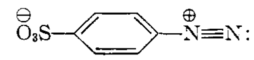
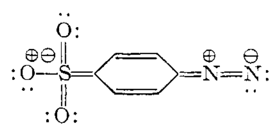
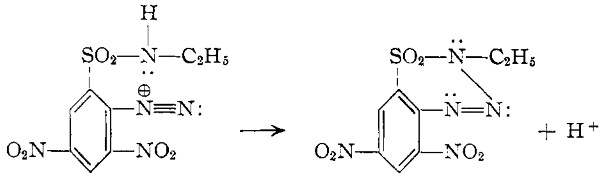
pound was found at 4.41 μ indicating some contribution of a quinoid structure such as XI.

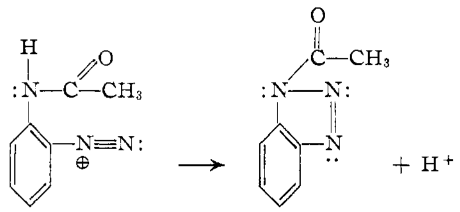

X


XI

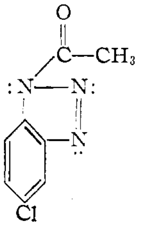
Diazonium Compound from 2-Amino-3,5-dinitrobenzene-N-ethylsulfonamide.—The product resulting from the diazotization of 2-amino-3,5-dinitrobenzene-N-ethylsulfonamide did not show an absorption band between 4 and 6 μ. The absence of the band characteristic of a nitrogen–nitrogen triple bond provides direct evidence that the diazonium ion cyclizes to form a benzothiatriazine by elimination of a proton.[18] Elemental analyses of the product agreed very closely with the theoretical values for the cyclic product and clearly showed that the compound was not a diazonium sulfate. Since the equilibrium would be shifted to the left to some extent in acidic solutions, the infrared spectrum of an acetic acid solution of the benzothiatriazine was measured in an attempt to observe the characteristic diazonium band. No trace of the band could be found, thus indicating that under these conditions the equilibrium is still far to the right. This conclusion is in agreement with the fact that in an acetic acid medium the diazonium compound couples very slowly with amines.[19]

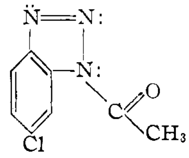


Diazonium Compounds from *o*-Aminoacetanilides.—It is well established that diazotization of *o*-aminoacetanilides results in the formation of 1,2,3-benzotriazoles[20] according to the equation

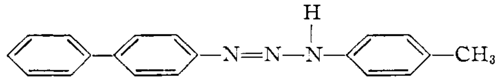


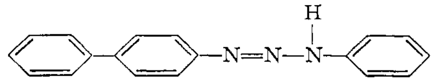
The infrared spectra of the products resulting from the diazotization of 2-aminoacetanilide and 2-amino-4-chloroacetanilide were consistent with this structure in that no characteristic diazonium band was observed. Elemental analyses of the product from 2-amino-4-chloroacetanilide were in agreement with those calculated for the triazole. The absence of sulfur showed that the compound was not a diazonium sulfate. No attempt was made to determine whether this product was the 1- or the 3-acetylbenzotriazole (XII and XIII) or a mixture of the two.[20]


XII


XIII

Triazenes.—The spectra of two diaryltriazenes XIV and XV, were measured.


XIV


XV

As expected, neither of those compounds showed characteristic absorption in the 4 to 6 μ region.

KINGSPORT, TENN.

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[18] Reference 6, p. 253.

[19] Unpublished data obtained in this Laboratory.

[20] Reference 6, pp. 247–250.

[JOINT CONTRIBUTION FROM THE INSTITUTO DE QUÍMICA, UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO, AND THE CHEMISTRY DEPARTMENT, ACTON TECHNICAL COLLEGE]

Absorption Spectra of Azo- and Related Compounds. II.[1] Substituted Phenylnitrones

BY OWEN H. WHEELER[2a] AND PETER H. GORE[2b]

RECEIVED FEBRUARY 10, 1956

The ultraviolet absorption of a number of substituted phenylnitrones (N-phenylbenzaldoximes) has been measured, and the spectra are discussed with reference to the electronic and steric properties of the substituents. Comparison is made with the spectra of azoxybenzenes.

