neopentyl alcohol (1030 cm.$^{-1}$), allyl alcohol (1030 cm.$^{-1}$) and benzyl alcohol (1010 cm.$^{-1}$). Likewise in the tertiary series these shifts are found: methylethylisobutylcarbinol (1142 cm.$^{-1}$), methylethylphenylcarbinol (1100 cm.$^{-1}$) and triphenylcarbinol (1009 cm.$^{-1}$). Considerable caution, however, is necessary in dealing with C–O bands appearing at lower frequencies than about 1050 cm.$^{-1}$, for it is quite apparent that the sensitivity of this band with respect to variation in structure diminishes very rapidly as the frequency approaches 1000 cm.$^{-1}$ (compare benzyl alcohol, benzhydrol, trityl alcohol and tri-*p*-anisylcarbinol). It is also important to note that no C–O band absorptions have been identified beyond 1000 cm.$^{-1}$. This limit of sensitivity is ascribed to increasing vibrational interaction between the C–O and a C–C bond frequency as these frequencies approach one another in magnitude. The resultant coupling acts to prevent any further approach to each other and to cause a loss of identity in their absorption bands.[17] Another limiting factor may be the *mass-symmetry effect* discussed below.

It is evident that while consistency is observed within a given alcohol series, primary, secondary or tertiary, in relation to electronic effects, it does not exist among the three classes of alcohols on the same terms. This is well illustrated by the alcohols, *t*-butanol (1205 cm.$^{-1}$), isopropyl alcohol (1105 cm.$^{-1}$) and methanol (1030 cm.$^{-1}$). This second effect, independent of the C–O bond force constant and demonstrably of large magnitude and opposite in operation to that of the electronic effect, may be interpreted in terms of mass symmetry. This is to say that an increase in the masses and in the symmetry of the masses of the substituents attached to the hydroxylated carbon atom results in a C–O band shift to higher frequencies. This effect is most clearly observed in saturated alcohols, inasmuch as alkenyl and aryl groups strongly displace the C–O band frequency to lower values and mask the symmetry effect, as in the case of tri-*p*-anisylcarbinol.[18] In alicyclic alcohols, both secondary and tertiary, the restrictions in freedom of the substituents may be considered in terms of the decrease in symmetric properties to account for displacements to lower frequencies than those of the aliphatic type. Exceptions are, of course, cyclopropanol and cyclobutanol.

Tentative conclusions can be drawn from a correlative point of view. The appearance of the C–O band in the region of 1205–1125 cm.$^{-1}$ is indicative of a tertiary alcohol, saturated and aliphatic, or a highly symmetrical secondary alcohol. From 1125 to 1085 cm.$^{-1}$ it is highly probable that the alcohol is a saturated secondary aliphatic, an α-unsaturated or cyclic tertiary carbinol. If the band lies between 1100 and 1085 cm.$^{-1}$ the secondary alcohol is probably branched on one α-carbon atom. Between 1085 and 1050 cm.$^{-1}$ the alcohol is an α-unsaturated secondary, a straight-chain primary or an alicyclic secondary carbinol having a five- or six-membered carbon ring skeleton. Beyond 1050 cm.$^{-1}$ are grouped di-unsaturated secondary, both α-branched and unsaturated secondary, α-branched and/or unsaturated primary, highly unsaturated tertiary and seven- and eight-membered alicylic secondary alcohols.

Studies on the intensities of the C–O absorption bands and solvent and temperature effects on these bands are incomplete. In general, the band is shifted toward lower frequencies when the alcohol is measured in benzene, chloroform or carbon disulfide.

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(17) We are indebted to Professor J. G. Kirkwood, Professor R. S. Halford of Columbia University and Professor R. C. Lord of the Massachusetts Institute of Technology for discussions of this and other theoretical points.

(18) Hydrogen atoms are not regarded here as contributory toward this effect for the reason that their interactions with C–O bonds are undoubtedly quite small in comparison to that of C–C–O.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Absorption Spectra of Tetracyclones

BY STEPHEN B. COAN,[1] DONALD E. TRUCKER[1,2] AND ERNEST I. BECKER[3]

RECEIVED JULY 3, 1952

The absorption spectra of a series of tetracyclones have been measured. Those with substituents in the *p*-position of the 2-phenyl ring affect mainly the absorption maximum at 512 mμ, while those with substituents in the *p*-position of the 3-phenyl ring affect mainly the absorption maximum at 342 mμ. On the basis of these data assignments of excited electronic paths in the tetracyclone molecule have been made to include the 2-phenyl (Y-path) and the 3-phenyl (X-path) rings.

