S, 25.99.

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(18) M.p. 132–134°[14] has been observed once. This discrepancy may be due to crystallization and drying conditions.

Many-membered Carbon Rings. XIV. Transannular Ring Cleavage of Certain Cycloalkane Derivatives[1]

BY A. T. BLOMQUIST AND PETER R. TAUSSIG[2]

Pyrolysis of cyclononyl acetate at 500° affords mainly 1,8-nonadiene (70%) together with *cis*-cyclononene (27%) and *trans*-cyclononene (1.5%). Thermal decomposition of cyclononyl S-methyl xanthate at various temperatures indicates that formation of 1,8-nonadiene occurs only at temperatures above 400°. Pure *trans*-cyclononene rearranges at 500° to 1,8-nonadiene (85%) and *cis*-cyclononene (15%) while pure *cis*-cyclononene, at 500°, yields only *ca.* 20% 1,8-nonadiene and 80% unchanged *cis*-cyclononene. Conformational analysis suggests two possible paths for the formation of the diene from cyclononyl acetate.

The discovery in recent years of transannular reactions[3,4] has done much to stimulate research in the chemistry of medium size rings. This has included several studies concerned with the course of elimination reactions of various derivatives of the cycloalkanes such as their amines, halides, acetates and xanthates.[5–7] This article presents studies of the thermal decomposition of the acetate and S-methyl xanthate of cyclononanol. In an earlier study of the pyrolysis of cyclodecyl acetate and cyclodecyl xanthate,[6] it was observed that a mixture of *cis*- and *trans*-cyclodecenes was produced rather than exclusively one stereoisomer as might have been expected. Further, it was noted that pyrolysis of cyclodecyl acetate gave, as a minor

product, a low boiling "dienoid" substance. The latter was not fully characterized at that time.

Pyrolysis of cyclononyl acetate[8] at 500 ± 10° under the same conditions employed in the thermal decomposition of cyclodecyl acetate[6] afforded a pyrolyzate (78%) which interestingly contained only 30% of the expected mixture of *cis*- and *trans*-cyclononenes (IIa and IIb). The principal constituent (70%) of the pyrolyzate was found to be a low boiling compound analogous to the minor product formed in the thermal degradation of cyclodecyl acetate. This low boiling substance was readily identified as 1,8-nonadiene (I).

The structure of this hydrocarbon I was established as indicated below. Its properties agreed with those reported for 1,8-nonadiene by van Pelt[9] and by Everett.[10] Elementary analysis of I was in accord with the composition C_9H_{16} and quantitative catalytic hydrogenation of I indicated the presence of two double bonds. On oxidative ozonolysis I gave an acid (18%) which did not depress the melting point of an authentic sample of pimelic acid. Finally, the infrared absorption spectrum of I showed maxima at 10.07 and 10.97 μ, characteristic of a vinyl group, and was identical with the spectrum of 1,8-nonadiene obtained by pyrolysis of 1,9-nonanediol diacetate.

(1) (a) For the preceding paper in this series see A. T. Blomquist and P. R. Taussig, THIS JOURNAL, **77**, 6399 (1955). (b) Presented before the Division of Organic Chemistry at the National Meeting of the American Chemical Society at Miami, Florida, April 7–12, 1957.

(2) Du Pont Post-Graduate Teaching Fellow. The work reported here was abstracted from part of the dissertation presented by Peter R. Taussig in September, 1956, to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) V. Prelog and K. Schenker, *Helv. Chim. Acta*, **35**, 2044 (1952); V. Prelog, K. Schenker and W. Küng, *ibid.*, **36**, 471 (1953); V. Prelog, H. J. Urech, A. A. Bothner-By and J. Würch, *ibid.*, **38**, 1095 (1955); V. Prelog and V. Boarland, *ibid.*, **38**, 1776 (1955).

(4) A. C. Cope, S. W. Fenton and C. F. Spencer, THIS JOURNAL, **74**, 5884 (1952).

