ture. The good correlation which is obtained, however, in the case of those groups of compounds which are known with more certainty strongly suggests that equally good correlation may be expected for the other compounds when our knowledge of their properties is increased. On that basis the method appears to be decidedly worthy of consideration in the critical analysis of data reported in the literature.

It is fully appreciated that the correlation would perhaps be even more striking if the physical constants used were taken under more comparable conditions such, for instance, as vapor pressures at the same reduced temperatures or were given in more comparable units such as molecular volumes expressed as fractions of the respective critical volumes. This, however, could not be done because the necessary data are practically entirely lacking.

The method is not limited to the one group of compounds, nor to the property used here. A similar study has been made of the boiling points of alkanes and the plot obtained closely resembles that one given here for the molecular volumes.[6] A preliminary investigation has also indicated that alkenes will plot in an orderly fashion on the diagram prepared from normal alkanes. Indeed, it would seem that the only requisite is to have available as a basis of comparison one series of compounds in any one class, such as normal alkanes, normal primary alcohols, etc., the data for which are known with a sufficient degree of accuracy. Of course, the accuracy obtainable on the branched chain isomers will always depend on the accuracy of the data on the homologous series which is used as a basis of comparison.

The authors wish to express to Prof. Frank C. Whitmore of Pennsylvania State College their appreciation for permission to include in the plot some unpublished data on several nonanes.

Summary

A graphical method is described for the critical comparison of data on any one of the physical properties of large groups of homologs and isomers. The illustration chosen covers the density (molecular volume) of the alkanes, and suggests the necessity of obtaining more and better data in the range C_9 to C_{12}.

DETROIT, MICHIGAN RECEIVED NOVEMBER 29, 1935

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[6] Prints of Fig. 1 and of the corresponding plot of boiling points, 70 × 70 cm., will be furnished upon request, by the authors.

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 489]

The Decomposition of Di-ortho-tolyliodonium Iodide

BY H. J. LUCAS, E. R. KENNEDY AND C. A. WILMOT

Introduction

The belief that organic reactions may take place via the mechanism of a positive organic ion in which the carbon atom carries the positive charge is not new.[1] The important role which the positive ion plays in certain molecular rearrangements has been pointed out by others.[2] Recently, Whitmore[3] has interpreted molecular rearrangements on the basis of electron structures.

A reaction which may proceed via the mechanism of an intermediate, positively charged positive ion is the decomposition of di-*o*-tolyliodonium iodide. From the nature of the reaction product one may draw conclusions in regard to the mechanism.

There are two possible mechanisms by which this decomposition might take place: (a) migration of the iodide iodine to one of the benzene rings in a position ortho or para to the C–I bond, followed by the scission of a C–I bond; (b) the scission of a C–I bond, followed by the attachment of the resulting positive organic ion to the negative iodide ion. These two mechanisms are pictured below.

On the assumption that the two iodine atoms are held together by a covalent bond (I), the migration of iodine to an ortho or para position on the benzene ring is quite plausible since atoms or radicals attached to other electronegative atoms (oxygen and nitrogen especially) readily migrate. If migration is the first step, then scission of a

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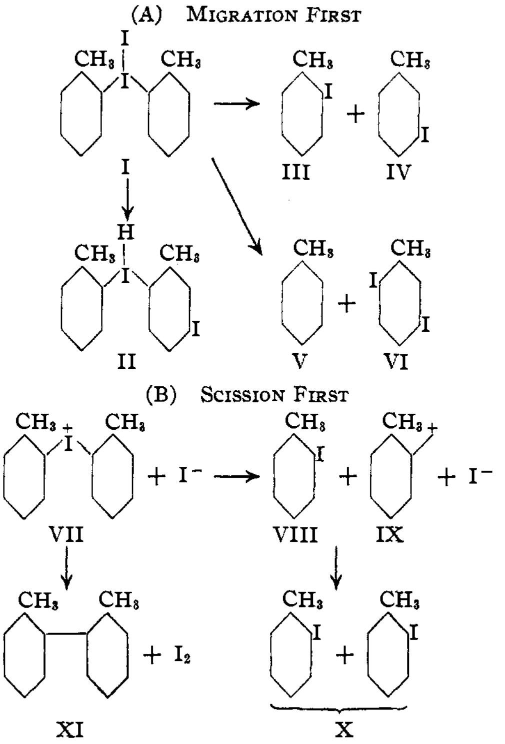
[1] Euler, *Ber.*, **39**, 2726 (1906); Biilmann, *Ann.*, **388**, 330 (1912); Holmberg, *Ber.*, **59**, 1569 (1926).