I. Introduction

The specific assignment of particular excited electronic paths in a molecule to observed ultraviolet and visible absorption maxima has been carried out on only a few types of systems. Jones[4,5] has studied naphthalene and anthracene most thoroughly. Lewis and Calvin[6] have summarized data in the triphenylmethane dyes. In each class, it has been possible to associate a particular excited electronic structure with certain absorption maxima. However, only in anthracene has a broad

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(1) Taken from the Dissertations of S. B. Coan and D. E. Trucker presented to the Graduate Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the Ph.D. degree.

(2) Research fellow, June, 1949, to May, 1951, supported by the U. S. Army Signal Corps.

(3) To whom correspondence concerning this paper should be directed.

(4) Y. Hirshberg and R. N. Jones, *Can. J. Research*, **27B**, 437 (1949).

(5) R. N. Jones, *Chem. Revs.*, **41**, 353 (1943).

(6) G. N. Lewis and M. Calvin, *ibid.*, **25**, 273 (1939).

TABLE I

R_1-SUBSTITUTED TETRACYCLONES

	Starting materials							Analyses, %					
	R_1-Dibenzyl ketone		Benzil			Yield,[b]		Carbon		Hydrogen		Halogen	
R_1	g.	Mole	g.	Mole	M.p.,[a] °C.	g.	%	Calcd.	Found	Calcd.	Found	Calcd.	Found
H	21.0	0.10	21.0	0.10	220.0–221.0	30.4	79	90.59	90.58	5.24	4.93		
OCH_3	1.20	.005	1.05	.005	190.0–190.5	1.0	48.5	86.92	86.73	5.35	5.48		
CH_3	11.2	.05	10.5	.05	190.7–191.0	12.6	63.0	90.42	90.47	5.57	5.80		
F	4.56	.02	4.2	.02	211.0–212.0	6.8	85.0	86.54	86.73	4.75	4.81		
Cl	9.0	.022	4.5	.022	188.3–188.8	3.1	34.5	83.14	83.40	4.57	4.80	8.46	8.40
Br	7.25	.25	5.25	.025	200.4–200.8	10.1	86.0	75.16	75.15	4.13	4.17	17.25	17.43

[a] All melting points are corrected. [b] The yields are for once-recrystallized products.

TABLE II

R_2-SUBSTITUTED TETRACYCLONES

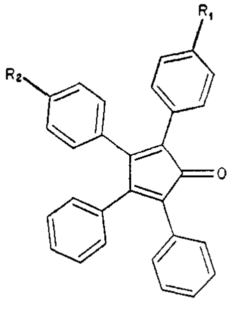
	Starting materials							Analyses, %					
	Dibenzyl ketone,		R_2-Benzil,			Yield		Carbon		Hydrogen		Halogen	
	g.	Moles	g.	Moles	M.p., °C.	g.	%	Calcd.	Found	Calcd.	Found	Calcd.	Found
$(CH_3)_2N$	10.0	0.048	12.0	0.048	220–221	5.5	55[a,b,c]						
OCH_3	2.1	.01	2.4	.01	217.6–218.0[d]	1.7	41[a,e]	86.92	86.72	5.35	5.50		
CH_3	10.5	.05	11.2	.05	223.8–224.2	13.6	68.5[e]	90.42	90.02	5.57	5.87		
Cl	0.86	.0041	1.0	.0041	211–212	1.55	91[b]	83.14	82.80[f]	4.57	4.77		
Br	10.5	.05	14.5	.05	211.5–212	12.8	56[e]	75.16	75.30	4.13	4.00	17.25	16.90

[a] Reference 10. [b] The yields are as obtained from the reaction mixture. [c] An ethiodide was prepared in 14% yield, m.p. 193–194°. [d] Reported[10] m.p. 213–214°. [e] The yields are for once-recrystallized products. [f] Average of three analyses.

systematic approach been effected to determine steric as well as electronic factors, yet even here the variations with the entering substituent affect both major absorption peaks.

