3. Dichloro-keto-hexahydro-α-triazines from Phosphorus Trichloride and the Compounds in 2.—The decomposition temperatures, formulas and analytical data of these triazines are summarized in Table III.

TABLE III

DICHLORO-KETO-HEXAHYDRO-α-TRIAZINE AND HOMOLOGS

Derivative	Decompn. temp., °C.	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Chlorine, %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
. . .	265–270	$C_3H_5N_3OCl_2$	21.18	21.20	2.94	3.21	24.71	25.00	41.15	41.00
Methyl	260–270	$C_4H_7N_3OCl_2$	26.08	26.00	3.80	3.80	22.82	22.83	38.58	38.56
Dimethyl	250–260	$C_5H_9N_3OCl_2$	30.31	30.30	4.54	4.54	21.20	21.32	35.85	35.75
Methylethyl	240–245	$C_6H_{11}N_3OCl_2$	33.50	33.41 33.20	5.19	5.30 5.10	19.81	19.60 19.62	33.65	33.50 33.46
Methylpropyl	230–235	$C_7H_{13}N_3OCl_2$	37.18	37.10	5.75	5.80	18.59	18.40	31.39	31.46

Experiments carried out with *iso*butyrylacetyl did not yield the expected dihydroxytriazine derivative. A soluble compound was formed whose constitution we have not yet determined.

Summary

1. Semicarbazide hydrochloride reacts with the sodium bisulfite addition products of glyoxal, methylglyoxal and 1,2-aliphatic diketones with the formation of dihydroxy-keto-hexahydro-α-triazines, compounds insoluble in the usual organic solvents except acetic acid, in which they are slightly soluble. They do not melt, but begin to decompose at definite temperatures; soluble in acids; stable against alkalies.
2. The above compounds yield with phosphorus trichloride dichloro-keto-hexahydrotriazines which resemble the original substances in their properties.
3. The sodium bisulfite addition products of a number of 1,2-diketones have been prepared.

BOULDER, COLORADO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS[

THE REDUCTION OF AROMATIC NITRO COMPOUNDS WITH SODIUM ALCOHOLATES

BY C. M. SUTER[1] AND F. B. DAINS

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Nearly 100 years ago (1834) Mitscherlich[2] used a solution of potassium hydroxide in ethyl alcohol as a reducing agent and obtained with nitrobenzene, azoxybenzene and the potassium salt of an organic acid. Since that time investigations in this field have been confined mainly to the action of various aromatic nitro compounds upon solutions of sodium in

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[1] From a dissertation presented by C. M. Suter to the Faculty of the Graduate School of the University of Kansas in partial fulfilment of the requirement for the degree of Doctor of Philosophy.

[2] Mitscherlich, *Ann.*, **12**, 311 (1834).

methyl or ethyl alcohol or sodium or potassium hydroxide dissolved in water or the same alcohols.[3] In general azoxybenzene or its derivatives were isolated, together with acids such as carbonic, oxalic, etc., and occasionally the formation of primary amines was noted, while with halogen nitrobenzenes some of the halogen might be displaced, yielding phenols or phenol ethers.

As a result of some observations on the action of sodium butylate on bromonitrobenzene, it was decided to investigate especially the reduction of nitro aromatic compounds with the higher sodium alcoholates in other than alcohol solutions. Benzene was chosen as solvent because it would diminish the ionizing effect of the excess of alcohol and would without question speed up the reaction, as was shown by Brühl[4] in his study of activated sodium methylate in xylene, where he obtained a quantitative yield of azoxybenzene.

Experimental

The general procedure was as follows. Sodium (0.1 mole) was added to the alcohol (2–4 moles) dissolved in benzene (100–450 cc.). The mixture was then refluxed for several hours until the metal had been changed to the alcoholate. To the cooled solution was added the nitro compound (0.05 mole) dissolved in a little benzene if a solid, in small portions so that the reducing agent was always in excess. The reaction usually began in the cold but for completion the mixture was heated on a water-bath for two hours. It was then distilled with steam, which removed the benzene solvent A, and other readily volatile substances such as excess alcohol and traces of aldehyde and ketones.