[2] McKenzie, Rogers and Mills, *J. Chem. Soc.*, **778** (1926); Meerwein and Wortmann, *Ann.*, **435**, 190 (1924); Meerwein and Montfort, *ibid.*, **435**, 214 (1924); Meerwein, *ibid.*, **453**, 16 (1927).

[3] Whitmore, THIS JOURNAL, **54**, 3274 (1932).



C–I bond in the hypothetical intermediate (II) should lead to the formation of a mixture of equal parts of *o*-iodotoluene (III) and *m*-iodotoluene (IV) or a mixture of equal parts of toluene (V) and 2,5-diiodotoluene (VI) or a mixture of all four compounds.

On the other hand, if the original compound is ionized, the iodide iodine would not migrate to the ring. A plausible mechanism of the rearrangement might involve first the formation, from di-*o*-tolyliodonium ion (VII), of equal amounts of *o*-iodotoluene (VIII) and positive *o*-tolyl ion (IX) by the scission of a C–I bond, and second the combination of this ion with the negative iodide ion, to form a second molecule of *o*-iodotoluene (X). The reaction product would then be pure *o*-iodotoluene. In case both C–I bonds should break simultaneously, the reaction products would be *o,o'*-bitolyl (XI) and iodine. If the reaction product should prove to be pure *o*-iodotoluene unmixed with the meta isomer or with diiodotoluene, then mechanism B would appear to be established.

The ionic character of iodonium compounds has been generally recognized for years. However, it is now known definitely that the I–I bond in diphenyliodonium iodide is an ionic, not a covalent, bond.[4] Since the reaction product was found to be almost pure *o*-iodotoluene uncontaminated by any isomeric product the evidence indicates that the decomposition proceeds through an intermediate, positively charged *o*-tolyl ion in which the positive charge is carried by a carbon atom. The conclusion that a C–I bond rather than a C–H bond breaks first is in agreement with bond energy values.[5]

Although Heilbronner[6] concluded that *o*-iodotoluene was the product of this rearrangement, his method of identification did not exclude the presence of the meta isomer. In the present work the reaction product was converted into the arylmagnesium iodide and this by reaction with carbon dioxide, into the corresponding toluic acid. This proved to be the pure ortho acid, unmixed with any metatoluic acid or with any methylphthalic acid. The steps involved in the preparation and decomposition of the iodonium compound are

$$CH_3C_6H_4I \longrightarrow CH_3C_6H_4ICl_2 \longrightarrow CH_3C_6H_4IO \longrightarrow$$
$$CH_3C_6H_4IO_2 \longrightarrow (CH_3C_6H_4)_2I\text{–}I \longrightarrow CH_3C_6H_4I \longrightarrow$$
$$CH_3C_6H_4MgI \longrightarrow CH_3C_6H_4COOH$$

Experimental

Materials.—*o*-Iodotoluene was prepared, through the diazo reaction, from colorless *o*-toluidine purified by distillation *in vacuo* after having been crystallized three times, in the form of the nitrate, from water. *m*-Iodotoluene was prepared from *m*-nitrotoluene through *m*-toluidine. The *m*-nitrotoluene was purified by freezing three times, with removal of unfrozen material, to give a product melting at 16°. The *p*-iodotoluene was prepared from *p*-toluidine (Eastman pract.). The yields of final purified iodotoluenes from the toluidines were, ortho 80%, meta 76% and para 74%.