Tetracyclone (I), a deep purple compound which has a central five-membered ring, exhibits two easily measured absorption maxima—at 346 mμ and and at 512 mμ. Its synthesis—the alkali-catalyzed condensation of benzil with dibenzyl ketone—permits a wide scope of variations merely by choosing the appropriately substituted reactants for the condensation. Further, and not the least important, two different excited electronic paths may be written for the molecule suggesting a possible separation of absorption bands.

Therefore, the purpose of this investigation is to show that an empirical relationship exists between the two major absorption peaks of tetracyclone and the two major electronic structures which can be written for it.



I, $R_1 = R_2 = H$
II, $R_1 = H, R_2 = (CH_3)_2N$
III, $R_1 = OCH_3; R_2 = H$
IV, $R_1 = H; R_2 = OCH_3$
V, $R_1 = CH_3; R_2 = H$
VI, $R_1 = H; R_2 = CH_3$
VII, $R_1 = F; R_2 = H$
VIII, $R_1 = Cl; R_2 = H$
IX, $R_1 = H; R_2 = Cl$
X, $R_1 = Br; R_2 = H$
XI, $R_1 = H; R_2 = Br$

II. Synthesis of Unsymmetrically Substituted Tetracyclones

A. R_1-Substituted Tetracyclones.—The desired tetracyclones required the synthesis of monosubstituted dibenzyl ketones. This was effected by condensing the appropriate phenylacetic ester with phenylacetonitrile or, as in the cases of VII and VIII, the appropriate halo-phenylacetonitrile with ethyl phenylacetate using sodium ethoxide in ethanol.[7] Hydrolysis and decarboxylation of the resulting acetoacetonitrile gave the substituted ketone. The condensations to the tetracyclones were effected without particular difficulty according to the general procedure of Dilthey[8,9] (see Table I).

B. R_2-Substituted Tetracyclones.—By condensing the appropriately monosubstituted benzil with dibenzyl ketone, the requisite tetracyclone was obtained. The monosubstituted benzils were prepared by oxidation of the corresponding benzoins either with copper sulfate–pyridine or by oxidation of the corresponding desoxybenzoins with selenium dioxide–acetic anhydride.

C. Ultraviolet Absorption Spectra.—The absorption spectra were determined using 1-cm. quartz cells and a concentration of 1.5×10^{-4} molar in benzene (see Figs. 1, 2 and Table III). It was found necessary to measure the spectra at once after making up the solutions unless protected from light since the absorption characteristics changed on standing.[11] Two experiments were performed to establish the nature of the change. A 3×10^{-5} molar solution of tetracyclone in cyclohexane was irradiated in a quartz flask arranged for cooling and stirring.[12] From Fig. 3 in which the absorption of the solution was plotted against time, the rapid change can be seen.

In a second experiment one gram of tetracyclone in 50 ml. of benzene was irradiated for 37.5 hours at which time the solution was yellow. Distillation of the solvent at re-

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(7) S. B. Coan and E. I. Becker, unpublished results.

(8) W. Dilthey and F. Quint, *J. prakt. Chem.*, **128**, 139 (1930).

(9) J. R. Johnson and O. Grummitt, *Org. Syntheses*, **23**, 92 (1943).

(10) W. Dilthey, O. Trösken, K. Plum and W. Schommer, *J. prakt. Chem.*, **141**, 331 (1934).

(11) F. J. Thaller, D. E. Trucker and E. I. Becker, THIS JOURNAL, **73**, 228 (1951).

(12) The light source was a 300-watt mercury sunlamp of the Burdick Corporation, Milton, Wisconsin, consisting of a straight quartz discharge tube 7.6 cm. long and 1.9 cm. in diameter mounted in front of a semi-cylindrical reflector. The radiation from this lamp is largely continuous with reported emission maxima of 200 microwatts/cm.²/sec. at 269 mμ, and 450 microwatts/cm.²/sec. at 318.5 mμ. At the close range employed, it was necessary to cool the flask.