The ultraviolet absorption of a number of phenylnitrones[3a] and other nitrones[3b,c] has been reported very generally. No systematic study of substituent effects in the spectra of phenylnitrones has been made. This paper records the absorption (Table I) of a number of phenylnitrones, some of them new compounds, and an interpretation of the data.

The spectra fall into three distinct regions (at *ca.* 230, 280 and 320 mμ). Each of the bands is of high intensity (ε > 5,000) and, therefore, due to

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[1] Part I, THIS JOURNAL, **78**, 2160 (1956).

[2] (a) Universidad Nacional Autónoma de Mexico, México, D. F. (b) Acton Technical College, London.

[3] (a) P. Grammaticakis, *Bull. soc. chim. France*, 965 (1951); (b) 664 (1947); (c) G. von Fodor and P. Csokán, *Ann.*, **535**, 284 (1938).

TABLE I

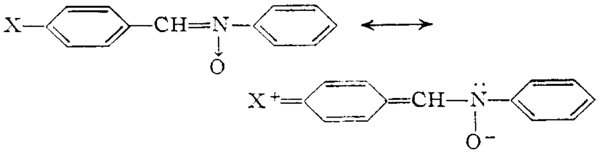
ABSORPTION SPECTRA OF PHENYLNITRONES[a]

	Substituent[b]		Bands[c]				
	α-Phenyl	N-Phenyl	E_1	E_2	K	$\Delta\lambda$[d]	$\Delta\epsilon$[d]
I	....	...	227 (9,850) 236 (9,060)	....	315 (14,000)	..	...
II	4-NO_2	...	228 236 (8,500)	251 (8,470) 266 278 (10,400)	350 (10,400)	+35	−3600
III	3-NO_2	...	228 237 (12,600)	251 (9,200) 258 (10,900) 270 280 (12,600)	314 (13,300)	− 1	− 700
IV	2-NO_2	...	227 (13,600)	284 (9,680)	320 (9,680)	+ 5	−4300
V	4-OH	...	228 237 (11,100)	....	333 (19,600)	+18	+5600
VI	4-OMe	...	227 (9,800)	280 (7,950)	330 (11,800)	+15	−2200
VII	3-OH	...	227 (9,540) 237 (7,840)	280 (5,510)	302 (7,000)[e] 315 (7,840)[e] 320 (7,000)[e]	0	−6100
VIII	2-OH	...	226 237 (11,700)	305 (11,300)	328 343 (8,500)	+23[f]	−5500
IX	4-OH 3-OMe	...	228 (16,300)	280 (8,000) 310 (9,700)	330 (7,800)	+15	−6200
X	4-OH	2-Me	224 (17,600)	292 (18,400)	319 (19,150)	+ 4	+5200
XI	4-OH	Et[g]	228 (7,850)	306 (17,700)	....	..	....
XII	...	4-Me	236 (10,300)	251 257 (5,700)	316 (15,800)	+ 1	+1800
XIII	...	4-Cl	228 237 (8,480)	254 (7,620)	318 (20,900)	+ 4	+6900

[a] Present determinations, in ethanolic solution. [b] See reference 4. [c] Absorption maxima (λ) in mμ; molar extinction coefficients (ε) in parentheses. [d] Δλ and Δε for main maximum of K-band. [e] Inflection. [f] Center of band taken as 338 mμ. [g] α-4-Hydroxyphenyl-N-ethylnitrone.

electronic transitions (E- and K-bands) and not to radical transitions (R-bands).[4] The band near 230 mμ is little affected by substituents, and the same band is found in azoxybenzenes (Part I)[1] and in anils and azobenzenes (see subsequent papers in this series). This is ascribed[1] to electronic transitions in the benzene nuclei (E-band) and is the E-band of benzene (~205 mμ, ε 6,300[5]), which is displaced to a higher wave length. In many of the compounds studied, the band consists of two maxima, at 227–228 mμ and 236–237 mμ. The former maximum may be assigned to transitions in the α-phenyl ring,[6] since α-4-hydroxyphenyl-N-ethylnitrone (XI) shows a single maximum, whereas the corresponding aryl analog, α-4-hydroxyphenyl-N-phenylnitrone (V), exhibits both maxima, and the maximum at *ca.* 236 mμ is probably due to transitions in the other ring. The effect of substituents is only to increase the intensity of absorption, and compound XI with only one benzene ring shows diminished absorption.