(5) A. T. Blomquist, R. E. Burge and A. C. Sucsy, *ibid.*, **74**, 3636 (1952).

(6) A. T. Blomquist and A. Goldstein, *ibid.*, **77**, 1001 (1955).

(7) A. C. Cope, R. A. Pike and C. F. Spencer, *ibid.*, **75**, 3212 (1953); A. C. Cope, D. C. McLean and N. A. Nelson, *ibid.*, **77**, 1628 (1955).

(8) M. Kobelt, D. Barman, V. Prelog and L. Ruzicka, *Helv. Chim. Acta*, **32**, 256 (1949).

(9) A. J. van Pelt, Jr., and J. P. Wibaut, *Rec. trav. chim.*, **60**, 55 (1941).

(10) J. L. Everett and G. A. R. Kon, *J. Chem. Soc.*, 3131 (1950).

After completion of the characterization of I, it became apparent that the "dienoid" product formed in the pyrolysis of cyclodecyl acetate[6] was probably 1,9-decadiene (III). This was confirmed by preparing an authentic sample of III *via* pyrolysis of 1,10-decanediol diacetate and comparing the infrared absorption spectra of the two hydrocarbons. They were indistinguishable.

With the object of ascertaining, to some extent, the generality of this ring cleavage of cycloalkyl esters, the pyrolysis of cycloöctyl acetate[8] was examined. Here it was found that about 10% of the pyrolyzate had properties differing from the cycloöctenes but possessing an infrared absorption spectrum very similar to those of 1,8-nonadiene and 1,9-decadiene. All of the foregoing suggests that ring cleavage in the thermal degradation of medium sized cycloalkyl acetates is general, but it is a major reaction only for the nine-membered ring.

Estimation of the amount of *cis*- and *trans*-cyclononene (IIa and IIb, respectively) in the cyclononene fraction obtained in the pyrolysis of cyclononyl acetate was done by the quantitative infrared analysis method used previously for *cis*- and *trans*-cyclodecene.[1] The per cent. IIa in the mixture of cyclononenes was determined by noting the intensity of the absorption maximum at 13.16 μ with reference to a base line drawn from the minimum at 12.90 μ. The per cent. IIb was determined by measuring the intensity of the absorption maximum at 10.15 μ with reference to a base line drawn from the minimum at 10.60 μ. Application of the method to analyses of known mixtures of pure cyclononenes indicated that it was accurate to about ±5%. Using the above method it was found that the cyclononene fraction resulting from the acetate pyrolysis comprised 90% IIa and 5% IIb.

In order to complement the pyrolysis study of cyclononyl acetate, it seemed desirable to examine the thermal decomposition of cyclononyl S-methyl xanthate (IV) at various temperatures. In these experiments (Table II) it was observed that the formation of I did not occur until the pyrolysis temperature was about 400°. At 500° the pyrolyzate from IV contained about 50% I. It was noted further that as the content of I increased in the pyrolyzate of IV, the per cent. IIb in the cyclononene fraction decreased.

The foregoing suggested that perhaps cyclononenes were intermediates in the formation of I. Accordingly, both IIa and IIb were pyrolyzed under conditions similar to those used for the decomposition of the cyclononyl esters. The pure hydrocarbon IIa at 500° afforded a pyrolyzate comprising *ca.* 20% I, the remainder (80%) being unchanged IIa. The pure hydrocarbon IIb at 500° gave a product which contained 85% I and 15% of a mixture of IIa and IIb. The cyclononene in this latter mixture was very largely the *cis* isomer IIa (see Table I).

