mole) of V. Dry nitrogen was passed through the bubbler until the air had been displaced, and this nitrogen stream was continued throughout the reaction. The flask was heated in an oil bath to a bath temperature of 140°, at which point evidence of reaction appeared in bubbling of the reaction mixture and in the appearance of distillate. Over the course of 20 min., the bath temperature was raised from 140° to 190° and maintained at the latter point for 5 min. During this period material was collected of b.p. 60–80°. Redistillation of the liquid product gave 8.2 g. (72%) of I, b.p. 70°, n_D^{20} 1.4253, d_D^{20} 0.7670, λ_{max} 250 mμ, log ϵ 2.32 (hexane).

Anal. Calcd. for C_7H_{10}: C, 89.25; H, 10.71. Found: C, 89.50; H, 10.73.

When 5.1 g. of I was redistilled after having been stored at 0° for 3 months, 4.9 g. (96%) of I, b.p. 69–71.5° was obtained and 0.1 g. of residue (2%) was left.

Adduct of I *with maleic anhydride.* To 0.98 g. (0.01 mole) of maleic anhydride dissolved in 20 ml. of ether contained in a 125-ml. Erlenmeyer flask was added 0.94 g. (0.01 mole) of I. No heat was evolved and no precipitate formed on standing overnight at room temperature; however, when the solution was cooled in a refrigerator, the adduct crystallized as white needles, 1.90 g. (99%), m.p. 91–92° (petroleum ether, b.p. 30–40°).

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.80; H, 6.56.

1,1-Dimethylcyclopentane from I. In a 500-ml. hydrogenation bottle were placed 50 ml. of glacial acetic acid, 8.1 g. (0.093 mole) of I, and 0.30 g. of platinum oxide. This mixture was hydrogenated at 3 atm. at room temperature, and in 15 min. 17 lb. of hydrogen pressure was taken up corresponding to 98% reaction. The reaction mixture was filtered, and the solution fractionally distilled using a Precision Distillation GE-118 concentric tube column. An azeotropic mixture, constant boiling at 83.5–84°, was obtained. The azeotrope plus material boiling to 92° was washed with three 15-ml. portions of water, five 15-ml. portions of saturated sodium bicarbonate solution, and three 15-ml. portions of water. After drying the hydrocarbon over phosphorus pentoxide, distillation gave 5.07 g. of 1,1-dimethylcyclopentane, b.p. 87–88°, n_D^{25} 1.4097, d_4^{25} 0.7487 (lit.[4] n_D^{25} 1.4091, d_4^{25} 0.7599). The infrared spectrum of this sample was identical in all respects with that[10] reported for authentic 1,1-dimethylcyclopentane.

Acknowledgment. After the appearance of our abstract[1] Dr. C. F. Wilcox of Cornell University kindly sent us a copy of his manuscript before publication.

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Cyclic Products from Hydrazines. I. Nitroindoles, Nitrotetrahydrocarbazoles, Nitroindolenines, and Nitrotetrahydrocarbazolenines

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The present investigations have been restricted to a study of the behavior of some nitrophenylhydrazones of ketones[1,2] in the presence of different condensing reagents. It has been found that cyclization of 2-nitro-, 4-nitro-, 2-chloro-4-nitro-, 4-chloro-2-nitro-, 2-iodo-4-nitro-, 4-iodo-2-nitro-, 2,4-dinitro-, and 4,6-dinitro-3-methylphenylhydrazones of methyl ethyl, diethyl, and methyl propyl ketones to the corresponding indoles and those of unsubstituted and 4-methylcyclohexanones to the corresponding tetrahydrocarbazoles takes place whether the phenylhydrazone has one or two nitro groups. But in case of nitrophenylhydrazones of methyl isopropyl ketone and 2-methylcyclohexanone (where the ring closure yields the corresponding indolenines and tetrahydrocarbazolenines, respectively), cyclization takes place only when one nitro group is present. Attempts to prepare dinitroindolenines and dinitrotetrahydrocarbazolenines have not been successful under similar experimental conditions.

Of the different condensing agents used[3-5] concentrated hydrochloric acid functions best for cyclizing the mononitrophenylhydrazones to indoles, tetrahydrocarbazoles, indolenines, and tetrahydrocarbazolenines while a mixture of concentrated sulfuric acid and acetic acid is preferable for preparing the dinitroindoles and dinitrotetrahydrocarbazoles from the corresponding phenylhydrazones.

