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John J. Courtney
State University of Iowa

Lothar E. Geipel
State University of Iowa

R. L. Shriner
State University of Iowa

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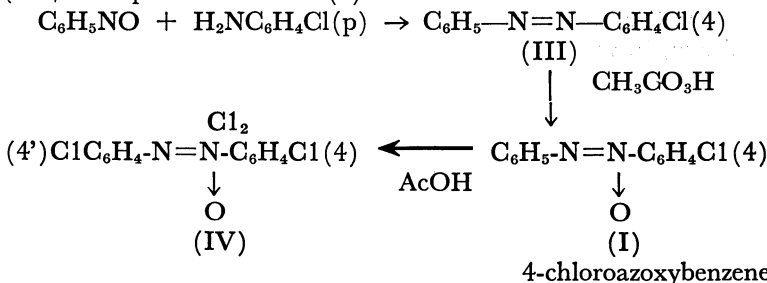
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Reactivity of the Halogen in the Isomeric 4- and 4'-Chloroazoxybenzenes

By JOHN J. COURTNEY, LOTHAR E. GEIPEL AND R. L. SHRINER

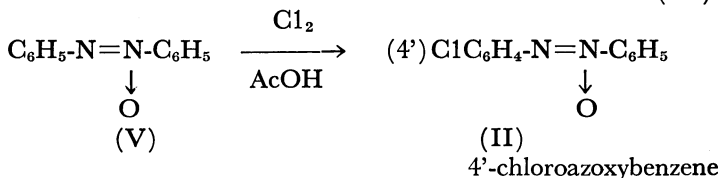
The relative ease of displacement of a halogen in the benzene ring by anionic reagents is markedly influenced by the character of other substituents in the ring. A thorough survey of the literature on these aromatic nucleophilic substitution reactions has been given by Bunnett and Zahler (1). These authors discuss the influences exerted by various groups in the *ortho*, *meta* and *para* positions, the effects of different electron donor reagents and variations in experimental conditions. Since no data are available concerning the effect of the azoxy group, it was desirable to synthesize some chloro-substituted aromatic azoxy compounds and compare them with chloro-nitro-compounds and chloro-azo-compounds. The azo-grouping has only a slight activating effect (2) being reported by Badger, Cook and Vidal (3) to be about one-sixth as effective as a nitro group.

Since Angeli and his collaborators (4) have shown that the azoxy-grouping is unsymmetrical, it is necessary to prepare the two isomeric chloroazoxybenzenes shown by formulas (I) and (II). The first isomer was made by condensing nitrosobenzene with *p*-chloroaniline and selectively oxidizing the *p*-chloroazobenzene (III) with peracetic acid to (I).



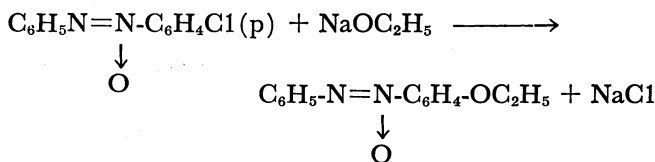
4-chloroazoxybenzene

The structure of (I) was shown by the fact that it could be chlorinated to 4,4'-dichloroazoxybenzene (IV). The second isomer (II) was obtained by chlorination of azoxybenzene (V). This isomer (II) is not further chlorinated to the dichloroderivative (IV).



These reactions parallel those described by Angeli (3) on bromo- and nitro-azoxybenzenes.

The effect of the azoxy group on the ease of displacement of the chlorine in compounds I and II was determined by refluxing solutions of these compounds with an excess of sodium ethoxide in ethanol. The amount of ionic chloride formed by the displacement reaction was determined gravimetrically. The results are shown



in Table I which includes data on 4-chloroazobenzene and 4-chloronitrobenzene for comparison.

Table I

Compound	% Chlorine 10 hrs. (A)	Displaced in 20 hrs. (B)
4 -chloroazoxybenzene (I)	1.6	5.0
4'-chloroazoxybenzene (II)	2.8	7.3
4-chloroazobenzene (III)	trace	trace
4-chloronitrobenzene	46.3	54.6

(A) This series used 0.001 mole of each compound in 50 ml. of 0.42 N sodium ethoxide in ethanol.

(B) This series used 0.002 mole of each compound in 100 ml of 0.37 N sodium ethoxide.

The results show that the azoxy-group slightly increases the reactivity of the halogen atom over that shown by the azo-grouping but that these groups are much weaker in their effects than the nitro group. It is of interest that isomer (II) reacted to a slightly greater extent than isomer (I) and that the latter was more reactive than the azo compound (III). These may be explained on the basis of differences contributed by various structures to the resonance hybrid.

EXPERIMENTAL

4-Chloroazoxybenzene (I). To a solution of 32.5 g. of 4-chloroazobenzene in 370 ml. of glacial acetic acid was added 70 ml. of 30% hydrogen peroxide. After standing at 25° for 7 days, a

crop of yellow crystals amounting to 11 g. and melting at 57-61.5° was obtained. Dilution of the filtrate with an equal volume of water gave 13 g. of product melting 57-59.5°. Further addition of two volumes of water gave 2.5 g. melting at 59-61°. Each of these fractions was recrystallized from a series of solvents, methanol, ethanol, Skellysolve D, toluene and dioxane in order to try to find any isomers. Only one compound was found in 75% yield which melted constantly at 59-61.5° after recrystallizations from the above solvents.

Anal. Calcd. for: $C_{12}H_9ON_2Cl$: C, 61.80; H, 4.14; N, 12.04

Found: C, 61.92; H, 3.89; N, 12.09

4,4'-Dichloroazoxybenzene (IV). To 17.2 ml. of a molar solution of chlorine in glacial acetic acid was added 2.84 g. of 4-chloroazoxybenzene and an additional 20 ml. of glacial acetic acid. After standing 8 days at 25° in the dark, the mixture was poured into ice-water. The precipitate was collected on a filter and thoroughly washed with water. The solid was recrystallized twice from ethanol and once from methanol after which it melted constantly at 153-154.5° and did not depress the melting point of an authentic sample of 4,4'-dichloroazoxybenzene which had been synthesized from p-chloronitrobenzene.

Analysis Calculated. for $C_{12}H_8ON_2Cl_2$: Cl, 26.54; N, 10.48

Found: Cl, 26.50; N, 10.47

4'-Chloroazoxybenzene. To a solution of 4.8 g. of chlorine in 100 ml. of glacial acetic acid was added 13.4 g. of azoxybenzene. The mixture was kept in the dark at 25° for 6 days. The orange-red solution was poured into 500 ml. of ice water. The solid product was collected on a filter, thoroughly washed with water and recrystallized from 95% ethanol. There was obtained 15 g. of very pale yellow crystals melting sharply at 67.5-68°.

Analysis Calculated for $C_{12}H_9ON_2Cl$: N, 12.04

Found: N, 11.88

Reaction with Sodium Ethoxide. Solutions of 0.42 N and 0.37 N sodium ethoxide in absolute ethanol were prepared. Fifty and one-hundred milliliter aliquots of these solutions were brought to reflux on a hot plate, and when boiling had begun, samples of the chloro-compounds were added. At the end of 10 or 20 hours, the reaction mixtures were poured into cold, distilled water, and the resultant mixtures made acid with nitric acid and filtered. Silver nitrate was then added to precipitate the chloride ion. The silver chloride was filtered, dried and weighed. The results are recorded in Table I.

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CHEMISTRY LABORATORY
STATE UNIVERSITY OF IOWA
IOWA CITY, IOWA