Properties of the Iodotoluenes.—The ortho isomer was purified by distillation at 745 and 24 mm., the meta and para by distillation at 745 mm. The latter was crystallized from alcohol–water mixture. The ortho and meta were obtained as colorless liquids which slowly darkened in the light, and the para as a cream-colored solid. They remained unchanged for months when kept in the dark and in an atmosphere of carbon dioxide. The properties of the iodotoluenes differ somewhat from previous values. They are shown in Table I.

Table I

Physical Constants of Iodotoluenes

Isomer		Ortho	Meta	Para
B. p., °C., corr.	745 mm.	205.5	210.0	....
	24 mm.	95.5	....	....
Sp. gr. 20/20		1.7090	1.6981	....
Ref. index, n^{20}_D		1.6030	1.6012	....
M. p., °C., corr.		....	....	34.5–35.0

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[4] Medlin, This Journal, 57, 1026 (1935).

[5] These values are: C–I, 56.5 kg. cal. per mole; C–H, 97.7 kg. cal.

[6] Heilbronner, *Ber.*, 28, 1815 (1895).

Conversion of Iodotoluenes to the Toluic Acids.—This was done in order to obtain the pure toluic acids and to investigate the yields to be expected when working with small quantities (about 15 g.) of iodotoluenes. The Grignard reagents were first prepared from each of the three pure iodotoluenes. After passing in dry carbon dioxide, dilute sulfuric acid was added. The toluic acids were extracted from the ether with sodium carbonate solution and recovered by acidification of the latter. No essential difference was observed in the behavior of the three iodotoluenes, all giving a yield of about 50%. The addition of a small amount of methyl iodide to the magnesium and ether (1% of the ether by volume) two hours before adding the iodotoluene raised the yield to about 75%. Bitolyl was a by-product, resulting from a Wurtz coupling. Its formation accounts in part for the low yields.

The crude acids melted as follows: ortho, 102.5–103.6°; meta, 108–109°; para, 175–177°; and after crystallization from hot water, ortho, 103.5–103.7°; meta, 110.6–111.2°; para, 178.5–178.8°. Titration against 0.05 N sodium hydroxide, standardized against Merck analytical benzoic acid, gave equivalent weights as follows: ortho. 136.1; meta, 136.8; para, 136.5; theoretical is 136.1.

Preparation of Iodosotoluenes.—In order to obtain the intermediate iodosochlorides pure, and in good yield, the method of Willgerodt[7] was modified by concentrating the chloroform solution and then filtering off the solid iodosochlorides; yield of iodosotoluene, 70%.

The purity of the iodosotoluene was established by iodimetry. In the analysis, the liberation of iodine in a solution containing hydrogen and iodide ions is markedly accelerated by the addition of a few ml. of chloroform. The analytical results indicate that the iodosotoluenes form monohydrates which are stable at room temperature. Thus, three samples of *o*-iodosotoluene dried in the air for three days averaged 92.0% pure on the basis of their oxidizing power, but when dried over sulfuric acid *in vacuo* they averaged 100.4%. The theoretical oxidizing power of the monohydrate is 92.9% that of the anhydrous.

Preparation of *o*-Iodoxytoluene.—The use of hypochlorous acid as the oxidizing agent[8] for converting the iodoso to the iodoxy compound proved to be unsatisfactory, for an excess of hypochlorite destroys the compound. Steam distillation of the iodosotoluene, according to the procedure of Willgerodt, was found to be satisfactory, since the recovered iodotoluene could be utilized. Two preparations from 50 g. of *o*-iodosotoluene gave *o*-iodoxytoluene in yields of 38 and 34% and iodotoluene in yields of 36 and 49%.

The first sample of iodoxytoluene was dried for two days in air, the second for one day *in vacuo* over concentrated sulfuric acid. Iodometric titration showed the first to have an oxidizing strength of 97.5% on the basis of iodoxytoluene and the second. 98.3%.