Discussion of Results

The observations presented in the foregoing can be accounted for by a careful conformational analysis of the nine-membered carbocycle. The most probable conformation for cyclononane itself would

be that in which there is maximum distance between the non-bonded atoms. Stylized projection representations for two views of such a conformation derived from a Fisher–Hirschfelder–Taylor model is given in Fig. 1. According to this model (Fig. 1) there are eight *quasi-axial* hydrogens, attached to carbon atoms 1,2,3,4,5,2',3' and 4', directed inward toward the center of the ring. Four of these are on the upper side of the ring and four below. The eight *quasi-equatorial* hydrogens attached to these carbon atoms and arranged about the periphery of the ring are directed outward and at an angle essentially perpendicular to the ring axis. The hydrogen atoms attached to the carbon labeled 1' appear to be unique in that they extend away from the ring in a direction midway between the *quasi-axial* and *quasi-equatorial* hydrogens. On the basis of this model three principal conformations are theoretically possible for cyclononyl acetate. The acetoxy group may be *quasi-equatorial*, *quasi-axial* or at the intermediate position on C_1'. At 500° all of these should exist and their interconversion should be facile. From these conformations of the acetate the realization of the requisite transition state for 1,2-elimination of acetic acid, a planar six-membered ring arrangement of the atoms H–C–C–O—C=O,[11,12] would

$$\overset{|}{C}H_3$$

appear to involve the least amount of "steric strain" under the circumstance that the hydrogen atom and acetoxy group on adjacent carbons both be in *quasi-equatorial* positions. Such a transition state would lead to IIb. Further, according to the models, the formation of *all* of those transition states which would lead to IIa is rendered more difficult because of steric factors. For the above reasons, IIb should be the principal product of the thermal 1,2-elimination of acetic acid from cyclononyl acetate.

The observations that (1) the pyrolyzate from cyclononyl acetate comprises principally I (70%) and IIa (*ca.* 30%) and (2) pyrolysis of the cyclononenes themselves affords I (*ca.* 20% from IIa and *ca.* 85% from IIb), suggests that the formation of I possibly involves two discrete steps. Initially, cyclononyl acetate affords, *via* 1,2-elimination of acetic acid, a mixture of cyclononenes containing mainly the *trans* isomer. Subsequently, the cyclononenes, especially the *trans* isomer, undergo transannular intramolecular rearrangement to the open-chain diene I. A possible path for this rearrangement is indicated in the diagram below. It involves a transannular shift of a *quasi-axial* hydrogen on carbon five to carbon one of the double bond with a concomitant redistribution of electrons.
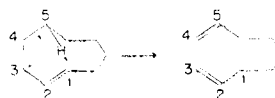
Examination of molecular models of IIa and IIb indicates that the rearrangement should be particularly facile for IIb. In this olefin IIb the

(11) E. R. Alexander and A. Mudrak, THIS JOURNAL, 72, 1810, 3194 (1950).

(12) W. Hückel, W. Tappe and G. Legutke, Ann., 543, 191 (1940).

TABLE I

THERMAL DECOMPOSITION OF CYCLONONENES AT 500°

Cyclononene used Wt., g.	Compn.	Total yield in g. and %	Diene yield, g. and % of total	Pyrolyzate obtained Cyclononone yield, g. and % of total	Compn
7.7	100% cis	6.7 (87)	1.2 (18.5)	5.5 (81.5)	100% cis
3.4	95% cis 5% trans	2.7 (78)	0.5 (20)	2.2 (80)	100% cis
8.4	65% cis 35% trans	5.8 (69)	2.5 (44)	3.3 (56)	91.2% cis 3.7% trans
10.3	100% trans	7.9 (77)	6.7 (85)	1.2 (15)	93.4% cis 6.2% trans

quasi-axial hydrogen at position five appears to be easily within bonding distance of position one, and further the movement of this hydrogen from C_5 to C_I is not obstructed by other *quasi-axial* hydrogen atoms. The situation with respect to IIa is quite different. The C_5-*quasi-axial*-hydrogen is at a greater distance from C_1 than in IIb, and also there are *quasi-axial* hydrogen atoms on C_3 and C_9 blocking the migration (see Fig. 2).

