# Synthesis of Substituted Mono- and Diazidobenzenes

PAUL A. GRIECO and J. PHILIP MASON
Department of Chemistry, Boston University, Boston, Mass. 02215

**The syntheses of pentachloroazidobenzene, 5-chloro-2,4-diazidonitrobenzene, *o*-azidonitrobenzene, and *p*-azidonitrobenzene have been accomplished by the reaction of sodium azide in dimethyl sulfoxide at room temperature with pentachloronitrobenzene, 2,4,5-trichloronitrobenzene, o-dinitrobenzene, and *p*-dinitrobenzene, respectively. *p*-Chloronitrobenzene, 2,4,6-trichloronitrobenzene, and 1,3,5-trinitrobenzene reacted with sodium azide at elevated temperatures in dimethyl sulfoxide to give *p*-aziodnitrobenzene, 4-chloro-2,6-diazidonitrobenzene, and 1-azido-3,5-dinitrobenzene, respectively. 1-Chloronitrobenzene afforded, at elevated temperatures, benzofurazan *N*-oxide. Some 1-benzotriazole derivatives have been prepared from the azides.**

RECENT work in the authors' laboratories has led to the direct syntheses of 3-azidophthalic acid and tetra-azidophthalic acid by the displacement of a nitro group from 3-nitrophthalic anhydride and four chlorines from tetrachlorophthalic anhydride with sodium azide in aprotic media (*5*). The synthesis of some previously known and some new substituted azidobenzenes by the displacement of chlorine and nitro groups from a benzene ring has now been achieved under similar conditions in dimethyl sulfoxide (DMSO).

## EXPERIMENTAL

Extreme caution should be taken when working with the azides described in this paper. The compounds should not be heated above their melting points. All of the azides prepared are unstable to light and decompose slowly. Infrared spectra were taken in Nujol on a Perkin-Elmer Model 237 spectrophotometer. Analyses were performed by the Scandinavian Microanalytical Laboratories, Herlev, Denmark, and by the Spang Microanalytical Laboratory, Ann Arbor, Mich. Melting points were determined using a Thomas-Hoover capillary melting point apparatus and are uncorrected.

**Method.** The general method of preparing these azides can be illustrated by the reaction of *p*-dinitrobenzene with sodium azide. To 1.68 grams (0.01 mole) of *p*-dinitrobenzene in 30 ml. of dimethyl sulfoxide, 0.65 gram (0.01 mole) of sodium azide was added. After stirring the mixture for 2 hours, during which time the mixture became homogeneous, 200 ml. of ice water were added to precipitate the *p*-azidonitrobenzene. Stirring was continued until the precipitate appeared to have an adequate particle size to be filterable, usually about 30 minutes. The dried product was recrystallized by dissolving it in absolute ethanol and adding water gradually; yield 1.5 grams, 91%, m.p: 74° C. Identification in this case was made by a comparison of the melting point and infrared spectrum with those of a known sample of *p*-azidonitrobenzene prepared by the procedure described by Smith and Boyer (*9*) for the ortho isomer. Variations in this procedure for the azides prepared are given in Table I.

**Identification of Pentachloroazidobenzene.** Even though the analysis was unsatisfactory, the compound is believed to be pentachloroazidobenzene, since the infrared spectrum showed a strong band at 2140 cm.$^{-1}$, and there were no bands to indicate the presence of a nitro group. The compound was reduced to form pentachloroaniline. To a suspension of lithium aluminum hydride (0.03 gram, 0.75 mmole) in 20 ml. of ether, 0.2 gram (0.70 mmole) of pentachloroazidobenzene in 20 ml. of ether was added and the mixture refluxed for 0.75 hour. The excess lithium aluminum hydride was decomposed with water, the ether layer dried over anhydrous magnesium sulfate, and the ether evaporated. The resulting solid, pentachloroaniline (*1*), when dried, melted at 232° C. The infrared spectrum showed two bands at 3380 and 3470 cm.$^{-1}$, while the azide band at 2140 cm.$^{-1}$ had disappeared.

