[CONTRIBUTION FROM THE CENTRAL EXPERIMENT STATION, U. S. BUREAU OF MINES]

Aromatic Cyclodehydrogenation. IX. Further Studies on Ring Oxygen Compounds[1]

BY MILTON ORCHIN,[2a] LESLIE REGGEL[2a] AND R. A. FRIEDEL[2b]

The work reported here was initiated as part of a study of the preparation and properties of 1-keto-2-(1′-tetralylidene)-1,2,3,4-tetrahydronaphthalene, I, referred to in the following discussion as tetralylidenetetralone. This compound has obvious usefulness as an intermediate in the synthesis of polynuclear compounds, but it has as yet not been so employed. Indeed, its only previously reported preparation was a fortuitous one in which Cook and Lawrence[3] isolated it from a Grignard reaction involving 1-tetralone.

The preparation of I is conveniently achieved by treatment of 1-tetralone with hydrogen chloride in a manner analogous to the preparation of cyclohexylidenecyclohexanone from cyclohexanone.[4a] The yield of I was 24% over-all, or 68% based on unrecovered 1-tetralone.

Catalytic hydrogenation of the unsaturated ketone, I, at room conditions with a palladium catalyst resulted in the absorption of one mole of hydrogen per mole of compound. The composition and properties of the product indicated that reduction had occurred only at the double bond, leaving the carbonyl group intact, and that a mixture of the two racemates of 1-keto-2-(1′,2′,3′,4′-tetrahydro-1′-naphthyl)-1,2,3,4-tetrahydronaphthalene, II, was formed.

Much study has been devoted[4b] to the establishment of the position of the double bond in cyclohexylidenecyclohexanone, a compound that may be considered to be the lower homolog of our compound, I. In our investigation an effort was made to determine by infrared spectrometry whether the double bond in I is exocyclic as shown, rather than endocyclic. The spectrum of I (Fig. 1) shows that, in the C–H vibration region at 3.0 microns, there are two bands typical of aromatic C–H and two bands characteristic of aliphatic CH_2 groups. If the double bond in I were endocyclic (Fig. 1, Ib), the grouping $=\overset{|}{C}-H$ would exist and should produce a band between these two groups of bands; such a band is not found. In addition, if the double bond were endocyclic, the grouping $-\overset{|}{\underset{|}{C}}-H$ would exist and might produce a band at a wave length longer than that of the CH_2 bands; such a band is not found in the spectrum of I. This band is present, however, in the spectrum of II (Fig. 1), which has two $-\overset{|}{\underset{|}{C}}-H$ groupings. This evidence indicates that the double bond in I is exocyclic (Fig. 1, Ia). The spectra of both I and II showed no absorption in the OH region, and the C=O bands (not shown) were of approximately equal intensity.

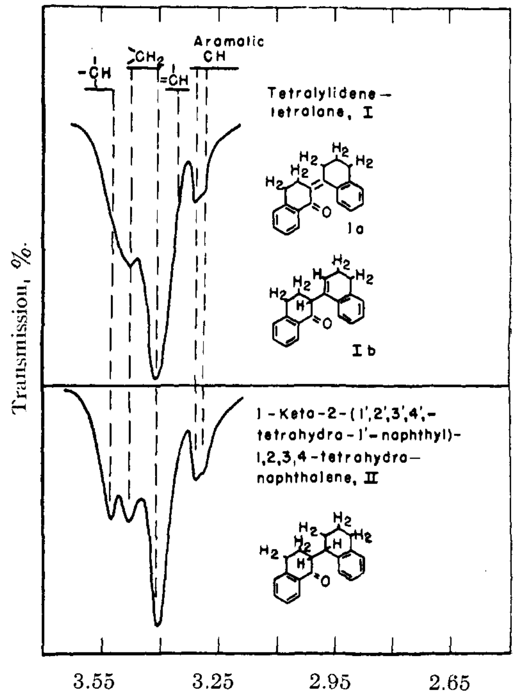

Fig. 1.—Infrared spectra of tetralylidenetetralone and 1-keto-2-(1′,2′,3′,4′-tetrahydro-1′-naphthyl)-1,2,3,4-tetrahydronaphthalene in the 3.4 micron C–H vibration region.