The water distillate, B, was found to contain the amine, unchanged nitro product and benzaldehyde when benzyl alcohol was used. The residue, C, in the flask consisted of non-volatile products and sodium salts.

The different portions were worked up as follows. The benzene solution, A, was extracted with water to remove traces of aldehyde or ketone that might be formed and then with dilute sulfuric acid, which dissolved any amine present. The water distillate, B, was acidified with sulfuric acid and separated from any unchanged nitro product. The acid solutions were then made up to a definite volume and the total amine determined by titration with a bromate–bromide solution, using the method of Francis and Hill.[5] It was found that the small amounts of alcohol present in the solution had but little effect on the accuracy of the titration in the cold but did not interfere if the solutions were warm.

The non-volatile reduction products in the flask, C, (mainly azoxybenzenes) which separated from the water solution as solids or oils, were isolated, washed with water, dried and weighed and their identities determined. The water solution in C contained the sodium salts of aliphatic or amino acids, occasionally small amounts of phenolic compounds and sodium halides from halogen nitrobenzenes. In some cases the volatile acids were determined qualitatively in the distillate after acidifying with sulfuric or

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[3] Otto and Voigt, *J. prakt. Chem.*, [1] **36**, 98 (1887); (b) Claus, *Ber.*, **5**, 364 (1872); (c) Schmidt and Schultz, *Ann.*, **207**, 328 (1881); (d) Leuckart, *Ber.*, **15**, 81 (1882); (e) **16**, 81 (1883); (f) Meisenheimer, *Ann.*, **355**, 255 (1907); (g) Lachman, THIS JOURNAL, **24**, 1178 (1902); (h) Smith with Lyons, *ibid.*, **48**, 3165 (1926).

[4] Brühl, *Ber.*, **37**, 2066 (1904).

[5] Francis and Hill, THIS JOURNAL, **46**, 2498 (1924).

phosphoric acid. No effort was made to ascertain the nature of the phenolic compounds and in only a few cases was the amount of halogen removed from the ring determined.

The following tables give a résumé of the results obtained followed by a discussion of the special points. In general halogen nitro compounds