TABLE III

SPECTRAL CHARACTERISTICS OF TETRACYCLONES

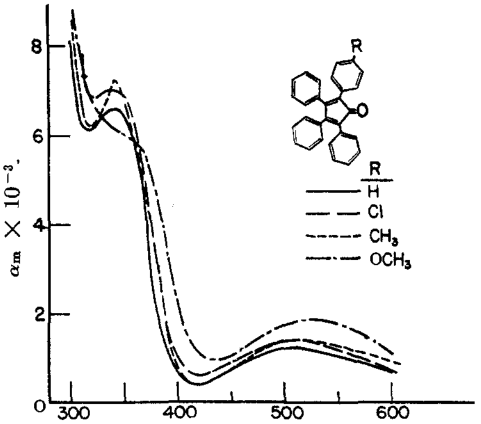
	Compound					
	R_1	R_2	λ_1[a]	αm_1[b]	λ_2	αm_2
I[c,d]	H	H	342	6760	512	1320
II[d]	H	$(CH_3)_2N$	428[e]	9610	...	..
			420[f]	10100		
III[g]	OCH_3	H	342 (infl.)	6100	525	1870
IV[d]	H	OCH_3	370	9040	512	1210
V	CH_3	H	340	6300	515	1510
VI[d]	H	CH_3	351	7860	513	1250
VII[h]	F	H	340	7060	510	1520
VIII	Cl	H	340	7020	510	1460
IX[d]	H	Cl	345	7740	510	1360
X[h]	Br	H	340	6780	510	1460
XI[d,h]	H	Br	342	7700	510	1260
XII[d]			300	6740	425	389

[a] Millimicrons. [b] See M. G. Mellon, *Anal. Chem.*, **21**, 3 (1949). [c] The ultraviolet absorption spectrum of tetracyclone has also been reported in dioxane, E. D. Bergmann and Y. Hirshberg, *Bull. soc. chim. France*, 1091 (1950). [d] Taken on a Beckman spectrophotometer, model DU. [e] Benzene solution. [f] Cyclohexane solution. [g] Carey recording spectrophotometer, model 11. [h] The fluoro and bromo compounds have been shown only in Table III because their curves are similar to ones already drawn and to avoid confusion in the figures.

duced pressure and recrystallization of the remaining solid gave a colorless product, m.p. 232.5–233.5°, whose analysis corresponded to a dibenzoylstilbene (λ_{max} 252 mμ, ϵ 33,200).

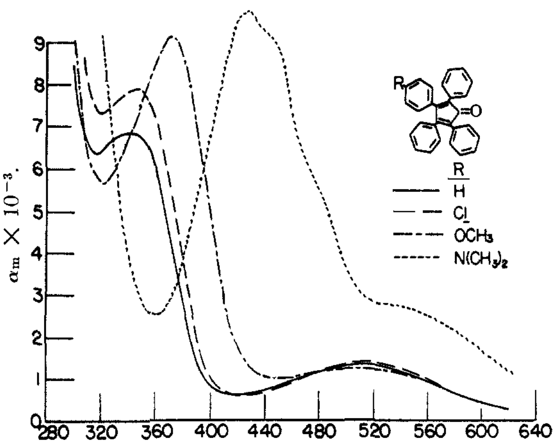
Anal. Calcd. for $C_{28}H_{20}O_2$: C, 86.57; H, 5.19. Found: C, 86.23; H, 5.38.

Japp and Klingemann[13] reported that the *cis*-dibenzoylstilbene and *trans*-dibenzoylstilbene melt at 212–214° and 232°, respectively. More recently, Kuhn, *et al.*,[14] have reported the absorption characteristics for the *cis* compound (λ_{max} 255 mμ, ϵ 28,900) and the *trans* compound (λ_{max} 252 mμ, ϵ 32,900). It thus appears that the product obtained upon irradiation of tetracyclone is *trans*-dibenzoylstilbene.[15]



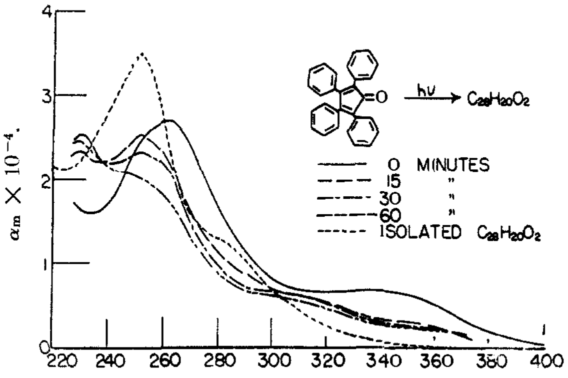
Wave length (mμ).