The ultraviolet spectrum of II (Fig. 2) is, as expected, very similar to that of 1-keto-1,2,3,4-tet-

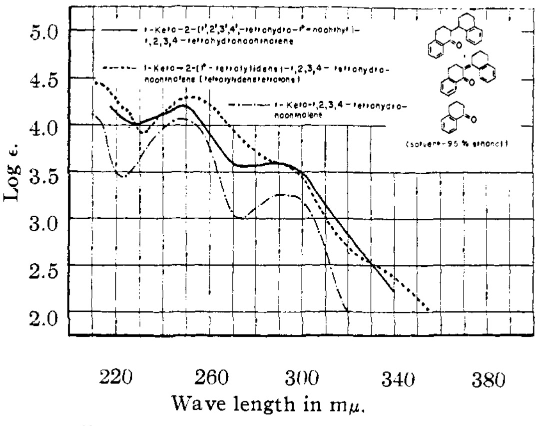

Fig. 2.—Ultraviolet absorption spectra.

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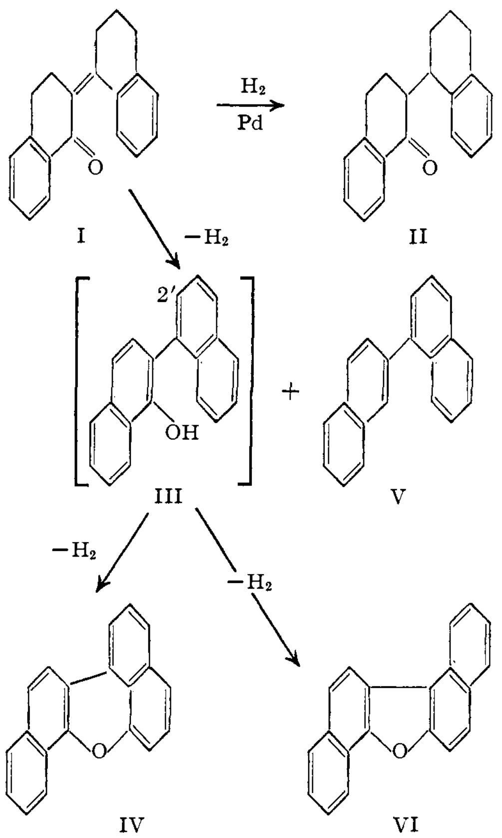
(3) Cook and Lawrence, *J. Chem. Soc.*, 1431 (1936).

(4) (a) Rapson, *ibid.*, 15 (1941); (b) Reese, *Ber.*, **75B**, 384 (1942).

rahydronaphthalene (1-tetralone); the shoulder at 275 mμ in II is indicative of the weakly absorbing tetralin nucleus. The spectrum of I is not very similar to that of 1-tetralone or II and shows less distinct structure because of the extensive double-bond conjugation.



Liquid-phase dehydrogenation of I with a palladium catalyst at 300° gave a mixture of products that were separated into a Claisen[5] (methanolic) alkali-soluble fraction and a neutral portion. The alkali-soluble product could not be crystallized, and attempts to prepare an acetate were unsuccessful. This product was probably 2-(1'-naphthyl)-1-naphthol, III, and the resemblance of its ultraviolet absorption spectrum to that of 1,2'-dinaphthyl, V, (Fig. 3) tends to confirm this supposition; the slight shoulder at 320–325 mμ in III is to be expected, since the hydroxyl group would increase the steric hindrance and further inhibit the coplanarity of the compound.[6] The neutral portion of the dehydrogenation product was separated further by chromatography. Small amounts of naphthalene and of 1,2'-dinaphthyl, V, were obtained, but the main product was a yellow crystalline compound, $C_{20}H_{12}O$, melting point 166.2–166.8°, which fluoresced strongly. We regard this compound as dibenzo[c,kl]xanthene, IV. The only alternate structure which need seriously be considered is the isomeric dinaphtho[1,2-b,1',2'-d]furan, VI, which could arise from cyclization of III into the 2'-position of the naphthalene nucleus. We have shown previously[7] that treatment of 2-(1'-naphthyl)-cyclohexanone, VII, or 2'-hydroxy-1-phenylnaphthalene, VIII, with a palladium catalyst under the conditions of the present experiment leads to the formation of the known 1,9-benzoxanthene, IX, containing a six-membered ring, rather than to the formation of the isomeric benzo[b]-naphtho[1,2-d]furan, X, containing a five-membered ring. The intense fluorescence of 1,9-benzoxanthene and the deep color of its complexes with 2,4,7-trinitrofluorenone and *s*-trinitrobenzene are also features of the compound we regard as IV. In contrast, the known benzo[b]naphtho[2,3-d]-furan (brazan), which contains a five-membered oxygenated ring, is weakly fluorescent and forms lighter-colored complexes.[8] The ultraviolet absorption spectrum of the compound we regard as IV has considerable resemblance to that of 1,9-benzoxanthene (Fig. 4); both compounds have the same type of band structure, with the expected shifting of the bands of the dibenzo[c,kl]xanthene to longer wave lengths.