TABLE I

TABLE OF RESULTS

No.	Na, moles	Alcohol	C_6H_6, cc.	Nitro comp., moles	Amine, %	Azoxy, %	Other products
I	0.3	CH_3	450	0.15 *p*-$C_6H_4CH_3NO_2$	1.3	..	Conds. prods.
II	.1	CH_3	150	.05 *p*-$C_6H_4ClNO_2$	3.5	4.6	HCOOH
III	.1	C_2H_5	C_6H_6	*p*-$C_6H_4CH_3NO_2$	..	..	(Less resins than with CH_3)
IV	.1	C_2H_5	C_6H_6	*p*-$C_6H_4ClNO_2$	Trace	..	
V	.2	*iso*-C_3H_7, 200 cc.	...	.125 $C_6H_5NO_2$	...	Little	...
VI	.1	*iso*-C_3H_7	150	.05 *p*-$C_6H_4ClNO_2$	29	33	(Trace acetone, HCOOH, resins)
VII	.1	*n*-C_4H_9	150	.05 $C_6H_5NO_2$	28.8	Little	
VIII	.1	*n*-C_4H_9	150	.05 *p*-$C_6H_4ClNO_2$	19.6	49.5	...
IX	.1	*n*-C_4H_9	150	.05 *p*-$C_6H_4ClNO_2$	29	40	...
X	.1	*n*-C_4H_9	150	.05 *p*-$C_6H_4ClNO_2$	23	48.5	HCOOH
XI	.1	*n*-C_4H_9	150	.05 *p*-$C_6H_4ClNO_2$	33.8	Pres.	HCOOH
XII	.1	*n*-C_4H_9	150	.05 *p*-$C_6H_4ClNO_2$	27.7	55	HCOOH
XIII	.1	*n*-C_4H_9	150	.05 *p*-$C_6H_4ClNO_2$	32.2	54	...
XIV	.1	*n*-C_4H_9	150	.05 *p*-$C_6H_4ClNO_2$	28.2	42.7	...
XV	.1 NaOH	*n*-C_4H_9, 100 cc.	...	.05 *p*-$C_6H_4ClNO_2$	10	56	...
XVI	.1	*n*-C_4H_9	150	.05 *m*-$C_6H_4ClNO_2$	25	56	...
XVII	.1	*n*-C_4H_9	150	.05 *p*-$C_6H_4BrNO_2$	30.8	48.5	...
XVIII	.1	*n*-C_4H_9	200	.05 *p*-$C_6H_4INO_2$	27.4	43	...
XIX	.1	*iso*-C_4H_9	150	.05 *p*-$C_6H_4ClNO_2$	32.6	37	...
XX	.1	*iso*-C_4H_9	250	.05 *p*-$C_6H_4ClNO_2$	42.5	45	...
XXI	.1	*sec.*-C_4H_9	150	.05 *p*-$C_6H_4ClNO_2$	32.6	14.8	...
XXII	.1	*sec.*-C_4H_9	100	.05 *p*-$C_6H_4BrNO_2$	Pres.	Pres.	HAc, ketone test
XXIII	.1	*iso*-C_5H_{11}	C_6H_6	.05 *p*-$C_6H_4ClNO_2$	25	67 azo, mainly	HCOOH
XXIV	.1	$C_6H_5CH_2$	100	.05 $C_6H_5NO_2$	..	Pres.	C_6H_5COOH
XXV	.1	$C_6H_5CH_2$	100	.05 *m*-$C_6H_4(NO_2)_2$	..	Pres.	C_6H_5COOH
XXVI	.1	$C_6H_5CH_2$	150	.05 *p*-$C_6H_4CH_3NO_2$	..	Little	C_6H_5COOH, C_6H_5CHO
XXVII	.1	$C_6H_5CH_2$	150	.05 2-$C_{10}H_7NO_2$	..	Tar	C_6H_5COOH, C_6H_5CHO
XXVIII	.1	$C_6H_5CH_2$	150	.05 *p*-$C_6H_4ClNO_2$	..	100	C_6H_5COOH
XXIX	.1	$C_6H_5CH_2$	250	.05 *p*-$C_6H_4ClNO_2$	..	100	C_6H_5COOH, 73%; C_6H_5CHO
XXX	.1	$C_6H_5CH_2$	300	.05 *p*-$C_6H_4ClNO_2$	..	95	C_6H_5COOH
XXXI	.1	$C_6H_5CH_2$	100	.05 *m*-$C_6H_4ClNO_2$	..	Pres.	C_6H_5COOH
XXXII	.1	$C_6H_5CH_2$	100	.05 *m*-$C_6H_4ClNO_2$	..	Pres.	C_6H_5COOH
XXXIII	.1	furfural	300	.05 *p*-$C_6H_4ClNO_2$	..	91	...
XXXIV	.1	*n*-C_3H_7	300	.05 *o*-$C_6H_4OCH_3NO_2$	Found	Tar	...

were used as oxidizing agents, both for ease in the separation of the reduction products and to compare the effect of halogen in the ortho, meta and para positions.

Discussion

The results point out distinctive differences between the action of methyl and ethyl alcohols and those from propyl on, while series VI–XXIII brings out clearly the special activity of the higher aliphatic alcohols in that nearly 40% of the reduction products appear as amines and not as azoxy derivatives. In XV, where butyl alcohol alone was used as solvent, the decreased amount of amine (15%) illustrated the definite effect of the benzene solvent. The amines are evidently formed directly and not through intermediate azoxybenzenes, since sodium butylate had no reducing effect on *p,p'*-dichloro-azoxybenzene under the same conditions. The reductions with benzyl alcohol (XXIV–XXXII) are noteworthy in that there is practically no amine formation but instead high yields of azoxybenzene and of benzoic acid or the intermediate benzaldehyde, which has been isolated for the first time. This absence of amine may be due to the stability of the benzoic acid, which remains unchanged while the aliphatic acids are oxidized further to acids with less carbon content and even to formic acid and are hence more effective reducing agents. Aliphatic aldehydes and ketones, the first oxidation products, speedily disappear. Only in VII was a trace of acetone and in XXII evidence of a ketone obtained and acetic acid absolutely proved.

o-Halogen Nitrobenzenes with Sodium Alcoholates

These reactions are grouped by themselves in Table II since they offer some interesting differences as compared with the *p*- and *m*-halogen isomers. While the experimental results have shown the usual formation of amines,[6] it has been found that the azoxybenzenes were replaced almost entirely by α-amino acids, *o*-halogen $C_6H_4NHCH(R)COOH$, when *n*-propyl or alcohols of the type RCH_2-CH_2OH were used.