Fig. 1.—Absorption spectra of monosubstituted cyclones.



Wave length (mμ).

Fig. 2.—Absorption spectra of monosubstituted cyclones.

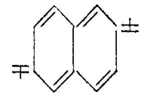


Wave length (mμ).

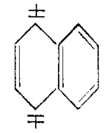
Fig. 3.—Absorption spectra of tetracyclone upon ultraviolet irradiation.

Discussion

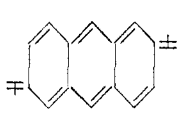
Jones[4,5] has shown that in naphthalene and in anthracene it is feasible to divide the effect of substituents on the absorption spectra of the parent hydrocarbons on the basis of whether the substituent lies in the long conjugated path (X-direction) or in the transverse path (Y-direction).



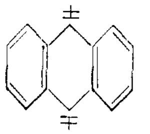
X-path



Y-path



X-path



Y-path

Assignment of the X- and Y-paths was made in each case by examining the change in absorption maxima of the two major peaks upon the introduction of substituents at the 1- or 2-positions in naphthalene and at the 1- or 2-positions in anthracene. The empirical assumption was made that the peak which responded with the largest shift was the one associated with the particular excited state containing the substituent. This assumption was also made here.

Compounds III, V, VII, VIII and X have substituents at R_1 in the tetracyclone molecule. From Fig. 1 and Table III it is seen that the λ_1 peak has remained remarkably constant while the λ_2 peak has

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[13] F. R. Japp and F. Klingemann, *J. Chem. Soc.*, *Trans.*, 662 (1890).

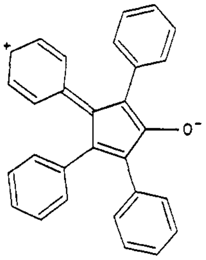
[14] L. P. Kuhn, R. E. Lutz and C. R. Bauer, THIS JOURNAL, **72**, 5058 (1950).

[15] A parallel reaction was reported by W. Dilthey, S. Henkels and M. Leonhard, *J. prakt. Chem.*, **143**, 189 (1935), in the conversion of phencyclone to 9,10-dibenzoylphenanthrene. This reaction also has been verified here.

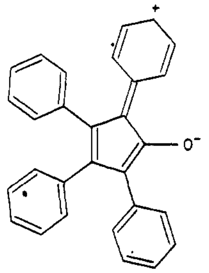
shown shifts in absorption maximum and for molar absorbancy in accord with the electronic effect of the substituent. Thus, the effect on molar absorbancy of the groups is $H < Cl < CH_3 = Br < F < OCH_3$. As expected OCH_3 effects an appreciable bathochromic shift of the λ_2 peak.

With the substituents in R_2, it is again seen that only absorption peak is shifted appreciably—the λ_1-peak (Fig. 2). Here, the λ_2-peak is shifted only with $N(CH_3)_2$; now the λ_2-peak is overpowered by the large bathochromic effect of $N(CH_3)_2$ on λ_1, and is manifest only as an inflection on the bathochromic slope of the λ_1-peak. The order of the bathochromic effect of the substituents is $H = Br < Cl < CH_3 < OCH_3 < N(CH_3)_2$.

The results are consistent with the assignment of Ia to represent the excited path for λ_1, and of Ib for λ_2. This choice is consonant with the assignment of the longer path to the longest wave length. The interaction of the substituent groups through the molecule with the carbonyl group is also in agreement with the dipole moment measurements of tetracyclone and certain of its chloro derivatives carried out by Professor C. P. Smyth.[16]



Ia



Ib

It was of interest to see what effect there would be on the absorption spectrum of tetracyclone if two of the phenyl groups were removed and replaced by alkyl. Accordingly, the absorption spectrum of 2,5-diethyl-3,4-diphenylcyclopentadienone (XII) was taken.[17] As expected there is a large hypsochromic shift of the λ_2-peak along with a somewhat smaller hypsochromic shift of the λ_1-peak (Fig. 4). This is in accord with the fact that the ethyl groups cannot conjugate with the double bonds as well as phenyl, except by hyperconjugation which is not measurable in these experiments.