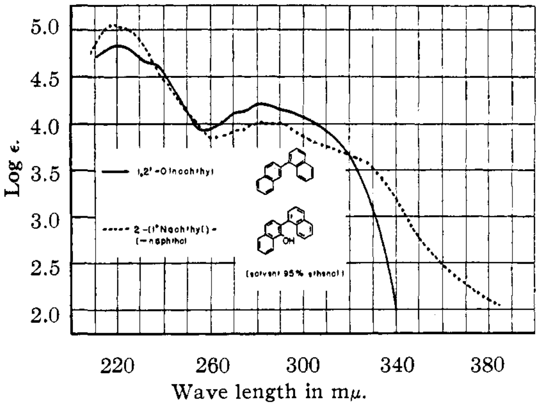
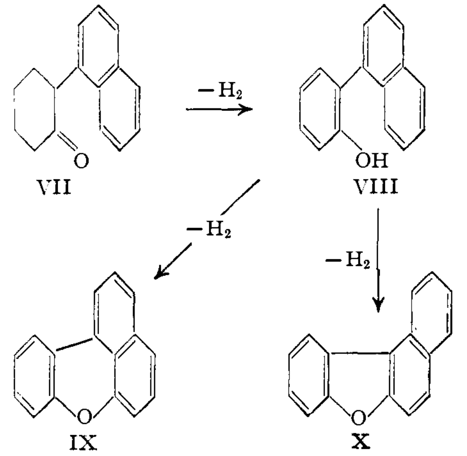


Fig. 3.—Ultraviolet absorption spectra.



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[5] "Organic Reactions," John Wiley and Sons, New York, N. Y., Vol. 2, 1944, p. 28.

[6] Friedel, Orchin and Reggel, THIS JOURNAL, **70**, 199 (1948).

[7] Orchin, *ibid.*, **70**, 495 (1948).

[8] Orchin and Reggel, *ibid.*, **70**, 1245 (1948).

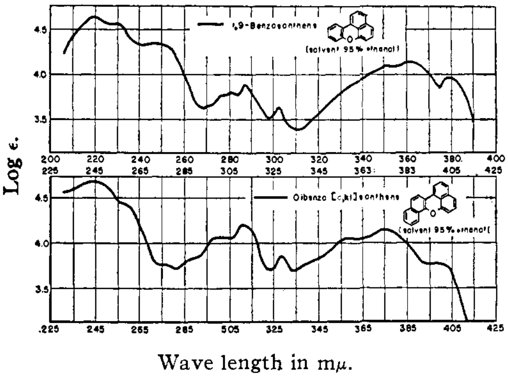

Fig. 4.—Ultraviolet absorption spectra.

The formation of IV probably occurs through III just as IX was shown to be formed by cyclodehydrogenation of VIII.[7] An attempt was made to prepare III by dehydrogenation of I in the presence of an inert solvent.[9] The alkali-soluble portion of the product could not be crystallized; its ultraviolet absorption spectrum indicated its probable identity with the alkali-soluble product from the dehydrogenation of I in the absence of solvent. Treatment of this material under conditions whereby I gave IV resulted in a mixture, the ultraviolet absorption spectrum of which indicated that a major component was dibenzo[c,kl]xanthene, IV. The spectrum of IV was subtracted from the mixture spectrum to obtain the curve shown in Fig. 5. This may be the isomeric dinaphtho[1,2-b,1′,2′-d]furan, VI; comparison with the spectrum of the corresponding hydrocarbon, 1,2,5,6-dibenzfluorene, is interesting but inconclusive.

