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REACTION OF BENZOFURAN WITH IODINE AZIDE: FORMATION OF *cis*- AND *trans*-2,3-DIAZIDO-2,3-DIHYDROBENZOFURANS

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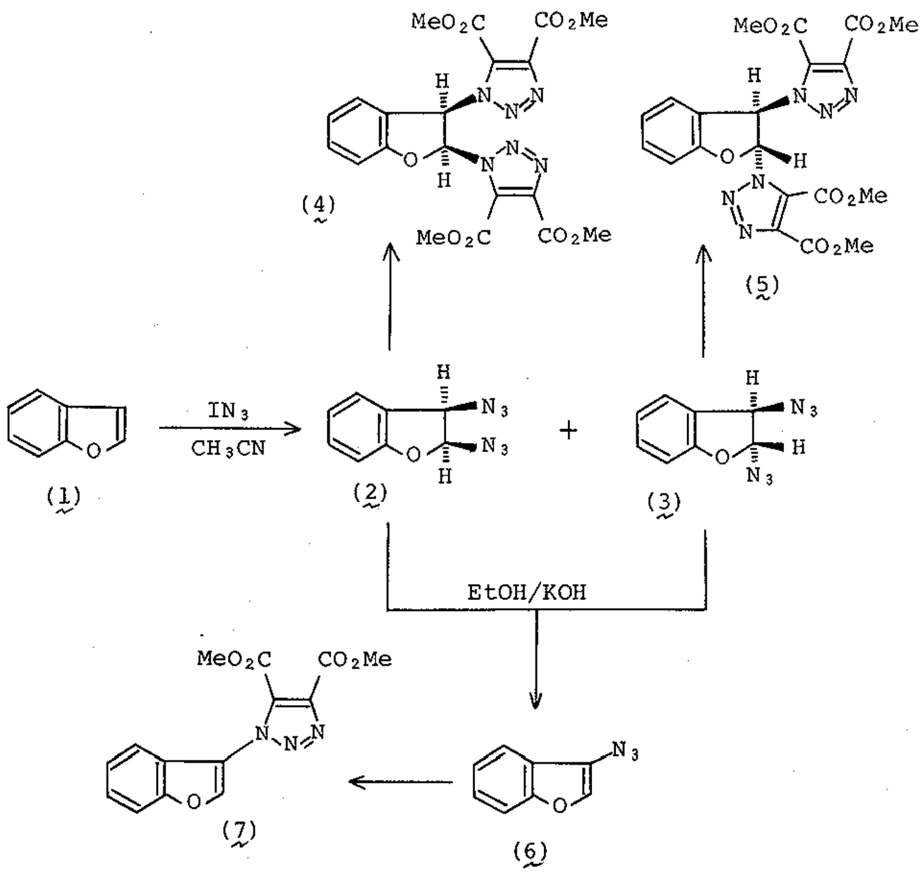
Benzofuran reacted with IN_3 to give in good yields *cis*- and *trans*-2,3-diazido-2,3-dihydrobenzofurans, both of which were readily converted to 3-azidobenzofuran.

Iodine azide (IN_3) is well known as an efficient reagent for introduction of azide function to olefins.[1] Recently we have reported that the reaction of some indoles with IN_3 provides a simple method for preparation of various indole derivatives containing azide function.[2,3] We describe here that benzofuran also reacted with IN_3 to give in good yields *cis*- and *trans*-2,3-diazido-2,3-dihydrobenzofurans (**2**) and (**3**), both of which were readily converted to 3-azidobenzofuran (**6**).