Two differently substituted indoles can be obtained from the phenylhydrazones of unsymmetrical ketones of the type $RCH_2CH_2COCH_3$, as one or the other α-carbon atom is linked with the benzene ring. Only one isomer, however, could be isolated in each case. The structure of such compounds has been assigned by methylating[6,7] them. Thus, the product of methylation of the indole from 4-nitrophenylhydrazone I of methyl ethyl ketone is either IV or V as its structure is II or III. It has been found to be identical with IV obtained from the cyclization of VI and different from the isomeric product V, the cyclization product of VII. The indole formed from I is, therefore, II.

Similar studies, carried out with the indoles obtained from 2-nitro-, 4-chloro-2-nitro-, 2-chloro-4-nitro-, 4-iodo-2-nitro-, and 2-iodo-4-nitrophenylhydrazones of methyl ethyl ketone, confirm the pre-

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(1) E. Fischer and E. Jourdan, *Ber.*, **16,** 2241 (1883); E. Fischer and O. Hess, *Ber.*, **17,** 559 (1884); E. Fischer, *Ber.*, **19,** 1563 (1886).

(2)(a) A. Von Baeyer, *Ber.*, **22,** 2185 (1889); *Annalen*, **278,** 105 (1894); (b) W. Borsche, *Annalen*, **359,** 53 (1908); W. H. Perkin and S. G. P. Plant, *J. Chem. Soc.*, **119,** 1825 (1921).

(3) A. E. Arbuzov and V. M. Tichvinski, *Ber.*, **43,** 2301 (1910); A. Korczynski and L. Kierzek, *Gazz. Chim. ital.*, **55,** 361 (1925); *Roczniki Chemji*, **5,** (1–3), 23 (1925).

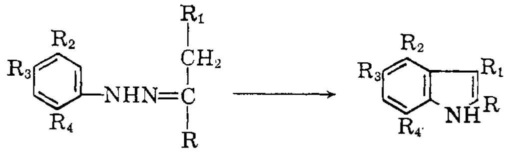
(4)(a) H. Bauer and E. Strauss, *Ber.*, **65,** 308 (1932). (b) K. Schofield and R. S. Theobald, *J. Chem. Soc.*, 796 (1949); 1506 (1950); (c) S. G. P. Plant, *J. Chem. Soc.*, 955 (1933).

(5) C. U. Rogers and B. B. Corson, *J. Amer. Chem. Soc.* **69,** 2910 (1947).

(6) E. Fischer, *Ann.*, **242,** 348 (1887); E. Fischer and A. Steche, *Ber.*, **20,** 2199 (1887); E. Fischer and J. Meyer, *Ber.*, **23,** 2629 (1890).

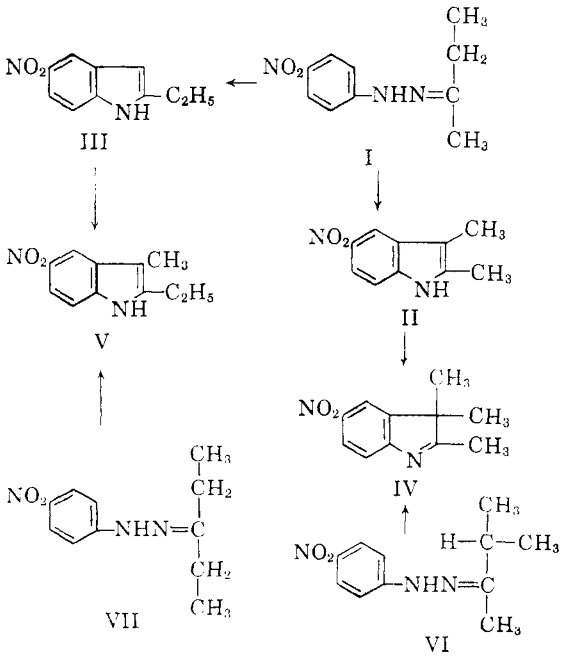
(7) G. Ciamician, *Ber.*, **37,** 4227 (1904).