Preparation of Di-*o*-tolyliodonium Iodide.—Following the method which Meyer and Hartman[9] used when they obtained a 93% yield of diphenyliodonium iodide, that is, agitation for two days of an equimolar mixture of iodoso and iodoxy compound with an excess of silver oxide suspended in water, only an 18% yield of the *o*-tolyl compound resulted. It was found preferable to grind in a mortar equimolal amounts of the iodosotoluene, iodoxytoluene and freshly precipitated moist silver oxide (9.0, 9.3 and 10.0 g., respectively) with 10 ml. of chloroform and a few ml. of water. At intervals the water was poured off into a flask, more water was added to the mixture in the mortar and the grinding continued. Finally the mixture was allowed to stand overnight. The combined aqueous extracts were reduced by sulfur dioxide, resulting in the precipitation of di-*o*-tolyliodonium iodide. A much whiter product is obtained by adding a solution of potassium iodide instead of reducing with sulfur dioxide. The yield of washed and dried product was 44%. A duplicate experiment, using however only 0.5 g. of silver oxide (1/20 molal ratio), gave practically the same yield (43.5%). A third preparation, using 16.5 g. of the iodoso (a slight excess), 16.3 g. of the iodoxy compound and 1.0 g. of silver oxide gave 20.7 g. of the iodide, a yield of 73%. In this case the mixture was allowed to react for two days and the silver oxide was added in two portions.

These results indicate that the rate with which the tolyliodonium ion is formed is much slower than the rate of formation of the corresponding phenyl compound. This may be due in part to lower solubilities of the tolyl compounds and in part to steric hindrance. The results also indicate that silver oxide catalyzes the reaction by which the iodonium compound is formed. The reaction presumably is as follows.

$$\mathrm{C_7H_7IO + C_7H_7IO_2 \xrightarrow{Ag_2O} (C_7H_7)_2I^+ + IO_3^-}$$

Decomposition of Di-*o*-tolyliodonium Iodide.—Preliminary experiments showed that the reaction did not take place until the solid was heated to 150°. The decomposition was effected by immersing in a glycerol bath at 155° a 100-ml. spherical flask containing approximately 16 g. of the iodide. The flask was provided with a 7-mm. diameter reflux tube. About two minutes after immersion the reaction started and was apparently complete within five seconds. A small amount of liquid condensed on the reflux tube but there was not enough to run back into the flask. A small amount of iodine vapor was visible. A small portion of the liquid was analyzed for free iodine and the refractive index determined (Table II).

TABLE II

DATA ON REACTION AND PRODUCT

Experiment		1	2
$(C_7H_7)_2I_2$ taken, g.		16.35	15.91
Bath temp., °C.		155	155
Loss during reaction	g.	0.11	0.34
	%	.07	.22
Iodine present	g.	.0045	.0055
	%	.38	.46
Refractive index, n^{20}_D		1.607	1.607

Identification of the Reaction Product.—The bulk of the reaction product was converted into the corresponding toluic acid by the method previously mentioned. with results shown in Table III.

The rearranged tolyl iodide is believed to be nearly pure *o*-iodotoluene for the following reasons: first, the refrac-

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(7) Willgerodt. *Ber.*, **26**, 357 (1893).

(8) Willgerodt. *ibid.*, **29**, 1568 (1896).

(9) Meyer and Hartman, *ibid.*, **27**, 426. 502 (1894).

TABLE III

CONVERSION OF REARRANGED TOLYL IODIDE TO TOLUIC ACID

$CH_3C_6H_4I$	g.	14.38[a]	15.32[b]
	mole	0.066	0.070
Magnesium	g.	1.8	2.2
	mole	0.074	0.090
Ether, ml.		70[c]	110[c]
Time, hours	Addition	3	6
	Stirring	3	12
Toluic acid	g.	5.75	6.05
	%	64.0	63.4
	m. p.	102.4–103.0	103.3–103.7
Residue	g.	1.55	1.50
	%	25	22.5

[a] Plus 15 ml. of anhydrous ether. [b] Plus 60 ml. of anhydrous ether. [c] Plus 0.90 ml. of methyl iodide.

