

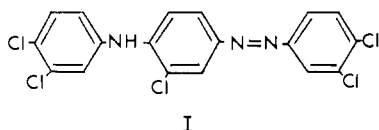
# Synthesis and Properties of 4-(3,4-Dichloroanilino)-3,3',4'-trichloroazobenzene

Joseph D. Rosen\* and Marie Siewierski

The synthesis of 4-(3,4-dichloroanilino)-3,3',4'-trichloroazobenzene is described. Preliminary stud-

ies indicate that the material is stable after incubation in soil or after irradiation by sunlight.

Spectroscopic evidence indicated that 4-(3,4-dichloroanilino)-3,3',4'-trichloroazobenzene (I) was formed by the action of sunlight on 3,4-dichloroaniline in the presence of riboflavin 5'-phosphate, sodium (FMN), (Rosen *et al.*, 1970) and by the action of soil microorganisms on the herbicide, 3,4-dichloropropionanilide (Linke, 1970). Because I represents a possible environmental residue of several



herbicides containing 3,4-dichloroaniline moieties, it was decided to synthesize enough of it to determine its toxicological significance and to obtain some indication of its persistence in the environment. Another goal was to establish definitively the structure of I as proposed by Rosen *et al.* (1970).

## EXPERIMENTAL

**Synthesis of 2,3',4'-Trichlorodiphenylamine.** A modification of a method of Hebký *et al.* (1961) was used. Sixty-three grams of 3,4-dichloroacetanilide (made by the dropwise addition of acetyl chloride to a solution of 3,4-dichloroaniline in benzene), 42.6 g of potassium carbonate, 3 g of copper powder, and 750 mg of iodine were thoroughly mixed. To this mixture was added 65.6 g of *o*-bromochlorobenzene, and the resulting mixture was heated in an oil bath at 200° to 210° C for 20 hr. After cooling, 100 ml of a 31% potassium hydroxide alcohol-water (70 to 30, v/v) solution was added and the mixture was refluxed for 10 hr. The mixture was filtered and the filtrate was concentrated to a dark brown oil which was dissolved in 300 ml of ether and successively extracted with 100 ml of 6*N* hydrochloric acid (twice), 100 ml of saturated sodium bicarbonate solution, and 100 ml of water. The ether solution was dried and evaporated to give 62 g of a dark brown tar. Adsorption chromatography on silica gel (J. T. Baker, 60–200 mesh) with hexane as eluent afforded unreacted *o*-bromochlorobenzene and elution with a solution of hexane-benzene (9 to 1) gave the desired product. Recrystallization from hexane gave a white solid (21.2 g, 40% yield) m.p. 45–45.5° C (uncorrected). The infrared spectrum (Nujol) had bands at 3413 (NH) 810 (two adjacent hydrogens), and 746 cm<sup>-1</sup> (four adjacent hydrogens). The mass spectrum exhibited a parent ion at *m/e* 271 whose isotope distribution Beynon, 1960) indicated three chlorine atoms.

**Synthesis of I.** A solution of 0.41 g of sodium nitrite in 0.67 ml of water was added dropwise to a mixture of 0.95 g of 3,4-dichloroaniline and 8.5 ml of 3.18*M* hydrochloric acid

at 0° to 7° C. The resultant yellow suspension was added to a chilled solution of 1.07 g of 2,3,4'-trichlorodiphenylamine in 45 ml of glacial acetic acid. The flask containing the undissolved 3,4-dichlorobenzenediazonium chloride was rinsed with 2 ml of glacial acetic acid and the washings were added to the reaction mixture, which became dark red within 2 hr. Upon standing overnight, a small amount of an orange-yellow material precipitated. The reaction mixture was allowed to stand in the dark for 34 days, during which time precipitation continued. The orange material was filtered, washed with water to remove acetic acid, and dried (0.56 g). The filtrate was treated with a saturated solution of sodium bicarbonate, extracted with ethyl acetate, dried, and evaporated to dryness to give 0.89 g of red oil. The solid and the oil were chromatographed separately on neutral alumina (Woelm) using hexane to elute the major impurities (two unidentified red materials) and a hexane-benzene (8 to 2) solution to elute I. The solid gave a total of 0.41 g of I, while 0.24 g was obtained from the oil for a total yield of 38%. The isolated material was chromatographically pure (tlc), melted at 146–7° C (uncorrected), and exhibited mass and infrared spectra identical with material obtained from the photolysis of 3,4-dichloroaniline (Rosen *et al.*, 1970).