TABLE I



No.	R	R_1	R_2	R_3	R_4	Yield % A	Yield % B	Yield % C	M.P.	Formula	Calcd.	Found
1	CH_3	CH_3	H	H	NO_2	70	62	59	164[a]			
2	CH_3	CH_3	H	NO_2	H	70	64	61	184[a]			
3	CH_3	CH_3	H	NO_2	Cl	68	62	64	230	$C_{10}H_9ClN_2O_2$	Cl 15.81	15.62
4	CH_3	CH_3	H	Cl	NO_2	64	61	58	202	$C_{10}H_9ClN_2O_2$	Cl 15.81	15.74
5	CH_3	CH_3	H	NO_2	I	55	50	[b]	255	$C_{10}H_9IN_2O_2$	I 40.19	40.21
6	CH_3	CH_3	H	I	NO_2	56	49	[b]	204	$C_{10}H_9IN_2O_2$	I 40.19	40.02
7	CH_3	CH_3	H	NO_2	NO_2	28	30	35	Above 360	$C_{10}H_9N_3O_4$	N 17.87	17.61
8	CH_3	CH_3	CH_3	NO_2	NO_2	20	24	30	-do-	$C_{11}H_{11}N_3O_4$	N 16.87	16.43
9	CH_3	C_2H_5	H	H	NO_2	62	50	56	138	$C_{11}H_{12}N_2O_2$	N 13.72	13.84
10	CH_3	C_2H_5	H	NO_2	H	65	60	54	194	$C_{11}H_{12}N_2O_2$	N 13.72	13.98
11	CH_3	C_2H_5	H	NO_2	Cl	58	40	43	228	$C_{11}H_{11}ClN_2O_2$	Cl 14.88	14.72
12	CH_3	C_2H_5	H	Cl	NO_2	56	45	44	175	$C_{11}H_{11}ClN_2O_2$	Cl 14.88	14.56
13	CH_3	C_2H_5	H	NO_2	I	44	40	[b]	253	$C_{11}H_{11}IN_2O_2$	I 38.48	38.39
14	CH_3	C_2H_5	H	I	NO_2	47	42	[b]	239	$C_{11}H_{11}IN_2O_2$	I 38.48	38.36
15	CH_3	C_2H_5	H	NO_2	NO_2	25	30	32	Above 360	$C_{11}H_{11}N_3O_4$	N 16.87	17.02
16	CH_3	C_2H_5	CH_3	NO_2	NO_2	25	28	30	-do-	$C_{12}H_{13}N_3O_4$	N 15.96	15.78
17	C_2H_5	CH_3	H	H	NO_2	68	60	65	106	$C_{11}H_{12}N_2O_2$	N 13.72	14.03
18	C_2H_5	CH_3	H	NO_2	H	72	65	50	182	$C_{11}H_{12}N_2O_2$	N 13.72	13.91
19	C_2H_5	CH_3	H	NO_2	Cl	68	62	48	189	$C_{11}H_{11}ClN_2O_2$	Cl 14.88	14.54
20	C_2H_5	CH_3	H	Cl	NO_2	63	55	43	147	$C_{11}H_{11}ClN_2O_2$	Cl 14.88	14.18
21	C_2H_5	CH_3	H	NO_2	I	55	41	[b]	244	$C_{11}H_{11}IN_2O_2$	I 38.48	38.31
22	C_2H_5	CH_3	H	I	NO_2	57	43	[b]	260	$C_{11}H_{11}IN_2O_2$	I 38.48	38.27
23	C_2H_5	CH_3	H	NO_2	NO_2	20	34	38	Above 360	$C_{11}H_{11}N_3O_4$	N 16.87	16.76
24	C_2H_5	CH_3	CH_3	NO_2	NO_2	20	32	34	-do-	$C_{12}H_{13}N_3O_4$	N 15.96	16.17

[a] Previously prepared see refs. 4b and 4c. [b] Iodine was liberated.



vious observation[4b,8,9] that in unsymmetrical ketones it is the methylene group of the longer chain that participates in the indole cyclization in preference to the methyl group.

The mononitroindoles and mononitrotetrahydrocarbazoles are neutral crystalline substances varying in color from yellow to brownish red. Their solubility also varies. Those from simple phenylhydrazines are soluble in alcohol and acetic acid. With an increase in the number of electronegative substituents, the solubility decreases so much that the dinitro derivatives are very slightly soluble in these solvents.