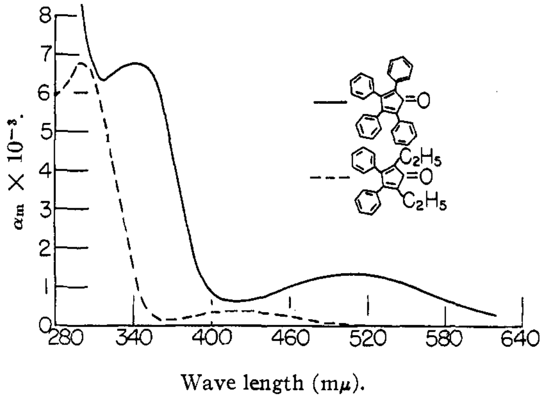


Fig. 4.—Absorption spectra of tetracyclone and 2,5-diethyl-3,4-diphenylcyclopentadienone.

It seems possible, therefore, to correlate the two major absorption peaks in tetracyclone with two paths in the molecule corresponding to the structures shown in Ia and Ib.

[16] A. Di Giacomo and C. P. Smyth, THIS JOURNAL, **74**, 4411 (1952).

[17] We are indebted to Dr. J. A. VanAllan of the Eastman Kodak Laboratories for a generous sample.

BROOKLYN, NEW YORK

[CONTRIBUTION FROM THE WORCESTER FOUNDATION FOR EXPERIMENTAL BIOLOGY, AND THE NATIONAL INSTITUTE OF MENTAL HEALTH COÖPERATIVE RESEARCH STATION AT THE WORCESTER FOUNDATION, PUBLIC HEALTH SERVICE, FEDERAL SECURITY AGENCY]

The 9–10 μ Region of Infrared Absorption Spectra of Steroids in Relation to Chemical Structure[1]

BY HARRIS ROSENKRANTZ AND LEONARD ZABLOW

RECEIVED AUGUST 20, 1952

The infrared fingerprint region of seven simple steroids studied in carbon disulfide has been presented. A comparison of the absorption characteristics in the 9–10 μ region of these steroids was made with spectra published in the literature. It has been suggested tentatively that steroid structures containing a C_3-α-hydroxyl group *cis* to a C_5-hydrogen give rise to an absorption band near 10 μ. This is in contrast to the band near 9.6 μ arising from any of the other three possible configurations involving the C_3- and C_5-centers. Steroids containing a Δ^5-double bond with a 3β-hydroxyl group at C_3 appeared to give rise to an appreciable band near 9.4–9.5 μ.

Many infrared spectroscopic studies have attempted to relate particular absorption bands to specific structural arrangements.[2–7] An extensive catalog of steroid spectra has permitted Jones and co-workers to characterize carbonyl groups and ethylene double bonds.[7,8] A band near 10.3 μ has been utilized by Jones[9] for detecting the pres-

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[1] The investigations described in this paper were aided by a grant from the U. S. Public Health (C-321) Service and supported in part by contract No. DA-49-007-MD-184 Medical Research and Development Board, Office of the Surgeon, Department of the Army.

[2] R. F. Furchgott, H. Rosenkrantz and E. Shorr, *J. Biol. Chem.*, **171**, 523 (1947).

[3] R. N. Jones and K. Dobriner, in R. S. Harris and K. V. Thimann's "Vitamins and Hormones," Vol. 7, 1949, p. 293.

[4] M. L. Josien, N. Fuson and A. S. Cary, THIS JOURNAL, **73**, 4445 (1951).

[5] H. Rosenkrantz, A. T. Milhorat and M. Farber, *J. Biol. Chem.*, **195**, 503 (1952).

[6] H. Rosenkrantz, A. T. Milhorat and M. Farber, *ibid.*, **195**, 509 (1952).

[7] R. N. Jones, V. Z. Williams, M. J. Whalen and K. Dobriner, THIS JOURNAL, **70**, 2024 (1948).

[8] R. N. Jones, P. Humphries, E. Packard and K. Dobriner, *ibid.*, **72**, 86 (1950).

[9] R. N. Jones, *ibid.*, **72**, 5322 (1950).