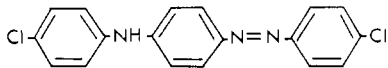
**Soil Experiments.** Twelve mg of I were thoroughly mixed with 24 g of Nixon sandy loam (pH 5.3) and the soil was moistened to 60% of capacity. The treated soil samples (four replicates) were incubated in closed pint Mason jars at room temperature for 60 days. Air was admitted daily and water was added weekly to maintain the moisture level. A control soil and a sample containing 12 mg of 3,4-dichloroaniline were also incubated under the same conditions. At the end of the incubation period each sample containing I was extracted with 200 ml of methanol in a Lourdes overhead mixer, filtered, and reextracted with 250 ml of methanol. The methanol extracts were combined and diluted to 500 ml. A 2-ml aliquot of this solution was diluted to 10 ml with methanol before determining its concentration on a Beckman DB Spectrophotometer at 408 nm ( $\epsilon = 31,000$ ). Extracts of the untreated soil samples treated in an identical manner had no absorption at 408 nm. The soil in which 3,4-dichloroaniline had been incubated was extracted with acetone and 3,3',4,4'-tetrachloroazobenzene was characterized by gas and thin-layer chromatography (Linke *et al.*, 1969).

**Photolysis Experiments.** A methanol solution of I (12 ppm) was exposed to a 450-watt Hanovia lamp for 10 hr through a 1.8-mm borosilicate glass filter. Such a filter effectively stops most of the light transmission below 297 nm (Calvert and Pitts, 1966). A solution of the same concentration was exposed to sunlight through a quartz window for 14 days. After the irradiation periods, the solutions were determined quantitatively by visible spectroscopy and qualitatively (after concentration) by tlc using sulfuric acid as spray reagent.

Department of Agricultural Chemistry, Rutgers, The State University of New Jersey, New Brunswick, N.J. 08903

## RESULTS AND DISCUSSION

The formation of I from 2,3',4'-trichlorodiphenylamine and 3,4-dichlorobenzediazonium chloride proceeded at a much slower rate than the analogous formation of 4-chloro-4'-(4-chloroanilino) azobenzene (II, Rosen *et al.*, 1970). One pos-



II

sible reason for this rate difference may be due to the much lower basicity of I as compared to II. The latter, upon formation in the acetic acid reaction medium, is immediately precipitated as the acetate salt. I is too weak a base to react with acetic acid. Another possible reason for the observed difference in reaction rate can be ascribed to the lowering of electron density by the *m*-chloro group at the point of diazonium ion attack in 2,3',4'-trichlorodiphenylamine. In any event, the slow rate allows several other reactions to compete more successfully against formation of I, thereby decreasing the overall yield of I, as well as creating an isolation problem. Attempts to accelerate the rate of formation of I by heating at 40°C for 1 hr resulted in even poorer yields and more products.

After 2 months incubation of I in soil, 104, 96, 94, and 92% of the starting material was recovered, indicating that I, under the conditions of the experiment, was stable. The observed formation of 3,3',4,4'-tetrachlorazobenzene from 3,4-dichloroaniline (Bartha and Pramer, 1967) served as a check on the biological activity of the soil used in these experiments.

Methanolic solutions of I exposed to sunlight for 2 weeks

and to light of wavelength greater than 297 nm for 10 hr remained unchanged. These results are a good indication that I is stable in sunlight, although sensitized or induced photochemical reactions are not ruled out by this experiment. It deserves mention that a sample of I, slightly contaminated with the two unidentified red coproducts, lost approximately half of its absorbance at 408 nm when exposed to sunlight for 15 min in acetone (but not methanol) solution. Upon standing in the dark overnight, the original intensity returned. This apparent *trans-cis* isomerization did not occur after the sample was purified.

## CONCLUSIONS

The synthesis of I as described above confirms the structure assigned previously (Rosen *et al.*, 1970). Preliminary results indicate that the material is stable towards two important environmental degradation processes—microbiological activity and direct photolysis.

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