The nitroindolenines and nitrotetrahydrocarbazolenines are basic crystalline compounds. The former are brownish yellow to red while the latter vary from silvery white to orange in color. Those having a nitro group in position 7 in the former and in position 8 in the latter are red and orange respectively. They are soluble in alcohol, acetic acid and benzene.

EXPERIMENTAL

Nitroindoles: 7-chloro-5-nitro-2,3-dimethylindole. Method A. A mixture of 4.8 g. (0.02 mole) of methyl ethyl ketone 2-chloro-4-nitrophenylhydrazone, and 48 ml. of concd. hydrochloric acid (*d.* 1.18) was heated on water bath. After half an hour the hydrazone dissolved forming a dark red solution. Subsequently, the solution became turbid and a brown sand-like compound started settling down. After heating for 4 hr., the product was filtered, washed with concentrated hydrochloric acid, and crystallized from alcohol in brown yellow plates.

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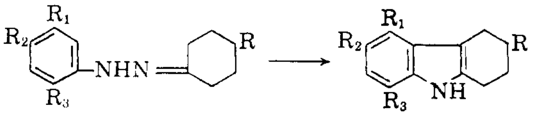
(8) A. Korczynski, W. Brydowna, and L. Kierzek, *Gazz. chim. ital.*, **56**, 903 (1926).

(9) Ng. Ph. Buu-Hoï and R. Royer *Rec. trav. Chim.*, **66**, 305 (1947).

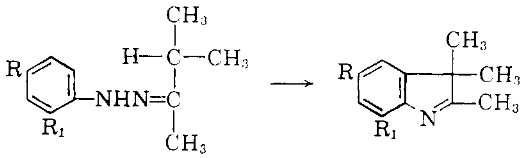
TABLE II



No.	R	R_1	R_2	R_3	Yield %			M.P.	Formula	Calcd.	Found
					A	B	C				
1	H	H	H	NO_2	90	82	84	148[a]			
2	H	H	NO_2	H	89	86	82	177[a]			
3	H	H	NO_2	Cl	83	78	74	218[a]			
4	H	H	Cl	NO_2	82	79	71	215[a]			
5	H	H	NO_2	I	75	68	[b]	245	$C_{12}H_{11}IN_2O_2$	I 37.17	36.91
6	H	H	I	NO_2	72	62	[b]	215	$C_{12}H_{11}IN_2O_2$	I 37.17	36.82
7	H	H	NO_2	NO_2	15	25	32	280	$C_{12}H_{11}N_3O_4$	N 16.09	16.21
8	H	CH_3	NO_2	NO_2	12	23	32	Above 360	$C_{13}H_{13}N_3O_4$	N 15.27	14.96
9	CH_3	H	H	NO_2	88	75	80	190[a]			
10	CH_3	H	NO_2	H	85	78	71	168[a]			
11	CH_3	H	NO_2	Cl	81	72	70	185	$C_{13}H_{13}ClN_2O_2$	Cl 13.42	13.26
12	CH_3	H	Cl	NO_2	83	74	68	206[a]			
13	CH_3	H	NO_2	I	62	60	[b]	209	$C_{13}H_{13}IN_2O_2$	I 35.67	35.49
14	CH_3	H	I	NO_2	64	59	[b]	220	$C_{13}H_{13}IN_2O_2$	I 35.67	35.32
15	CH_3	H	NO_2	NO_2	15	22	30	Above 360	$C_{13}H_{13}N_3O_4$	N 15.27	15.61
16	CH_3	CH_3	NO_2	NO_2	12	21	31	-do-	$C_{14}H_{15}N_3O_4$	N 14.53	14.27

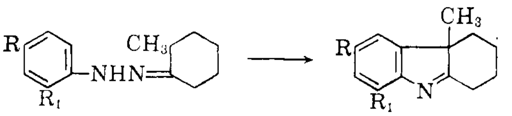
[a] Refs. 2 and 5. [b] Iodine was liberated.