Most of the phenylnitrones possess a second high intensity band (E_2-band) in the region 250–300 mμ, which, however, is absent in the parent phenylnitrone I, being apparently submerged in the E-band. The N-4-tolyl derivative XII has a double maxima at 251 and 257 mμ, and this also occurs in the nitro-compounds II and III. Substitution by −OH (or −OMe) groups results in bathochromic shifts of *ca.* 30 mμ. For α-4-hydroxyphenyl-N-phenylnitrone (V), the E_2-band is submerged in the high intensity K-band, but α-4-hydroxy-3-methoxyphenylnitrone (IX) and α-4-hydroxyphenyl-N-ethylnitrone (XI) both show this maximum. A similar band occurs in some azoxybenzenes, and it is probably due to transitions involving the central linkage and one aromatic ring, *e.g.*



All the phenylnitrones show a third maximum at *ca.* 320 mμ. This band is greatly affected by substitution and must be due to electronic transitions throughout the whole molecule (K-band). Azoxybenzenes also possess the same absorption band. The bathochromic effect of substituents in the α-4-position follows the sequence $NO_2 \gg OH >$ OMe, and α- *meta*-substituents (in III and VII) do not alter the position of the maximum; this is typical of the inductive effect of the substituents. Substitution in the α-2-position (*e.g.*, NO_2– and OH– groups in IV and VIII) leads to pronounced hypsochromic shifts and decreased intensity, as compared with the corresponding α-4- compounds (*cf.* II and V). This type of hypsochromic effect has been attributed[7] to steric hindrance to co-

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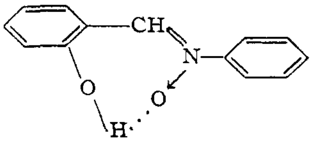
(4) A. Burawoy, *J. Chem. Soc.*, 1865 (1937).

(5) *Cf.* K. Bowden and E. A. Braude, *ibid.*, 1068 (1952).

(6) The nomenclature used is that of *Chemical Abstracts*. N- denotes substitution on the central nitrogen atom and α- on the central carbon atom.

(7) *Cf.* E. A. Braude, W. F. Forbes and F. Sondheimer, *Nature*, **173**, 117 (1954).

planarity, due to interaction between the large *ortho* groups and the atoms of the central linkage, resulting in an increase in the energy levels of the excited ionic states, causing absorption at shorter wave length. The α-2-hydroxyphenylnitrone (VIII) also has another maximum (at 343 mμ), and this probably is due to internal hydrogen-bonding of the *o*-hydroxyl group with the oxygen atom of the nitrone grouping



Such bonding would lower the energy of the excited state relative to that of the ground state, resulting in absorption at longer wave length. Similar effects have been noted in *o*-hydroxyazobenzenes[8a] and azonaphthalenes.[8b]

A comparison of the K-bands of α-4-hydroxyphenyl-N-2-tolylnitrone (X, λ_{max} 319 mμ) and α-4-hydroxyphenyl-N-phenylnitrone (V, λ_{max} 333 mμ) shows, instead of a bathochromic shift due to the additional methyl group in the former, a pronounced hypsochromic shift. This too must be due to steric inhibition of resonance, and this will be large because of the proximity of the *o*-methyl group and the nitrone oxygen atom.

The deformation angles for these compounds have been calculated (see Table II) using two methods (*cf.* Part I[1]), $\theta_1 = \cos^{-1}\epsilon/\epsilon_0$[7] and $\theta_2 = \cos^{-2}\epsilon/\epsilon_0$,[9] and the values confirm the above qualitative discussion. α-2,4,6-Trimethyl- and α-2,4,6-trichlorophenylnitrone have maxima at 298.5 (ϵ 8,900) and 286 mμ (ϵ 7,800), respectively.[3a] These bands, from their position, must be E_2-bands, and the steric hindrance caused by the doubly substituted *o*-positions is such that electronic transitions throughout the whole molecule are impossible.