Synthesis of Phenylamino Acids

α-*o*-Chloro-anilinopropionic Acid, $ClC_6H_4NHCH(CH_3)COOH$ (XXXVII–XLI).—Sodium (6.9 g.) was dissolved in benzene (250 cc.) and *n*-propyl alcohol (80 cc.). To this solution was added *o*-chloronitrobenzene (16 g.) and the mixture refluxed for two hours.

The reaction product contained 40% of *o*-chloro-aniline but no dichloro-azoxybenzene. From the alkaline solution was isolated on acidifying 12.5 g. of an acid melting at 150° after crystallizing from hot water, in which it is soluble to the extent of 0.44 g. per 100 cc. at the boiling point; at 30°, 0.094 g. per 100 cc.

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[6] Paal and Otten, *Ber.*, **23**, 2587 (1890); Miller and Plöchl, *Ber.*, **25**, 2020 (1892); Bischoff and Hausdörfer, *Ber.*, **25**, 2270, 2298 (1892); Bischoff and Mintz, *Ber.*, **25**, 2314, 2326 (1892); Dzierzgowski, *Ber.*, **27**, 1983 (1894); Bischoff, *Ber.*, **30**, 2303, 2464, 2760, 3169 (1897).

Anal. Calcd. for $C_9H_{10}ClNO_2$: N, 7.06; Cl, 17.73; mol. wt., 199.5. Found: N, 6.67, 6.86; Cl, 17.6; mol. wt., 230 in acetic acid.

Its identity was further proved by comparison with the acid synthesized as follows. A mixture of *o*-chloro-aniline (30 cc.), 2-bromopropionic acid (18 cc.) and water (60 cc.) was heated over a small flame for thirty minutes until the solution became homogeneous. It was then made alkaline, distilled with steam to remove excess aniline and the amino acid was precipitated with dilute sulfuric acid. It crystallized from hot water in white needles, m. p. 150°.

Anal. Calcd. for $C_9H_{10}ClNO_2$: N, 7.00. Found: 6.99, 6.97.

The acid was soluble in alkalies, sodium carbonate, dilute mineral acids and the usual organic solvents, though not in benzene near its freezing point. A drop of copper sulfate added to a water solution of the acid gave a green coloration characteristic of this class of compounds. When heated above 165°, it lost carbon dioxide with the formation of monoethyl-*o*-chlorophenylamine, which was identified by conversion into its phenylurea, m. p. 144°.

N-Ethyl-*o*-chloro-aniline, *o*-$C_2H_5NHC_6H_4Cl$.—This was prepared from *o*-chloroaniline and diethyl sulfate. The oil boiled at 219° (corr.) at 726 mm.; sp. g., 25°/4°, 1.104; 35°/4°, 1.0911. The hydrochloride melted at 138–139°.

Anal. Calcd. for $C_8H_{10}ClN$: N, 9.03. Found: 8.9, 9.1.

α-Ethyl-α-*o*-chlorophenyl-β-phenylurea made from the amine and phenyl isocyanate crystallized from alcohol in white needles which melted at 144°.

Anal. Calcd. for $C_{15}H_{15}ClN_2O$: N, 10.20. Found: 10.21, 10.37.

α-*o*-Chloro-anilinobutyric Acid, $ClC_6H_4NHC(C_2H_5)COOH$ (XLIV–XLV).—Sodium-*n*-butylate and *o*-chloronitrobenzene gave the amine and the amino acid, which was very soluble in organic solvents but less so in water than the lower homolog. It was best purified by crystallization from gasoline; the white rosets melted at 95°.

Anal. Calcd. for $C_{10}H_{12}ClNO_2$: N, 6.55. Found: 6.30, 6.20.