TABLE III



No.	R	R_1	Yield %		M.P.	Formula	Calcd.	Found
			A	B				
1	H	NO_2	65	40	201	$C_{11}H_{12}N_2O_2$	N 13.72	13.44
2	NO_2	H	68	53	128	$C_{11}H_{12}N_2O_2$	N 13.72	13.48
3	NO_2	Cl	60	45	168	$C_{11}H_{11}ClN_2O_2$	Cl 14.88	14.66
4	Cl	NO_2	58	40	186	$C_{11}H_{11}ClN_2O_2$	Cl 14.88	14.71
5	NO_2	I	50	41	192	$C_{11}H_{11}IN_2O_2$	I 38.48	38.41
6	I	NO_2	50	38	175	$C_{11}H_{11}IN_2O_2$	I 38.48	38.38

TABLE IV



No.	R	R_1	Yield %		M.P.	Formula	Calcd.	Found
			HCl	H_2SO_4				
1	H	NO_2	80	76	98	$C_{13}H_{14}N_2O_2$	N 12.17	12.26
2	NO_2	H	55	54	103[a]	$C_{13}H_{14}N_2O_2$	N 12.17	12.34
3	NO_2	Cl	69	62	152	$C_{13}H_{13}ClN_2O_2$	Cl 13.42	13.31
4	Cl	NO_2	70	64	110	$C_{13}H_{13}ClN_2O_2$	Cl 13.42	13.36
5	NO_2	I	58	53	205	$C_{13}H_{13}IN_2O_2$	I 35.67	35.48
6	I	NO_2	60	53	135	$C_{13}H_{13}IN_2O_2$	I 35.67	35.51

[a] 6-Nitro-1-methyltetrahydrocarbazole, m.p. 197°. (*Anal.* Calcd. for $C_{13}H_{14}N_2O_2$: N, 12.17. Found: N, 12.21), is also obtained in the reaction as an insoluble material.

Method B. Heating a mixture of 48 ml. of phosphoric acid (85%) and 4.8 g. (0.02 mole) of the above hydrazone for 4 hr. on water bath, followed by dilution with excess water gave a product that crystallized from alcohol to afford the pure nitroindole.

Method C. To a solution of 12 ml. of sulfuric acid in 36 ml. of glacial acetic acid was added 4.8 g. (0.02 mole) of the above hydrazone. The reaction mixture was refluxed for 3 hr. It was then diluted and the product that separated was crystallized from alcohol.

Nitrotetrahydrocarbazoles: 8-chloro-6-nitro-3-methyl-tetrahydrocarbazole. Method A. A mixture of 5.6 g. (0.02 mole) of 4-methylcyclohexanone 2-chloro-4-nitrophenylhydrazone and 56 ml. of concd. hydrochloric acid (*d.* 1.18) was heated on water bath. The hydrazone dissolved to give a dark red solution. After a few minutes the solution attained turbidity and the nitrotetrahydrocarbazole started separating. After being heated for 3 hr. the product was filtered and crystallized from alcohol.

Method B. A mixture of 5.6 g. (0.02 mole) of the 2-chloro-4-nitrophenylhydrazone and 56 ml. of phosphoric acid (85%) was heated on water bath for an hour. The mixture was diluted and the product that separated was crystallized from alcohol.

Method C. A solution of 14 ml. of concd. sulfuric acid in 42 ml. of glacial acetic acid was mixed with 5.6 g. (0.02 mole) of the above hydrazone. The mixture was refluxed for 2 hr. After dilution the product was crystallized from alcohol.

Nitroindolenines: 7-nitro-2,3-3-trimethylindolenine. Method A. A mixture of 2.2 g. (0.01 mole) of 2-nitrophenylhydrazone of methyl isopropyl ketone and 22 ml. of concd. hydrochloric acid (*d.* 1.18) was heated for 3 hr. The nitroindolenine, being basic, remained in solution. Any suspended matter in the solution was removed by filtration. The filtrate was made basic and the nitroindolenine was extracted with benzene. The benzene layer was separated and dried. On evaporating the solvent, the residue was crystallized from dilute alcohol to afford the pure indolenine.