**Identification of 4-Chloro-2,6-diazidonitrobenzene.** The C,H,N analysis and the infrared spectrum were consistent with either 4-chloro-2,6-diazidonitrobenzene or 6-chloro-2,4-diazidonitrobenzene. Since the nuclear magnetic resonance

Table I. Variations in Procedure for Preparation of Azides

| Substituted Benzene | $NaN_3$, G. | Mole Ratio[a] | DMSO, Ml. | Reaction Temp., ° C. | Time, Hr. | Product | M.P., ° C. | Yield, % |
|---|---|---|---|---|---|---|---|---|
| *p*-Dinitro- | 0.65 | 1 to 1 | 30 | [b] | 2 | *p*-Nitroazidobenzene[c] (*6*) | 74 | 91 |
| *p*-Nitrochloro | 1.30 | 1 to 1 | 60 | 85–90 | 7 | *p*-Nitroazidobenzene[c] | 74 | 75 |
| *o*-Dinitro- | 1.30 | 2 to 1 | 30 | [b] | 1.5 | *o*-Nitroazidobenzene[c] (*9*) | 51–2 | 87 |
| *o*-Nitrochloro- | 0.65 | 1 to 1 | 30[d] | 100 | 1 | Benzofurazan-*N*-oxide[c] (*9*) | 70–2 | 29[e] |
| 1,3,5-Trinitro- | 5.20 | 2 to 1 | 100 | Steam bath | 1 | 3,5-Dinitroazidobenzene[f] | 85–6 | 88[e] |
| Pentachloronitro- | 0.65 | 2 to 1 | 30 | [b] | 1.25 | Pentachloroazidobenzene[g] | 80 | . . |
| 2,4,6-Trichloronitro- | 0.97 | 3 to 1 | 30 | 80–90 | 1 | 4-Chloro-2,6-diazidonitrobenzene[h] | 116–8 | 71[e] |
| 2,4,5-Trichloronitro- | 2.60 | 2 to 1 | 60 | [b] | 8 | 5-Chloro-2,4-diazidonitrobenzene[c,i] | 97 | 54 |
| 1,4-Dichloro-2,6-dinitro- | 1.30 | 4 to 1 | 30 | 85 | 1 | 4-Chloro-2,6-dinitroazidobenzene (*2*) | 84–5 | 94[e] |

[a] Ratio of $NaN_3$ to reactant. [b] The reactants were mixed at room temperature. The exothermic reaction raised the temperature to 30° to 40° C., but neither external heating nor external cooling was used. [c] Recrystallized by dissolving in absolute ethanol at room temperature and adding water. [d] DMF instead of DMSO. [e] Before recrystallizing. [f] Recrystallized from chloroform by the addition of petroleum ether; Anal. Calcd. for $C_6H_3N_5O_4$: C, 34.46; H, 1.43; N, 33.50. Found: C, 34.47; H, 1.43; N, 33.40. [g] Anal. Calcd. for $C_6Cl_5N_3$: C, 24.73; Cl, 60.85; N, 14.43. Found: C, 24.49; Cl, 58.97; N, 16.26. [h] Recrystallized from absolute ethanol-water and then from benzene-cyclohexane. Anal. Calcd. for $C_6H_2ClN_7O_2$: C, 30.08; H, 0.84; N, 40.93. Found: C, 30.17; H, 1.05; N, 41.62. Anal. Calcd. for $C_6H_2ClN_7O_2$: C, 30.08; H, 0.84; Cl, 14.80; N, 40.93. Found: C, 29.99; H, 1.00; Cl, 14.90; N, 41.12.

spectrum showed only one proton signal, the compound was considered to be 4-chloro-2,6-diazidonitrobenzene.

**Identification of 5-Chloro-2,4-diazidonitrobenzene.** To determine the location of the azide group, this compound (0.3 gram) was dissolved in 35 ml. of 2-methoxyethanol, and cooled to 0°C. A solution of 6 grams of arsenic trioxide (*11*) and 16 grams of potassium hydroxide in 15 ml. of a 50% aqueous solution of 2-methoxyethanol was added dropwise with stirring. The reaction mixture was then quenched in ice water. The crystals which formed melted at 189–90° C. The infrared spectrum indicated the presence of amine and nitro groups, and the melting point was the same as that found by Morgan and Wooton (*7*) for 5-chloro-2,4-diaminonitrobenzene.