Experimental[10]

1-Keto-2-(1′-tetralylidene)-1,2,3,4-tetrahydronaphthalene, I.—1-Tetralone[11] (148.2 g.) was saturated with dry hydrogen chloride gas and then heated on a steam-bath for sixty-seven hours; hydrogen chloride was passed in again and heating continued for another twenty-four hours. The mixture was taken up in benzene, washed with 10% sodium hydroxide solution, washed, dried and distilled. There was obtained 94.79 g. (64.0%) of 1-tetralone and 41.94 g. of a viscous yellow gum, b. p. 220–225° at 1–2 mm. (bath 280–285°). This was dissolved in about 1.5 l. of absolute ethanol and the solution concentrated to 360 ml. The first crop (31.28 g.) formed large, pale-tan prismatic crystals, m. p. 131.6–135.5°. Another 2.79 g. was obtained from the mother liquor; total yield, 24.5%. A sample recrystallized from absolute ethanol formed white prisms, m. p. 132.5–134.2°. The 2,4-dinitrophenylhydrazone formed orange plates, m. p. 247–248° (dec.). Cook and Lawrence[3] give 130–130.5° and 249–250° (dec.), respectively, for the melting points of these compounds. The semicarbazone, prepared in pyridine–ethanol[12] and recrystallized twice from absolute ethanol, was a white powder, m. p. 236.5–240°. *Anal.* Calcd. for $C_{21}H_{21}N_3O$: N, 12.7. Found: N, 13.0.

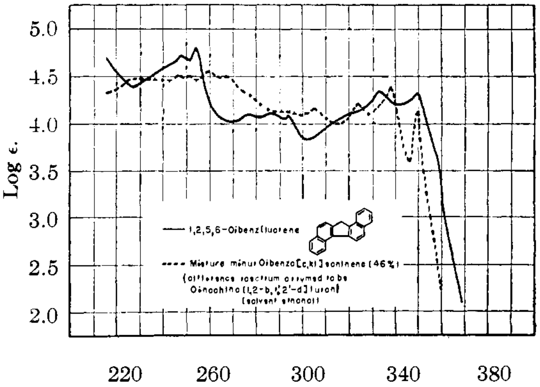

Fig. 5.—Ultraviolet absorption spectra.

1-Keto-2-(1′,2′,3′,4′-tetrahydro-1′-naphthyl)-1,2,3,4 tetrahydronaphthalene, II.—A solution of 2.75 g. of tetralylidenetetralone in 60 ml. of dioxane was hydrogenated at 1 atmosphere and room temperature, using 0.60 g. of palladium-on-charcoal catalyst.[13] After eighty minutes, 1.04 mole hydrogen had been absorbed per mole compound, and the rate of absorption had become very slow. The catalyst and solvent were removed and the residual oil crystallized from methanol, giving 1.55 g. of white crystals, m. p. 107.4–110.2°. Three recrystallizations (from methanol, benzene–ethanol, and ethanol) gave 0.91 g. of material, which began to soften at 100° and had m. p. 109.0–110.2°. *Anal.* Calcd. for $C_{20}H_{20}O$: C, 86.9; H, 7.3. Found: C, 87.0; H, 7.2. The marked sintering below the melting point may be due to the presence of a mixture of the two expected racemates, but this possibility was not further investigated. The 2,4-dinitrophenylhydrazone formed small, bright-red needles (from alcohol), m. p. 208–210° with sintering at 205°; the mixed melting point with 2,4-dinitrophenylhydrazine was 180–197°. *Anal.* Calcd. for $C_{26}H_{24}N_4O_4$: N, 12.3. Found: N, 11.8. A semicarbazone could not be prepared by the pyridine method.[12]