tive index 1.607 is higher than the value of 1.603 for *o*-iodotoluene, and for that reason the main impurity is not likely to be *m*-iodotoluene, the refractive index of which is 1.601; likewise, it is not likely to be bitolyl, for the refractive index of a 10% solution of crude bitolyl (from the Grignard reaction) in *o*-iodotoluene is 1.592; the presence of the dissolved iodine does not compensate for the influence of any dissolved material because 0.5% of dissolved iodine does not change the refractive index; second, the small percentage of free iodine in the decomposition product (0.46%) shows that less than 1% of the iodonium compound decomposed into iodine and bitolyl; third, the crude toluic acid obtained from the decomposition product is pure *o*-toluic acid, uncontaminated by methylphthalic acid or by any *m*- or *p*-toluic acid, as shown by (a) the equivalent weight (136.7 against theoretical of 136.1), (b) the high melting point of the crude acid, 103.3–103.7°, a value practically identical with the best value of recrystallized *o*-toluic acid obtained in this work, *viz.*, 103.5–103.7°; (c) the mixed melting point of the crude with the purest *o*-toluic acid, *viz.*, 103.4–103.7°; and (d) the lowering of the melting point of the crude acid by its admixture with the isomeric acids, 5% of which gave these values, meta, 99.5–101.6°; para, 98.5–100°.

Although the yield of *o*-toluic acid was 64%, a part of the reaction product, namely, 22–25%, was accounted for as bitolyl. The molecular weight of the crude bitolyl, as determined by the camphor method,[10] was found to be 204, whereas that of bitolyl is 182.

Since the yield of toluic acid was 64% and that of bitolyl 22–25%, 86–89% of the original material is accounted for. The presence of water in traces, during the preparation of the Grignard reagent, would lead to the formation of some toluene, which would be lost.

Summary

Di-*o*-tolyliodonium iodide decomposes at 155° into *o*-iodotoluene and not into a mixture of iodotoluenes. The nature of the reaction product indicates that the ditolyliodonium ion splits into *o*-iodotoluene and positively charged *o*-tolyl ion by a scission of the C–I bond. The combining of this ion with the negative iodide ion produces *o*-iodotoluene.

In the formation of di-*o*-tolyliodonium iodate from *o*-iodosotoluene and *o*-iodoxytoluene, silver oxide acts catalytically.

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[10] Smith and Young, *J. Biol. Chem.*, **75**, 289 (1927).

PASADENA, CALIFORNIA RECEIVED JULY 30, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

The Parachor and Molecular Refraction of Hydrazine and Some Aliphatic Derivatives

BY L. D. BARRICK, G. W. DRAKE AND H. L. LOCHTE

Since aliphatic hydrazines and related compounds were until recently relatively rare, little work has been done on their physical constants. The determination of their parachor values seemed especially desirable in view of the variety of nitrogen linkages available. The data on these compounds furnish an opportunity to compare the atomic constants of Sugden[1] with those reported later by Mumford and Phillips.[2]

With the highly purified materials available the molecular refraction and dispersion were also redetermined.

Preparation and Purification of Materials.—Anhydrous hydrazine was prepared according to the method of Hale and Shetterly.[3] Final drying was carried out by high vacuum distillation over freshly prepared calcium oxide; b. p. (corr.) 113° at 760 mm.[4]

Dimethylketazine was prepared according to the directions of Curtius[5] and dried over pellets of potassium hydroxide. The vapor of the fraction boiling at 132–133° was then passed, under vacuum, over fresh potassium hydroxide; m. p. −12.5°.

3,5,5′-Trimethylpyrazoline was prepared according to the method of Frey and Hoffmann[6] using oxalic acid as rearranging agent. The oxalate of the base was recrystallized from alcohol and the pyrazoline liberated by potassium hydroxide and dried like ketazine; b. p. 165–170° at 750 mm.

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(1) Sugden, *J. Chem. Soc.*, **125**, 1177 (1924).

(2) Mumford and Phillips, *ibid.*, 2112 (1929).

(3) Hale and Shetterly, THIS JOURNAL, **33**, 1071 (1911).

(4) This portion of the work was done under the direction of Prof. W. A. Felsing of this Laboratory.

(5) Curtius, *J. prakt. Chem.*, [2] **44**, 164 (1891).

(6) Frey and Hoffmann, *Monatsh.*, **22**, 760 (1901).