Although the above rationalizations appear to account satisfactorily for the experimental observations, the possibility of other operating mechanisms cannot be excluded. One of these was suggested in an earlier communication.[1] The proposed mechanism indicated the direct formation of the diene I from cyclononyl acetate by 1,4-trans-annular elimination of acetic acid via a six-membered cyclic transition state developed through interaction of the ethereal oxygen atom in *quasi-axial* cyclononyl acetate and the *quasi-axial* hydrogen atom on C_4. Examination of a molecular

I
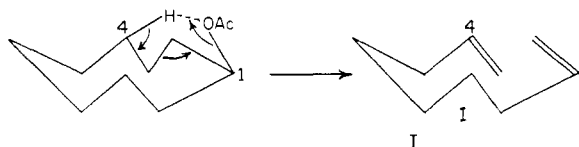
model of *quasi-axial* cyclononyl acetate suggests that the requisite transition state could be realized easily.

Acknowledgments.—The authors are indebted to Professor R. M. Hexter for his aid in obtaining and interpreting the infrared spectra data used in these studies. Also, the authors wish to express their sincere appreciation to Dr. Yvonne C. Meinwald for her assistance in the preparation of this article.

Experimental[13]

Materials.—*cis*-Cyclononene (IIa) was obtained by hydrogenation of cyclononyne[14] using Lindlar catalyst following a procedure similar to that described for the preparation of *cis*-cyclodecene.[6] The IIa obtained (83% yield) had $n^{25}D$ 1.4780. *trans*-Cyclononene (IIb), $n^{25}D$ 1.4782, was obtained as described previously.[14] 1,8-Nonadiene (I), prepared by pyrolysis of 1,9-nonanediol diacetate at 500°, showed b.p. 136–138° (740 mm.), and $n^{25}D$ 1.4250.[9,10] 1,9-Decadiene b.p. 162–163° (740 mm.), and $n^{25}D$ 1.4316, was prepared similarly from 1,10-decanediol diacetate. Its properties were in good agreement with those reported for it by Everett and Kon.[10] The cyclononyl acetate used[8] had b.p. 113–116° (12 mm.) and $n^{25}D$ 1.4629.

(13) All b.p.'s are uncorrected. Infrared absorption spectra were obtained by use of a Perkin–Elmer double beam infrared spectrophotometer, Model 21.

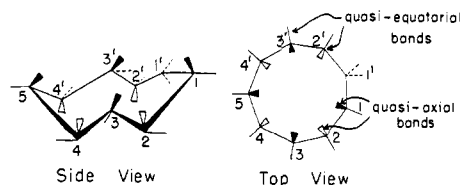(14) A. T. Blomquist, L. H. Liu and J. C. Bohrer, THIS JOURNAL, 74, 3643 (1952).
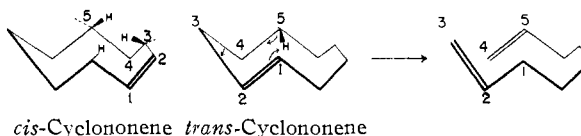
Fig. 1.—Conformation of cyclononane.

cis-Cyclononene   *trans*-Cyclononene

Fig. 2.—Conformations of the cyclononenes.

Cyclononyl S-Methyl Xanthate.—This xanthate was prepared using the same method described for cyclodecyl S-methyl xanthate.[6] From 36.7 g. of cyclononanol 72 g. of crude xanthate was obtained. This crude xanthate was used in the pyrolyses described subsequently. An analytical sample of the xanthate was secured by chromatographing the crude product on alumina and eluting with pentane. It was obtained as a clear, slightly yellow oil.

Anal. Calcd. for $C_{11}H_{20}OS_2$: C, 56.87; H, 8.62; S, 27.62. Found: C, 56.62; H, 8.38; S, 27.40.