Its identity was confirmed by comparison with the same acid prepared from *o*-chloro-aniline and 2-bromobutyric acid.

Discussion

The results tabulated show that only alcohols with the grouping CH_2-CH_2OH (XXXVI–XLVI, XLIX, L) thus far have yielded the amino acids. With ethyl alcohol (XXXVI) where it might be expected, the acetic aldehyde has resinified too quickly to condense with the nitrosobenzene. *Iso*butyl (XLVIII) and cinnamyl (LIII) alcohols with a single hydrogen attached to the second carbon gave none, while benzyl alcohol (LI–LII) showed the same behavior with all three isomers.

TABLE IIA

RESULTS OF EXPERIMENTS

No.	Other amino acids	M. p.,	°C., from	Nitrogen Calcd., %	Found, %
XLIX	α-*o*-Chloro-anilino-*iso*valeric	75,	dil. HAc	6.18	5.99 5.98
XLII	α-*o*-Bromo-anilinopropionic	162–164,	hot water	5.73	5.67 5.51
XLIV	α-*o*-Bromo-anilinobutyric	83,	gasoline	5.42	5.21
XLI	α-2,5-Dichloro-anilinopropionic	163,	hot water	5.96	5.77 5.81
L	α-*o*-Chloro-anilinophenylacetic	160,	yellow crystals, alcohol	5.37	5.10 5.27

TABLE IIB

REACTIONS OF *o*-HALOGEN SUBSTITUTED NITROBENZENES

No.	Na, moles	Alcohol	C_6H_6, cc.	Nitrobenzene deriv., moles	Amine, %	Azoxy, %	Amino acid, RNHCHRCOOH, %
XXXV	0.3	CH_3	450	0.15 *o*-Chloro	2.1	81	18.6 Cl from ring
XXXVI	.3	C_2H_5	450	.15 *o*-Chloro	17.5	Tar	. . .
XXXVII	.3	*n*-C_3H_7	300	.1 *o*-Chloro	40	. .	α-$ClC_6H_4NHCH(CH_3)$-COOH, 60
XXXVIII	.3	*n*-C_3H_7	300	.15 *o*-Chloro	35	. .	Same, 47
XXXIX	.1	*n*-C_3H_7	300	.1 *o*-Chloro	35	. .	Same, 50
XL	.1	*n*-C_3H_7	300	.05 *o*-Chloro	43	. .	Same, 26
XLI	.1	*n*-C_3H_7	250	.05 2,5-Dichloro	19.4	. .	$Cl_2C_6H_3NHCH(CH_3)COOH$, 60
XLII	.3	*n*-C_3H_7	300	.15 *o*-Bromo	23.8	. .	α-*o*-$BrC_6H_4NHCH(CH_3)$-COOH, 41
XLIII	.1	*n*-C_3H_7	250	.05 *o*-Iodo	23.7	Tar	157°, too little for anal.
XLIV	.3	*n*-C_4H_9	300	.15 *o*-Chloro	24.7	. .	α-*o*-$ClC_6H_4NHCH(C_2H_5)$ COOH
XLV	.3	*n*-C_4H_9	450	.15 *o*-Chloro	16.8	. .	Same
XLVI	.3	*n*-C_4H_9	300	.15 *o*-Bromo	14.5	Present	α-*o*-$BrC_6H_4NHCH(C_2H_5)$-COOH, 68.8
XLVII	.1	*iso*-C_4H_9	300	.15 *o*-Chloro	41.5	37	. . .
XLVIII	.3	*iso*-C_4H_9	300	.15 *o*-Chloro	42	Impure	. . .
XLIX	.1	*iso*-C_5H_{11}	300	.05 *o*-Chloro	24	Little	α-*o*-ClC_6H_4NHCH (*iso*-C_3H_7) COOH
L	.1	$C_6H_5C_2H_4$	250	.05 *o*-Chloro	32	. . .	α-*o*-$ClC_6H_4NHCH(C_6H_5C_2H_4)$ COOH, 27
LI	.1	$C_6H_6CH_2$	250	.05 *o*-Chloro	. .	Present	C_6H_5COOH, 98
LII	.1	$C_6H_5CH_2$	250	.05 *o*-Chloro	Trace	Present	C_6H_5CHO, C_6H_5COOH
LIII	.1	$C_6H_5CH{=}CH$	300	.05 *o*-Chloro	. .	Impure	$C_6H_5CH{=}CHCOOH$