In the reaction of 2,4,6-trichloronitrobenzene with azide ion in DMSO, the two chlorines ortho to the nitro group are replaced, while in the reaction with pentachloronitrobenzene, which also has two chlorines ortho to a nitro group, the nitro group is replaced with an azide group. The first reaction is similar to the reaction of 2,4,6-trichloronitrobenzene with methoxide ion to form 2-methoxy-4,6-dichloronitrobenzene (*4*). This type of reaction is explained by Hammond and Hawthorne (*3*) by assuming that the nitro group, originally in a noncoplanar conformation, may sandwich itself between the chlorine and the azide group in the transition state, thereby assuming an essentially coplanar conformation, and causing an increase in the resonance energy. In the case of pentachloronitrobenzene, apparently the combined inductive effects of the five chlorines is the dominant factor in causing the nitro group to be displaced by the azide ion.

**Reactions of o- and p-Azidonitrobenzenes , 3, 5-Dinitroazidobenzene, and 5-Chloro-2,4-diazidonitrobenzene with Benzyne.** The reactions with the first three of these compounds were carried out by refluxing a mixture of 0.05 mole of the azide and 6 grams (0.058 mole) of *n*-butyl nitrite in 200 ml of dichloromethane, and adding dropwise a solution of 7 grams (0.051 mole) of anthranilic acid in 60 ml. of acetone. The reaction mixture was evaporated to about one fourth of the original volume and this mixture was chromatographed through a column of alumina. The column was eluted with dichloromethane, the eluates evaporated to dryness, and the resulting residues recrystallized.

The 1-(4-nitrophenyl)-benzotriazole (*8*) was recrystallized from DMSO and melted at 239°C. The 1-(2-nitrophenyl)-benzotriazole (*10*) was recrystallized from benzene-cyclohexane and melted at 117–18° C. The 1-(3,5-dinitrophenyl)-benzotriazole was recrystallized from chloroform petroleum ether and melted at 169–9.5° C.

Anal. Calcd. for $C_{12}H_7N_5O_4$: C, 50.53; H, 2.46; N, 24.56. Found: C, 50.66; H, 2.58; N, 24.45.

In the reaction with 5-chloro-2,4-diazidonitrobenzene, 1.2 grams (0.005 mole) of this compound and 1.2 grams (0.012 mole) of *n*-butyl nitrite were dissolved in 50 ml. of dichloromethane at room temperature. A solution of 1.4 grams (0.01 mole) of anthranilic acid in 15 ml. of acetone was added dropwise over a period of 30 minutes. Evaporation of the solvents left a thick black oil, which was chromatographed on alumina. Elution with dichloromethane gave an oil which was crystallized from absolute ethanol; yield, 0.73 gram. After several recrystallizations from chloroform–petroleum ether, an analytical sample was obtained, m.p. 195–6° C. Anal. Calcd. for $C_{12}H_6ClN_7O_2$: C, 45.64; H, 1.90; N, 31.06. Found: C, 45.69; H, 2.07; N, 31.16. The infrared spectrum of the product in methylene chloride showed absorption bands at 2120 ($N_3$), 1580 (N=N), 1545 and 1340 cm.$^{-1}$ ($NO_2$). The product was identified as either 1-(5-azido-2-chloro-4-nitrophenyl)-benzotriazole or 1-(5-azido-4-chloro-2-nitrophenyl)-benzotriazole.

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# 3,3′-Keto Biscoumarins

L. L. WOODS and MIKE FOOLADI
Texas Southern University, Houston, Tex. 77004

**The Knoevenagel synthesis of 3,3′-keto biscoumarins has been expanded and several new related compounds have been produced. The properties of the compounds have been examined; the spectral characteristics, including fluorescence, have been determined and the 2,4-dinitrophenyl hydrazone derivatives prepared.**

SOME YEARS AGO Knoevenagel and Langensiepen (*2*) were able to synthesize 3,3′-keto biscoumarin, designated by them as di[coumarinyl-(3)]ketone. An examination of their publication showed this to be the only compound of its nature produced by them and a search of the literature failed to reveal the existence of any other generically related compounds. The compounds described in this report were all prepared by essentially the same conditions as those employed by Langensiepen.

When the reaction was tried with 2,4,6-trihydroxybenzaldehyde, *o*-vanillin, gentisaldehyde, and 3,5-dibromosalicylaldehyde, water-imbibing compounds were obtained