Dibenzo[c,kl]xanthene, IV, from Tetralylidenetetralone, I.—A mixture of 5.00 g. I and 0.54 g. 30% palladium-on-charcoal[13] was heated at 300° for thirty minutes and the temperature then raised to 350° during fifteen minutes. There was evolved 851 cc. of hydrogen (S.T.P.). The product was dissolved in benzene, filtered, and extracted with Claisen alkali,[5] giving 0.57 g. alkali-soluble material (A) and 4.18 g. neutral material. The neutral fraction was chromatographed on alumina–celite (1:1 by volume). The percolate gave 0.18 g. naphthalene, identified by its ultraviolet absorption spectrum and by melting point and mixed melting point of the *s*-trinitrobenzene complex. The bottom, non-fluorescent portion of the column gave 0.61 g. of 1,2′-dinaphthyl, V, identified by its ultraviolet absorption spectrum and by melting point and mixed melting point of the hydrocarbon and its dipicrate. The upper, blue-green fluorescent portion of the column was extracted and the material allowed to crystallize from benzene–ethanol; there was obtained 1.76 g. of yellow needles, m. p. 155.8–163.0° (sintering from 152°). Two recrystallizations from benzene–ethanol gave 0.93 g. of beautiful yellow needles, m. p. 166.2–166.8°. Two further crystallizations from alcohol did not change the melting point or the ultraviolet absorption spectrum. *Anal.* Calcd. for $C_{20}H_{12}O$: C, 89.5; H, 4.5. Found: C, 89.8; H, 4.6. The complex with 2,4,7-trinitrofluorenone[14] formed brownish-black needles (from benzene), m. p. 251.5–252.5°. *Anal.* Calcd. for $C_{33}H_{17}N_3O_8$: N, 7.2. Found: N, 7.1. The complex with *s*-trinitrobenzene

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[9] Mosettig and Duval, THIS JOURNAL, **59**, 367 (1937).

[10] All melting points corrected. Microanalyses by Mr. G. L. Stragand, University of Pittsburgh. We wish to thank Lois Harnack and Marion Springer for the spectra measurements.

[11] We wish to thank Dr. Gilbert Thiessen and The Koppers Company for a generous gift of 1-tetralone.

[12] McElvain, "The Characterization of Organic Compounds," The Macmillan Company, New York, N. Y., 1945, p. 198.

[13] Linstead and Thomas, *J. Chem. Soc.*, 1127 (1940); catalyst-d.

[14] Orchin and Woolfolk, THIS JOURNAL, **68**, 1727 (1946); Orchin, Reggel and Woolfolk, *ibid.*, **69**, 1225 (1947).

formed dark-red needles (from absolute ethanol), m. p. 177.2–179.0°. *Anal.* Calcd. for $C_{26}H_{15}N_3O_7$: N, 8.7. Found: N, 8.8. A picrate of the dibenzoxanthene could not be formed.

The mother liquors of the neutral fraction were intensively investigated by chromatography and crystallization of the material and of its trinitrofluorenone complexes, but no pure material could be isolated. The possible presence of the isomeric dinaphtho[1,2-b,1′,2′-d]furan, VI, was established by means of ultraviolet spectra, in the same manner as discussed above for the product obtained by cyclodehydrogenation of 2-(1′-naphthyl)-1-naphthol.

The alkali-soluble portion (Fraction A above) was a red oil that was exceedingly soluble in hexane and in alcohol. It could not be obtained in crystalline form, did not form a picrate, and was recovered unchanged after treatment with acetyl chloride; its properties were not improved by chromatography. The ultraviolet absorption spectrum (Fig. 3) was identical with that of the phenolic fraction obtained in the following experiment and is compatible with the spectrum to be expected of 2-(1′-naphthyl)-1-naphthol, III.

2-(1′-Naphthyl)-1-naphthol, III, from Tetralylidenetetralone, I.—A mixture of 10.00 g. I, 1.00 g. palladium-on-charcoal[13] and 100 cc. 1- and 2-methylnaphthalene was refluxed twenty-eight hours.[9] The product was taken up in benzene filtered and extracted first with 10% aqueous sodium hydroxide and then with Claisen alkali.[5] The Claisen-alkali extract gave 0.95 g. of a red oil which could not be crystallized.