TABLE II

NON-COPLANARITY ANGLES OF *o*-SUBSTITUTED PHENYLNITRONES

Substituent[a]	ϵ	ϵ_0[b]	θ_1	θ_2
α-2-OH	8,500	19,600	64°	49°
α-2-NO_2	9,680	10,400	21°	15°
α-4-OH, N-2-CH_3	19,200	21,400[c]	27°	19°

[a] All data taken from the present work. [b] Extinction of corresponding α-4-derivative. [c] Extrapolated from ϵ_{max} of α-4-hydroxyphenyl-N-phenylnitrone (V), by adding +1,800 for the methyl group; *cf.* compounds I and XII.

The phenylnitrones may be regarded as carbon analogs of azoxybenzenes, and it is interesting to compare their ultraviolet absorption (*cf.* Table III). For simple compounds, substitution of nitrogen for carbon has little effect on the chromophore[10]; however the K-bands[11] of the two series show distinct differences. The effect of substituents in the 4-positions of the azobenzenes is to give larger bathochromic shifts and higher intensity of absorption. Except for the effect of the 4-nitro-group on the spectra of phenylnitrone, the bathochromic shifts follow the order OH > OMe > Me, and the differences between the pairs of derivatives follow the order OH > OMe > H > NO_2, *i.e.*, the order of electron-releasing properties.

In a later paper comparison will be made between the spectra of phenylnitrones and anils.

TABLE III

K-BANDS OF PHENYLNITRONES AND AZOXYBENZENES[a]

	Phenylnitrones[b]		Azoxybenzenes[c]	$\Delta\lambda$
......	315 (14,000)	......	322 (19,100)	+ 7
α-4-NO_2	350 (10,400)	α-4-NO_2	339 (20,000)	−11
α-4-OH	333 (11,800)	α-4-OH	357 (22,900)	+24
α-4-OMe	330 (11,800)	α-4-OMe	353 (25,100)	+23
N-4-Me	316 (15,800)	β-4-Me	332 (25,100)	+16

[a] Wave lengths in mμ, ϵ in parentheses. All determinations in ethanolic solution. [b] From the present work. [c] L. Szegö, *Ber.*, 61, 2087 (1928); 62, 737 (1929).

Experimental

Hydroxylamines.—Phenylhydroxylamine was prepared by zinc dust and ammonium chloride reduction of nitrobenzene[12] and had m.p. 80° (lit. m.p. 80.5–81°[13]). *o*-Tolylhydroxylamine was similarly prepared from o-nitrotoluene,[14] m.p. 43° (lit. m.p. 44°[14]). *p*-Chlorophenylhydroxylamine was prepared by reduction of *p*-chloronitrobenzene with zinc dust and ammonium chloride, in 50% aqueous ethanol, and the product, m.p. 88° (lit. m.p. 86.5°[15]), extracted from the residue with boiling ethanol. Reduction of *p*-nitroanisole, under the same conditions, gave as product a mixture of *p*,*p*-dimethoxyazobenzene and *p*,*p*-dimethoxyazoxybenzene. Ethylhydroxylamine was prepared, as its hydrochloride, by

TABLE IV

PHYSICAL CONSTANTS OF NITRONES

	Substituents α-Phenyl	N-Phenyl	M.p., °C.	Reported m.p., °C.
I	....	...[a]	114	116[b]
II	4-NO_2	...	189	190[c]
III	3-NO_2	...	154	151[c]
IV	2-NO_2	...	137	94[c]
V	4-OH	...	212	210[d]
VI	4-OMe	...	116	118[c]
VII	3-OH	...	230[e]	....
VIII	2-OH	...	118	119[c]
IX	4-OH 3-OMe	...	215[f]	....
X	4-OH	2-Me	187[g]	....
XI	4-OH	Et	206[h]	....
XII	...	4-Me[a]	123	124–125[j]
XIII	...	4-Cl	181[i]	....