Thermal Decomposition of Cyclononyl Acetate.—The pyrolysis was carried out as described previously for the thermal decomposition of cyclodecyl acetate.[6] After the usual workup, the products were distilled through a 36-inch Podbielniak column to give two main fractions: (1) b.p. 140–144°, $n^{25}D$ 1.4260, d^{25} 0.748, which comprised 67–70% of the product, and (2) a mixture of *cis*- and *trans*-cyclononenes, b.p. 172–174°, $n^{25}D$ 1.4770, which comprised 33–30% of the product. The total yield of olefins amounted to 72–78%.

Analysis by infrared spectrophotometry indicated that fraction (2) consisted of 89–91% of IIa and 4–5% of IIb.

Thermal Decomposition of Cyclononenes (IIa and IIb).—The pyrolysis procedure used was identical with that employed in the cyclononyl acetate decomposition. The results are presented in Table I.

TABLE II

THERMAL DECOMPOSITION OF CYCLONONYL S-METHYL XANTHATE

Xanthate used, g.	Pyrolysis temp., °C.	Total, g. and %	Pyrolyzate % diene	% Cyclononenes and compn.
12.0	120 – 130	2.2 (34.4)	0	100—60% cis 40% trans
14.0	360 ± 10	3.3 (44)	0	100—55% cis 45% trans
14.0	400 ± 10	2.9 (38)	Trace	99+% 78% cis 19% trans
14.0	450 ± 10	3.4 (45)	10	90 80% cis 20% trans
14.0	500 ± 10	1.8 (24)	50	50 100% cis

Thermal Decomposition of Cyclononyl S-Methyl Xanthate. (A) Low Temperature Procedure.—Crude cyclononyl S-methyl xanthate (12 g.) was pyrolyzed in a 100-ml. flask at 120–130° according to the procedure previously described.[6] The product, a yellow liquid, was distilled at 56–64° (15 mm.) and weighed 4.1 g. The yellow contaminant was removed by chromatography. Subsequent distillation through a Podbielniak column at atmospheric pressure yield 2.2 g. (34.4%) of II, b.p. 168–173°, n^{25}D 1.4770. (B). High Temperature Procedure.—Crude cyclononyl S-

methyl xanthate (14 g.) was dropped through a carborundum packed column heated to the desired temperature as described for the acetate pyrolysis. After completion of the pyrolysis, the column was cooled and washed with pentane. The combined pyrolyzate and washes were worked up as in the low temperature procedure.

The results of the pyrolyses at various temperatures are summarized in Table II.

ITHACA, NEW YORK

Synthesis of Methoxyhydrophenanthrenes and Methoxyhydrocyclohepta[a]naphthalenes by Acylation of Ketones with Homoveratric Anhydride

BY GORDON N. WALKER
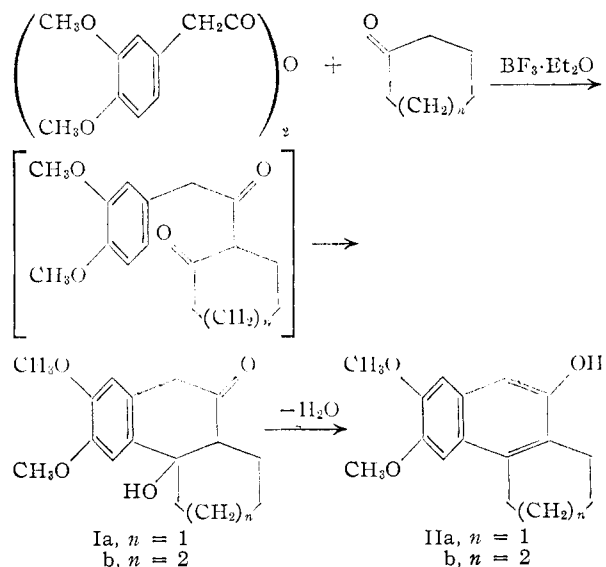
Acylation of cyclohexanone and cycloheptanone with homoveratric anhydride in the presence of boron trifluoride etherate is accompanied by cyclization, giving, after dehydration, compounds IIa and IIb, respectively. An intermediate hydroxyketone Ia is isolated in the first case. Acylation of cyclohexanone and cycloheptanone with homoveratric anhydride in the presence of boron trifluoride in acetic acid leads to formation of 1-acetyl-2-naphthol derivatives, XIa and XIb, respectively. Evidence confirming the structures of these products is presented, notably oxidation of compounds II to quinones VIII, and hydrogenation of compounds XI to octahydrophenanthrenes, XII. Angular methyl compounds V and VI have also been synthesized by acylation of 2-methylcyclohexanone with homoveratric anhydride.