Method B: methylation of 7-nitro-2,3-dimethylindole. A solution of 3.5 g. (0.02 mole) of 7-nitro-2,3-dimethylindole in 30 ml. of methyl alcohol and 2.8 g. (0.02 mole) of methyl iodide was refluxed in the presence of 2.1 g. (0.02 mole) sodium acetate for 12 hr. The solvent was removed and the residue on crystallization from dilute alcohol gave the pure 7-nitro-2,3,3-trimethylindolenine.

Nitrotetrahydrocarbazolenines: 8-nitro-11-methyltetrahydrocarbazolenine. A mixture of 4.9 g. (0.02 mole) of 2-nitrophenylhydrazone of 2-methylcyclohexanone and either 49 ml. of concd. hydrochloric acid (*d.* 1.18) or 49 g. of sulfuric acid (20%) was heated on water bath. After some time the mixture became almost clear. The solution was filtered and the filtrate made basic. The nitro-11-methyltetrahydrocarbazolenine was extracted with ether. After removing ether the residue was crystallized from alcohol.

Nitroindoles, nitrotetrahydrocarbazoles, nitroindolenines, and nitrotetrahydrocarbazolenines prepared by one or more of the methods described above together with their characteristics are described in Table I, II, III, and IV.

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Toluene Disproportionation[1]

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Aromatic disproportionation reactions are well-known.[2,3] However, the kinetics and mechanism of these disproportionation reactions have been only recently investigated in detail.[3] These studies are mainly concerned with the disproportionation reactions of the higher alkyl benzenes, and little work is reported on toluene disproportionation. Recent literature indicates that at 0 to 20° toluene is relatively inert toward aluminum bromide–hydrogen bromide and may be used as a reaction medium for reactions of the higher alkyl benzenes.[4] At 50°, and over relatively long time periods, toluene forms benzene, and higher molecular weight materials over aluminum bromide hydrogen bromide.[5]

The present investigation explored the possibility of selectively converting toluene into benzene and xylenes at moderate temperatures over an aluminum bromide–hydrogen bromide catalyst. During the course of these studies, the sole production of *m*-xylene in the C_8 benzene fraction was noted. It was also found that the *m*-xylene isomerized to an equilibrium mixture of *o*-, *p*-, and *m*-isomers on prolonged heating at 110°. The purpose of this note is to present these data and to offer an explanation for the observations.

Product distributions for the toluene disproportionation reaction over aluminum bromide–hydrogen bromide are depicted in Fig. 1 and 2. At 80.6°, a selective reaction occurs and xylene and benzene are produced. At this temperature, *m*-xylene comprises the entire xylene fraction. After about 60% toluene conversion, a small amount of C_9 and C_{10} aromatics appears. The C_9 fraction is, within experimental error, essentially all mesitylene. If it is assumed that the reaction is approaching equilibrium, then this apparent equilibrium may be compared with that calculated by assuming a multiple series of reactions and is shown in Column A of Table I.

In Figure 2, the results of the experiments at 110° are shown. Again, a rapid reaction occurs; however, this reaction produces C_{10} aromatics in higher amounts than found at 80.6°. It is also apparent from Figure 2 that both the xylenes and the C_9 aromatics have maxima in their concentration values. In addition, the benzene values appear to go through a maximum. At this temperature, only the C_{10} aromatic fraction continuously increases, and at the end of 240 minutes, this fraction is far above its calculated equilibrium value.

As in the experiments at 80.6°, the xylene fraction at 110° at initially pure *m*-xylene. However, this xylene isomer undergoes an isomerization reaction that increases as the disproportionation reaction progresses, Fig. 3. The isomerization reaction reaches an apparent equilibrium and values for *m*-, *p*-, and *o*-xylene at this equilibrium are compared in Column B of Table I with cal-

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[1] Presented at the 138th Meeting of the American Chemical Society, New York, September, 1960.

[2] D. V. Nightingale, *Chem. Revs.*, **25**, 329 (1939).

[3] K. L. Nelson and H. C. Brown, Chapter on Aromatic Substitution in Volume III of the *Chemistry of Petroleum Hydrocarbons* edited by Brooks, *et al.* Reinhold Pub. Corp., New York, N. Y., 1955.

[4] H. C. Brown and C. R. Smoot, *J. Am. Chem. Soc.*, **78**, 2176 (1956).

[5] K. S. Pitzer and D. W. Scott, *J. Am. Chem. Soc.*, **65**, 803 (1943).