While there is no experimental evidence for the real cause of the special reactivity of the *o*-halogen derivatives, it may be associated with the increased negative nature of the nitroso nitrogen due to the neighboring halogen atom and the increased ability of the nitroso nitrogen group to add an aldehyde complex and then rearrange as follows

$$o\text{-}XC_6H_4NO_2 + RCH_2CH_2OH = o\text{-}XC_6H_4NO + RCH_2CHO + NaOH = RCH_2CHOH\,(ONa)$$

$$o\text{-}XC_6H_4NO + RCH_2CHOH(ONa) = o\text{-}XC_6H_4N(OH)CRHCHOH(ONa) \text{ (rearrange) } o\text{-}XC_6H_4NHCH(R)COONa + H_2O$$

Where X is chlorine or bromine, the amino acid formation goes smoothly; with the less negative iodine (XLII), the yield is much diminished, while an *o*-methoxy group (XXXIV) gave only the amine and tar.

Summary

1. A study has been made of the action of sodium alcoholates on (mainly halogen) nitro aromatic compounds in benzene solution.

2. With the exception of *o*-halogen nitro derivatives, propyl, butyl and *iso*-amyl alcohols gave a yield of from 50–90% reduction products, consisting of amine and azoxybenzenes.

3. *o*-Halogen nitrobenzenes condensed with the methylene grouping of the alcohols RCH_2CH_2OH with the formation of amino acids, *o*-halogen $C_6H_4NHCH(R)COOH$.

4. Benzyl alcohol reduced the nitro compound to azoxybenzene and was fully oxidized to benzaldehyde and benzoic acid.

5. The aliphatic alcohols were oxidized to acids of less carbon content, among them formic.

LAWRENCE, KANSAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

NITROGEN TRICHLORIDE AND UNSATURATED HYDROCARBONS. II

BY GEORGE H. COLEMAN, G. M. MULLINS AND ELIZABETH PICKERING

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The reaction of nitrogen trichloride with the unsaturated hydrocarbons,[1] 1-butene, 2-butene and trimethylethylene has been reported in a previous communication, as has also its reaction with the unsaturated ketones,[2] benzalacetophenone and benzalacetone.

The reaction has now been studied with ethene, propene, methylpropene, 2-pentene and cyclohexene. There is a wide difference in the reaction rates of these hydrocarbons. Ethene reacts most slowly and methylpropene most rapidly. The degree of difference is indicated by the fact that at 20–25° two weeks or longer is required for the completion of the reaction with ethene, while with methylpropene the reaction, even at −45 to −50° is complete within two to three hours. The reaction rates of the other hydrocarbons fall between these two extremes.

The products of the reaction with ethene are nitrogen, ammonium chloride, ethylene chloride and 2-chloro-1-dichloro-amino-ethane. This compound was not isolated but was converted by hydrochloric acid to 1-amino-2-chloro-ethane. On further reduction with sodium amalgam ethylamine was obtained.

With propene, which reacts more rapidly than ethene but more slowly than the others, the products are similar to those obtained with ethene. Of the two possible addition products, $CH_3CHNCl_2CH_2Cl$ and $CH_3CHClCH_2NCl_2$, only the first was definitely shown to be formed. Attempts to prove the presence of the other isomer were not successful.

With methylpropene, although the products were much the same, the reaction differed in some respects from the others. In nearly all of the reactions thus far studied of nitrogen trichloride with unsaturated hydrocarbons, all or at least the greater part of the stable addition product remains in solution in the carbon tetrachloride as the dichloro-amino compound and is obtained as the hydrochloride of the corresponding amine by treatment with hydrochloric acid. In this case, however, most of the

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[1] Coleman and Howells, THIS JOURNAL, **45**, 3084 (1923).

[2] (a) Coleman and Craig, *ibid.*, **49**, 2593 (1927); (b) **50**, 1816 (1928).