There are several methods for synthesizing phenanthrenes and hydrophenanthrenes from simple aromatic compounds, depending upon cyclization reactions of appropriate functional groups with benzene carbon–hydrogen. These methods include the classical Pschorr procedure[1] and its modifications, the Haworth method[2] and cyclizations first described by Bardhan and SenGupta[3] and independently by Bogert[4] and Cook[5] and their collaborators. The Pschorr synthesis,[6,7] and another approach, namely, closure of ring B after elaboration of the A/C system,[8,9] have been adapted to synthesis of methoxy tricyclic compounds incorporating seven-membered rings (colchicine relatives). Efforts to circumvent difficulties inherent in these approaches have now led to discovery of a new cyclodehydration[10] reaction, described in this paper,[11] which accomplishes in one step the synthesis of certain hydrophenanthrenes and their C-ring homologs.

Experimental work was begun, acting upon the premise that if cyclic ketones could be C-acylated with phenylacetic anhydrides, it should be pos-

Ia, $n = 1$
b, $n = 2$

IIa, $n = 1$
b, $n = 2$

sible to bring about cyclization of resulting β-diketones through interaction of the benzene ring and the cyclic ketone moiety under acid conditions. Exposure of mixtures of phenylacetic anhydride and cyclohexanone to boron trifluoride under various conditions failed to yield recognizable products, an observation which agrees with earlier data.[12] However, it seemed likely that C-acylation did occur, for infrared spectra of the (presumably polymeric) products showed ketone (5.8–5.9 μ) rather than enol ester (5.7 μ) bands. Experiments with homoveratric anhydride were then tried, and these proved to be successful, inasmuch as C-acylation did occur, as supposed, and cyclization of resulting diketones in situ took place as well.

(1) See P. H. Leake in Chem. Revs., 56, 27 (1956).

(2) R. D. Haworth, et al., J. Chem. Soc., 1125, 1784, 2248, 2717, 2720 (1932).

(3) J. C. Bardhan and S. C. SenGupta, ibid., 2520, 2798 (1932).

(4) M. T. Bogert, et al., Science, 77, 289 (1933); J. Org. Chem., 1, 288, 300 (1936); THIS JOURNAL, 56, 185, 959 (1934).

(5) J. W. Cook and C. L. Hewett, Chemistry & Industry, 52, 451 (1933); J. Chem. Soc., 1098 (1933).

(6) J. W. Cook, J. Jack and J. D. Loudon, ibid., 1397 (1951), and preceding papers.

(7) H. Rapoport, et al., THIS JOURNAL, 73, 1414 (1951); 77, 670 (1955).

(8) C. D. Gutsche and F. A. Fleming, ibid., 76, 1771 (1954).

(9) D. Ginsburg, ibid., 76, 3628 (1954).

(10) A term used by C. K. Bradsher, Chem. Revs., 38, 447 (1946), to describe formation of aromatic rings through reactions involving loss of water. The synthesis presented here may be considered to fall into this category.

(11) A preliminary report of this work appeared in THIS JOURNAL, 78, 2340 (1956).

(12) J. T. Adams and C. R. Hauser, ibid., 67, 284 (1951).