[a] These compounds are colorless, all others are yellow. [b] G. Cusmano, *Gazz. chim. ital.*, **51**, 308 (1921). [c] Reference 3a. [d] E. Jolles, *Gazz. chim. ital.*, **68**, 488 (1938). [e] *Anal.* Calcd. for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57. Found: C, 72.88; H, 5.35; N, 6.43. [f] *Anal.* Calcd. for $C_{14}H_{13}NO_3$: C, 69.11; H, 5.39; N, 5.76. Found: C, 68.84; H, 5.55; N, 5.81. [g] *Anal.* Calcd. for $C_{14}H_{13}NO_2$: C, 73.98; H, 5.77; N, 6.16. Found: C, 74.02; H, 5.73; N, 6.06. [h] α-4-Hydroxyphenyl-N-ethylnitrone. *Anal.* Calcd. for $C_9H_{11}NO_2$: C, 65.43; H, 6.71; N, 8.48. Found: C, 65.21; H, 6.59; N, 8.53. [i] *Anal.* Calcd. for $C_{13}H_{10}NOCl$: C, 67.37; H, 4.35; N, 6.05; Cl, 15.32. Found: C, 67.13; H, 4.38; N, 6.17; Cl, 15.49. [j] E. Beckmann, *Ann.*, **367**, 273 (1909).

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(8) (a) A. Burawoy and J. T. Chamberlain, *J. Chem. Soc.*, 3734 1952); (b) A. Burawoy and A. R. Thompson, *ibid.*, 1443 (1953).

(9) H. B. Klevens and J. R. Platt, THIS JOURNAL, **71**, 1714 (1949).

(10) A. Maccoll, *J. Chem. Soc.*, 670 (1946); H. C. Barany, E. A. Braude and M. Pianka, *ibid.*, 1898 (1949).

(11) As noted above the E_1-bands are very similar and some derivatives of both series have E_2-bands.

(12) O. Kamm, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 445.

(13) E. Bamberger, *Ber.*, **27**, 1549 (1894).

(14) E. Bamberger and M. Rising, *Ann.*, **316**, 278 (1901).

(15) R. D. Haworth and A. Lapworth, *J. Chem. Soc.*, **119**, 768 (1921).

sodium and liquid ammonia reduction of nitroethane[16] and was immediately treated with *p*-hydroxybenzaldehyde in anhydrous ethanol in the presence of sodium bicarbonate.[16]

Nitrones.—The phenylnitrones were prepared by mixing centimolar equivalents of the appropriate phenylhydroxylamine and benzaldehyde, dissolved in the minimum quantity of alcohol, and allowing the mixtures to stand at room temperature overnight. The precipitates (yields 80–95%) were recrystallized from alcohol (see Table IV).

Ultraviolet spectra were obtained with lime-dried ethanol solutions, using a Unicam S. P. 500 spectrophotometer.

Acknowledgments.—O. H. W. is grateful to the Rockefeller Foundation, New York, for financial assistance. Some preliminary spectroscopic measurements were carried out by Mrs. I. Boston, Spectroscopic Laboratory, Chemistry Department, Imperial College, London. Analyses are by Mr. F. M. Oliver, Analytical Laboratory, of the same college, and by Dr. F. Pascher, Bonn.

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[16] G. W. Watt and C. M. Knowles, *J. Org. Chem.*, **8**, 540 (1943).

[CONTRIBUTION FROM THE ROHM AND HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

The Action of Lithium Aluminum Hydride and Organometallic Reagents on 4-Hydroxycoumarin[1]

BY JEREMIAH P. FREEMAN AND M. FREDERICK HAWTHORNE

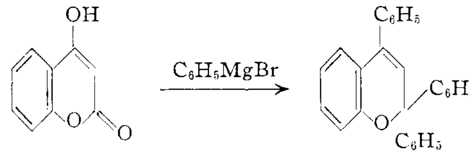
RECEIVED JANUARY 12, 1956

4-Hydroxycoumarin reacts with phenylmagnesium bromide to produce 2,2,4-triphenylbenzopyran, with phenyllithium to produce *o*-hydroxybenzophenone and acetophenone and with lithium aluminum hydride to yield *o*-hydroxypropiophenone and *o*-hydroxycinnamyl alcohol. The differences between the lithium reagent and the Grignard reagent are discussed in terms of the leaving group properties of the respective oxide ions.

