

The rate of bromination of the mixed fatty acids of poppy seed, soya bean, linseed and perilla oils is in direct relation to the acid constituents.

Under the influence of ultraviolet light the bromination of both the so-called pure acids and the mixed fatty acids proceeds beyond the bromination in the dark, which indicates the presence of unsaturated isomers which are not shown by present methods of analysis.

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THE CONSTITUTION OF ORTHO-NITROBENZALDEHYDE AND THE INTERFERENCE OF NITRO AND NITROSO GROUPS ON THE ZEREWITINOFF METHOD FOR THE QUANTITATIVE ESTIMATION OF ACTIVE HYDROGEN

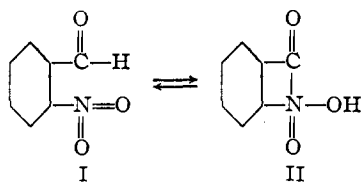
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Introduction

In connection with a study of the mechanism of the photochemical reactions of *o*-nitrobenzaldehyde and some of its condensation products, Tanasescu² has suggested recently that *o*-nitrobenzaldehyde is very probably an equilibrium mixture of the following forms:



The chief evidence brought forward in support of the cyclic hydroxy formula (II) is the quantity of methane evolved when *o*-nitrobenzaldehyde is treated with methylmagnesium iodide according to the method of Zerewitinoff.³ This quantitative method for the estimation of active hydrogens has been used very extensively and, on the whole, is eminently satisfactory.

However, Tanasescu is probably quite wrong in suggesting that *o*-nitrobenzaldehyde has the cyclic hydroxy formula (II) because the compound evolves methane when treated with methylmagnesium iodide. We do not say that a formula like (II) is impossible. If it is a likely formula it must find support in evidence other than that given by the Zerewiti-

¹ A preliminary report on this work was presented at Iowa City, May 7, 1927, before the Organic Division of the Iowa Academy of Science.

² Tanasescu, *Bull. soc. chim.*, 39, 1443 (1926).

³ Zerewitinoff, *Ber.*, 40, 2023 (1907), and numerous succeeding papers. The most recent reference is the *Z. anal. Chem.*, 68, 321-327 (1926) [*C. A.*, 21, 153 (1927)]. See also Chugaev, *Ber.*, 35, 3912 (1902), for earlier experimental work on the same method.

noff method. The present quantitative studies on the gases evolved show that the phenomenon of gas evolution is essentially an inherent property of the nitro and nitroso groups.

Tanasescu used methylmagnesium iodide in his studies and, as well as can be ascertained from his data, the gas evolved was merely measured and not analyzed to ascertain whether it was pure methane or a mixture of hydrocarbons. Such analyses have been carried out in our work and although the gas evolved when methylmagnesium iodide is used is largely methane, as one would expect if any hydroxyl group were present, the same is not true with other alkylmagnesium halides like the ethyl-, propyl- and butylmagnesium bromides. With these other alkylmagnesium halides varying amounts of unsaturated and R. R. hydrocarbons are evolved in addition to ethane, propane and butane.

Experimental

All of the experiments were carried out under the standard conditions of earlier workers. A few of the compounds were studied in *n*-butyl ether according to Zerevitinoff's³ technique. Most of the determinations, however, were made by the revised method of Moureu and Mignonac,⁴ in which ethyl ether is used as the medium. Ciusa⁵ also used the technique of Moureu and Mignonac. Blank runs with pure benzoic acid were made in both methods in order to assure ourselves of correct manipulation.

The compounds used were of the highest purity commercially available and in a few cases additional special purification processes were used.

The gases evolved were analyzed by standard methods of combustion, preceded by removal of ether, unsaturated hydrocarbons and oxygen.

An experiment with nitrobenzene and methylmagnesium iodide in *n*-butyl ether showed that most of the gas was evolved at room temperature during the first ten minutes.⁶ However, in order to displace any dissolved gas and to expedite the several determinations, the reaction flask was immersed in a beaker of water at 60–70°. It was allowed to stand under these conditions for fifteen minutes, after external heat was removed. At the end of this period the water-bath was removed, the flask cooled to room temperature and a reading was then made of the volume of gas evolved.

The analysis of the saturated gas by the explosion method followed by measurement of carbon dioxide and water showed that the quantity of saturated hydrocarbon that might have been formed by a coupling reaction (for example, ethane when methylmagnesium iodide was used) was generally quite small and did not exceed several per cent. In order to verify this, two large runs were made with *n*-butylmagnesium bromide and cyclohexylmagnesium bromide. Forty-nine and two-tenths g. (0.4 mole) of nitrobenzene dissolved in 100 cc. of dry ether was added slowly to 2.25 moles of *n*-butylmagnesium bromide—an amount which was sufficient to give a positive color test for RMgX compound. After hydrolysis, careful fractionation gave about 2 g. (1.6%)

⁴ Moureu and Mignonac, *Compt. rend.*, **158**, 1624 (1914).

⁵ Ciusa, *Gazz. chim. ital.*, **50**, II, 53 (1920); *C. A.*, **15**, 837 (1921).

