

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]
**THE INTERFERENCE OF NITRO AND AZO GROUPS ON THE
ZEREWITINOFF METHOD FOR THE QUANTITATIVE
ESTIMATION OF ACTIVE HYDROGEN**

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Introduction

It has recently¹ been shown that nitro and nitroso groups interfere with the Zerewitinoff² method for the quantitative estimation of active hydrogen. The presence of such groups in a molecule is directly responsible for the liberation of very significant volumes of gas when the compound is treated with RMgX compounds having an alkyl group of low molecular weight.

Zerewitinoff³ determined the number of active hydrogens in molecular compounds composed of substituted amines and trinitrobenzene, such as the trinitrobenzene complexes with *p*-amino-azobenzene and anthranilic acid. Each of these contains a primary amino group and it is known that one of the amino hydrogens reacts at room temperature and the second on heating. Zerewitinoff's results agree reasonably well on the basis of this general behavior, although there were more than the usual variations in quantity of gas evolved when the second hydrogen of primary amines is replaced. In view of our earlier work¹ it appeared that Zerewitinoff's results were incorrect, because the presence of trinitrobenzene in the complex molecule should have caused a larger evolution of gas than was reported by Zerewitinoff. We showed then that 1,3,5-trinitrobenzene evolved considerable gas when treated with ethylmagnesium bromide. This was contrary to the work of Ciusa⁴ who reported that trinitrobenzene contained no active hydrogen.

There was the possibility that the nitro groups in the complexes studied by Zerewitinoff might have been so masked by the amino component that normal values would be obtained. However, the present work shows that such is not the case. The complexes give decidedly higher values for active hydrogen than those calculated for the amino group alone. The unavoidable conclusion is that the nitro groups are very largely responsible for the abnormal results.

We do not say that the nitro group is entirely responsible in every case for the higher values, because the complex formed from *p*-amino-azobenzene and trinitrobenzene contains, in addition to the amino and nitro

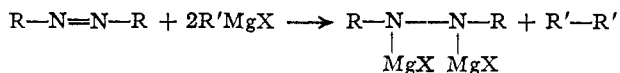
¹ Gilman and Fothergill, *THIS JOURNAL*, **49**, 2815 (1927).

² Zerewitinoff, *Ber.*, **40**, 2023 (1907) and numerous succeeding papers. The most recent reference is *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.

³ Zerewitinoff, *Ber.*, **43**, 3590 (1910).

⁴ Ciusa, *Gazz. chim. ital.*, **50**, II, 53 (1920) [*C. A.*, **15**, 837 (1921)].

groups, an azo group. Gilman and Pickens⁵ have shown that the following reaction takes place between azo compounds and the Grignard reagent.



In view of this reaction it is to be expected that azo compounds under certain conditions should evolve gases when treated with RMgX compounds having an alkyl group of low molecular weight. A study of several typical azo compounds shows that an appreciable quantity of gas is evolved under the conditions used in our determination of active hydrogen by Zerewitinoff's method. Accordingly, the azo group is to be added to the nitro and nitroso groups as a group that interferes with the quantitative estimation of active hydrogen.

TABLE I
RESULTS

Compound	Compound, g.	Solvent for compound	No. of active hydrogens	
			Room temp.	After warming to 70°
<i>p</i> -Amino-azobenzene-trinitrobenzene	0.2019	Xylene	2.17	3.46
	.1998	Xylene	1.88	3.18
	.2037 ^a	Xylene	2.09	3.62
Anthranilic acid-trinitrobenzene	.0972	Xylene	2.50	3.54
	.0975	Xylene	2.51	3.47
Azobenzene	.2004	<i>n</i> -Butyl ether	.24	.29
<i>p</i> -Dimethylamino-azobenzene	.2049	<i>n</i> -Butyl ether	.33	.42
<i>p</i> -Amino-azobenzene	.2035	<i>n</i> -Butyl ether	1.69	2.18
	.2008	<i>n</i> -Butyl ether	2.14 ^b	2.48 ^c
Benzene-azodiphenylamine	.2012	<i>n</i> -Butyl ether	1.26	1.42
				1.74 ^d
Benzoic acid ^e	.2168	Xylene	1.03	1.15

^a The methylmagnesium iodide used in this determination was prepared in *iso*-amyl ether, after the directions of Zerewitinoff.⁵ However, Zerewitinoff found 1.03 active hydrogens at room temperature, and 2.02 active hydrogens after warming to 85° for five minutes.

^b After standing at room temperature (31°) for fifteen hours.

^c After warming to 50–70° for six hours.

^d After warming to 70° and then standing for one and one-half hours at room temperature.

^e This check experiment was carried out to determine the reliability of xylene as a solvent.

⁵ Gilman and Pickens, *THIS JOURNAL*, **47**, 2406 (1925). The same mechanism, without proof, was offered earlier by Franzen and Deibel, *Ber.*, **38**, 2716 (1905). However, their reaction with ethylmagnesium bromide is incorrect, inasmuch as present studies show that the gases evolved from azobenzene and ethylmagnesium bromide contain 25–30% of ethylene. The results of this disproportionation reaction between azobenzene and other RMgX compounds will be reported later.

Experimental

The apparatus and general technique was that described by Zerewitinoff,² except that *n*-butyl ether was used as the medium for methylmagnesium iodide in all but one of the determinations. Xylene was used in some of the analyses as a solvent for the complexes with trinitrobenzene because of their low solubility in *n*-butyl ether. In each determination the amount of gas evolved by the reaction at room temperature was first determined, and then the reaction mixture was heated to 70° for fifteen minutes, after which it was cooled to room temperature for the second value.

Summary

The complexes of *p*-amino-azobenzene and anthranilic acid with trinitrobenzene have been shown to give higher active hydrogen values than those reported by Zerewitinoff. These abnormal results are due to the interfering effect of the nitro and azo groups.

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THE REACTION BETWEEN DUROQUINONE AND THE GRIGNARD REAGENTS¹

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Introduction and Historical Review. Statement of the Problem

In the first paper of this series² it was shown that the reaction between sodium malonic esters and duroquinone is not a simple addition reaction but is accompanied by oxidation leading to a product in which the malonic ester residue is linked by a double bond to what was originally one of the methyl groups of the quinone. This reaction involves the removal of both methylene hydrogen atoms of the malonic ester and both these hydrogen atoms are necessary in order for the reaction to take place.

In order to obtain more information concerning the addition of metallic derivatives to duroquinone, we have used in the present work a Grignard reagent. These reagents differ from sodium malonic ester in possessing no active "methylene" hydrogen atoms, and yet they have the advantage, in common with sodium malonic esters, of adding to carbonyl systems to give metallic derivatives which can be readily manipulated. By using the Grignard reagents we hoped to avoid the complicated oxidation reaction which accompanies the addition of sodium malonic ester and to

¹ Abstracted from a thesis by H. Marjorie Crawford, presented to the Graduate Faculty of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Smith and Dobrovlny, *THIS JOURNAL*, **48**, 1693 (1926).