It has been demonstrated in recent years that enolates of β-dicarbonyl compounds, which may be regarded as vinylogs of carboxylate ions,[2] react additively with Grignard reagents[2–5] and can be reduced with lithium aluminum hydride.[6,7] The course of these reactions is dependent upon the nature of the enolate and of the Grignard reagent and upon the concentration of the reagent and the temperature of the reaction. As 4-hydroxycoumarin (I) is the enol of a cyclic β-ketoester, its reactions with organometallic reagents and lithium aluminum hydride are of interest to this general field.

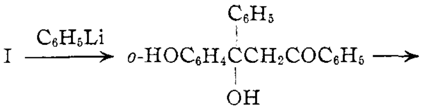
The reaction of 4-hydroxycoumarin with Grignard reagents has been investigated previously. Originally it was reported that the reaction produced chromenols.[8] The improbability of stable enol formation in this type of compound prompted a reinvestigation of the reaction, and it was recently reported that 4-hydroxycoumarin undergoes only salt formation with the Grignard reagent.[9] Its enol ether, however, reacted to produce chromanones indicating that the chromenol structure originally proposed for this type of compound was incorrect.

The resistance of the enolate of 4-hydroxycoumarin to further attack by the Grignard reagent seemed contradictory to the observed reactivity of other enols, and a re-examination of this reaction seemed necessary. It has now been found that 4-hydroxycoumarin does react with the phenyl Grignard reagent; the product obtained was 2,2,4-triphenylbenzopyran (II). Most of the 4-hydroxycoumarin was recovered unchanged, but the pyran was isolated in 22% yield.



I II

The reaction of 4-hydroxycoumarin with phenyllithium was next investigated to determine whether any differences existed between these two organometallic reagents with respect to their reaction with enolates. The products isolated from this reaction were acetophenone and *o*-hydroxybenzophenone, but these probably arise through hydrolytic cleavage of the primary reaction product, β-phenyl-β-(*o*-hydroxyphenyl)-β-hydroxypropiophenone (III).



$$\mathrm{I} \xrightarrow{C_6H_5Li} o\text{-}HOC_6H_4\underset{\underset{OH}{|}}{\overset{\overset{C_6H_5}{|}}{C}}CH_2COC_6H_5 \longrightarrow$$

$$\mathrm{III} \qquad o\text{-}HOC_6H_4COC_6H_5 + CH_3COC_6H_5$$

Finally the reduction of 4 hydroxycoumarin with lithium aluminum hydride was investigated. Two products were obtained upon hydrolysis of the reaction mixture: *o*-hydroxypropiophenone and *o*-hydroxycinnamyl alcohol.

$$\mathrm{I} \xrightarrow{LiAlH_4} o\text{-}HOC_6H_4COC_2H_5 + o\text{-}HOC_6H_4CH{=\!=}CHCH_2OH$$

Several reasonable reaction paths may be envisioned which would encompass all the reactions described. For conciseness one which involves a common intermediate for all the reactions is discussed in detail here. A reasonable first step in all

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[1] This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

[2] R. C. Fuson and L. R. Melby, THIS JOURNAL, **75**, 5402 (1953); R. C. Fuson, W. D. Emmons and G. W. Parshall, *ibid.*, **76**, 5466 (1954).

[3] G. F. Woods, *ibid.*, **69**, 2549 (1947).

[4] G. F. Woods and I. W. Tucker, *ibid.*, **70**, 2174 (1948).

[5] A. S. Dreiding and S. N. Nickel, *ibid.*, **76**, 3965 (1954).

[6] A. S. Dreiding and J. A. Hartman, *ibid.*, **75**, 939 (1953).

[7] A. S. Dreiding and J. A. Hartman, *ibid.*, **75**, 3723 (1953).

[8] I. M. Heilbron and D. W. Hill, *J. Chem. Soc.*, 2005 (1927).

[9] S. Wawzonek, R. C. Nagler and L. J. Carlson, THIS JOURNAL, **76**, 1080 (1954).