⁶ About 0.8 active hydrogen equivalent of gas was evolved during the first ten minutes. At the end of two hours, the equivalent of active hydrogen increased to 0.99. Finally, in this particular experiment, heating for fifteen minutes at 60–70° increased the active hydrogen equivalent to 1.35. This particular determination was the last of those made in the present study.

of *n*-octane and 6.0 g. or 3.6% of *n*-butyl alcohol. The reaction mixture of 0.17 mole of nitrobenzene and 0.4 mole of cyclohexylmagnesium bromide gave 2.4 g. or 3.6% of di-cyclohexyl.

TABLE I
RESULTS

No.	Compound	G. of compound	Grignard reagent	Gas evolved, (Cc. stand. cond.)	No. of active hydrogens
1	Benzoic acid	0.2034	CH ₃ MgI	33.2	0.89
		.2063		36.6	.96
		.2076		37.2	1.03 ^a
2	Nitrobenzene	.2876	CH ₃ MgI	51.2	0.98
		.2214		41.7	1.03
		.1993		34.4	0.95
		.4849		87.2	.99
3	Benzoic acid	.5206	C ₂ H ₅ MgBr	96.5	1.01 ^b
		4		Nitrobenzene	.6004
		.5724	155.7		1.50
5	<i>o</i> -Nitrotoluene	.6871	C ₂ H ₅ MgBr	180.0	1.60
					.3412
6	<i>p</i> -Nitrotoluene	.5872	C ₂ H ₅ MgBr	158.5	1.65 ^d
7	1,3,5-Trinitrobenzene	.1992	C ₂ H ₅ MgBr	31.2	1.49 ^e
8	<i>o</i> -Nitrobenzaldehyde	.5007	C ₂ H ₅ MgBr	121.9	1.65 ^f
					.5005
9	<i>m</i> -Nitrobenzaldehyde	.5297	C ₂ H ₅ MgBr	112.0	1.43 ^g
10	Nitrosobenzene	.4020	C ₂ H ₅ MgBr	91.8	1.09 ^h
11	<i>p</i> -Nitrosodiethylaniline	.5012	C ₂ H ₅ MgBr	46.4	0.74 ^h
12	Nitrobenzene	.6184	<i>n</i> -C ₄ H ₉ MgBr	213.8	1.90 ⁱ
13	Nitrobenzene	.7228	<i>n</i> -C ₄ H ₉ MgBr	221.6	1.68 ⁱ

^a When carried out at room temperature the number of active hydrogen was 0.98. However, when the reaction flask was heated to from 60–70° for fifteen minutes, then cooled and the gas measured, the number was 1.03. This slight increase was undoubtedly due to the expulsion of some dissolved gas. Accordingly, all other experiments with *n*-butyl ether were heated in like manner. With ethyl ether as the solvent the temperature of the water-bath was 40–45°.

^b This gas contained 0.5% of unsaturated compounds. Very probably this is due to a small quantity of ethylene formed in the preparation of ethylmagnesium bromide.

^c Included in this gas was 13% of unsaturated compounds.

^d There was 16.5% of unsaturation in this gas.

^e This includes 5.9% of unsaturation.

^f This includes 10.5% of unsaturation, and the other run giving 1.68 active hydrogen showed 8.0% unsaturation. The authors wish to thank the Eastman Kodak Company for the sample of *o*-nitrobenzaldehyde used in this study.

^g This includes 12.2% of unsaturation.

^h Includes 12.6% unsaturation, whereas the *p*-nitrosodiethylaniline has 9.6% unsaturation.

ⁱ Includes 10.8% unsaturation, whereas the experiment with *n*-butylmagnesium bromide gave 12.9% unsaturation.

Discussion of Results

The results in Table I show that all the nitro and nitroso compounds studied evolve varying amounts of gas when treated with alkylmagnesium

halides having an alkyl group of low molecular weight. In a way it is largely fortuitous that nitrobenzene shows but one active hydrogen when treated with methylmagnesium iodide;⁶ for, had ethylmagnesium bromide been used—a reagent which in the hands of others⁴ has given good results in estimating active hydrogen in a miscellany of compounds—the number of active hydrogens would have been about 50% greater. In this connection it is to be noted that *n*-propyl- and *n*-butylmagnesium bromides also give higher results than those obtained with methylmagnesium iodide.

The gas evolved from the two nitrobenzaldehydes studied is probably independent of the aldehyde group present, because benzaldehyde under corresponding conditions evolves no gas.

Tanasescu² got about one active hydrogen equivalent with *o*-nitrobenzaldehyde and less than one-third of an active hydrogen with *p*-nitrobenzaldehyde. He used methylmagnesium iodide, but on the basis of our results with different alkylmagnesium halides it is obvious that had he used a higher alkylmagnesium halide he would have found more active hydrogen. In this way he might have avoided the error of advancing formula (II), which is postulated as having one hydroxyl group largely because it evolves one equivalent of gas with methylmagnesium iodide.

Summary

The cyclic hydroxy structure proposed for *o*-nitrobenzaldehyde has no support on the basis of gas evolved when treated with an alkylmagnesium halide of low molecular weight. Gas evolution has been shown to be an inherent property of nitro and nitroso groups, and the Zerewitinoff method cannot be used with substituted aromatic nitro and nitroso compounds unless corrections are made for the gas evolved because of the nitro or nitroso group.

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