Cyclodehydrogenation of III.—The presumed 2-(1′-naphthyl)-1-naphthol, III, was treated with palladium-on-charcoal[13] at 325–350° for 30 minutes; 26 cc. (S. T. P.) of gas was evolved. The product was separated into neutral and Claisen alkali-soluble fractions. There was obtained 0.27 g. of apparently unchanged starting material (ultraviolet absorption spectrum) and 0.46 g. of neutral material. The neutral fraction was chromatographed on alumina–celite; the product was converted to the trinitrofluorenone[14] complex, which was recrystallized from benzene–ethanol (m. p. 236.5–238.5°) and then chromatographed on alumina. There was obtained 0.061 g. of material, m. p. 117–127°. Recrystallization from alcohol gave 0.045 g. of yellow needles, m. p. 120–132°. The ultraviolet absorption spectrum indicated the presence of a large amount of dibenzo[c,kl]xanthene, IV; evidence for the presence of another compound, probably dinaphtho[1,2-b,1′,2′-d]furan, VI, has been discussed above.

Summary

1-Keto-2-(1′-tetralylidene)-1,2,3,4-tetrahydronaphthalene, I, has been prepared from 1-tetralone. The location of the double bond was established by infrared absorption spectra.

Hydrogenation of I gave 1-keto-2-(1′,2′,3′,4′-tetrahydro-1′-naphthyl)-1,2,3,4-tetrahydronaphthalene.

Liquid-phase cyclodehydrogenation of I with a palladium catalyst at 300° gave a compound of the probable structure of dibenzo[c,kl]xanthene, IV. Evidence was obtained for the presence of dinaphtho[1,2-b,1′,2′-d]furan, VI, and 2-(1′-naphthyl)-1-naphthol, III. III is probably formed as an intermediate in the conversion of I to IV and VI.

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[CONTRIBUTION FROM THE WHITMORE LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE COLLEGE]

Synthesis and Properties of Compounds with a Framework of Alternate Silicon and Carbon Atoms[1]

BY LEO H. SOMMER, FRANK A. MITCH AND GERSHON M. GOLDBERG

In extension of previous work,[2] the present paper deals with the synthesis and physical properties of compounds of the type $CH_3[(CH_3)_2SiCH_2]_nSi(CH_3)_3$ in which *n* is 1 to 4. As methylene analogs of the well-known family of trimethylsilyl end-blocked linear methylpolysiloxanes, $CH_3[(CH_3)_2SiO]_nSi(CH_3)_3$,[3] these compounds should provide valuable data concerning the relative effects of Si-O-Si and Si-CH_2-Si on physical properties.

While the unusual physical properties of the linear methylpolysiloxanes have in previous discussions been taken as indicative of low intermolecular forces resulting from the influence of siloxane linkages, complete proof of this hypothesis was formerly unavailable. With the exception of 2,2,4,4-tetramethylpentane and di-*t*-butyl ether, hydrocarbon and ether analogs of the methylpolysiloxanes are unknown. Since the effect of branching of a carbon chain on physical properties is known to be very pronounced, the possibility existed that the extensive branching found in the methylpolysiloxanes might be responsible for their unusual physical properties. Furthermore, while the effect of one silicon atom on physical properties in the tetraalkylsilanes was shown to be slight,[4] nothing was known of the effect on physical properties of chains containing alternate silicon and carbon atoms as compared to chains of alternate silicon and oxygen atoms in the methylpolysiloxanes.

One of the major objectives of the present work was to determine whether the siloxane linkages in the methylpolysiloxanes are indeed largely responsible for the unusual physical properties of these compounds. The physical properties of the compounds herein reported furnish a direct answer to this question, since the structural features of the methylpolysiloxanes are held

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(1) XXII in a series on organosilicon chemistry. For XXI see THIS JOURNAL, **71**, 1509 (1949).

(2) Sommer, Goldberg, Gold and Whitmore, *ibid.*, **69**, 980 (1947).

(3) (a) Patnode and Wilcock, *ibid.*, **68**, 358 (1946); (b) Hurd, *ibid.*, **68**, 364 (1946); (c) Wilcock, *ibid.*, **68**, 691 (1946); (d) Hunter, Warrick, Hyde and Currie, *ibid.*, **68**, 2284 (1946).

(4) Whitmore, Sommer, DiGiorgio, Strong, Van Strien, Bailey, Hall, Pietrusza and Kerr, THIS JOURNAL, **68**, 475 (1946).