Treatment of benzofuran (25 mmole) with IN_3 [prepared *in situ* from iodine monochloride (50 mmole) and sodium azide (56 mmole)] in dry acetonitrile at 0° for 1 hr and then at room

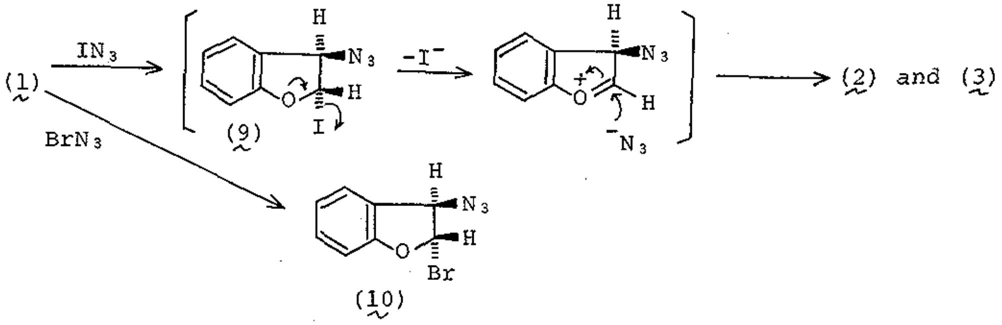


temperature overnight gave 93% yield of a mixture of (2) and (3) in a ratio of 42:58 (by nmr spectroscopy). The mixture was separated by preparative tlc to give pure cis- (2) [31% yield, an oil, ir ν_{max} 2100 cm^{-1} (N_3); nmr δ ($CDCl_3$) 5.83 (1H, d, H-2), 4.87 (1H, d, H-3)] and trans-isomers (3) [43% yield, an oil, ir ν_{max} 2100 cm^{-1} (N_3); nmr δ ($CDCl_3$) 5.76 (1H, d, H-2), 4.61 (1H, d, H-3)]. The structures of the adducts were assigned on the basis of their spectral and chemical data. Refluxing (2) and

(3) with dimethyl acetylenedicarboxylate in toluene for 6 hr gave the corresponding 1:2 cycloadducts (4), mp 172-174°,[4] and (5), mp 67-69°, in 50 and 18% yields, respectively.

The stereochemistry of (2) and (3) was defined by a comparison of the spin-coupling pattern between H-2 and H-3 [$J_{2,3}$=7 Hz for (2) and $J_{2,3}$=1.5 Hz for (3)[5]] as well as their behavior toward alkali. Treatment of (2) and (3) with 15% ethanolic KOH gave oily 3-azidobenzofuran (6)[6] [ir ν_{max} (CHCl$_3$) 2100 cm^{-1} (N$_3$); nmr δ (CDCl$_3$) 7.50 (1H, s, H-2)] in 83 and 87% yields, respectively, but the reaction proceeded appreciably faster with the *cis*-isomer (2) than with the *trans*-isomer (3). Thus, after 1 hr at room temperature (2) was completely converted to (6), whereas (3) was converted to (6) only after ca. 24 hr at room temperature. When compound (6) was refluxed with dimethyl acetylenedicarboxylate in toluene for 1 hr, crystalline adduct (7), mp 123-124°, was obtained in 21% yield.

The behavior of benzofuran toward IN$_3$ closely resembles that of 1-acylindoles,[2] and the formation of (2) and (3) may be rationalized by the assumption that the initially formed 1:1



adduct (9) undergoes the carbon-iodine bond cleavage followed by attack of azide anion to lead to the observed products. Attempts to detect (9) have thus far proved unsuccessful,[8] but the closely related trans-3-azido-2-bromo-2,3-dihydrobenzofuran (10) has been isolated from the reaction of benzofuran with bromine azide.[9]

REFERENCES AND FOOTNOTES

1. A. Hassner, Accounts Chem. Res., 1971, **4**, 9.
2. Y. Tamura, S. Kwon, F. Tabusa, and M. Ikeda, Tetrahedron Letters, 1975, 3291.
3. M. Ikeda, F. Tabusa, N. Nishimura, S. Kwon, and Y. Tamura, Tetrahedron Letters, 1976, 2347.
4. All new crystalline compounds gave satisfactory elemental and spectroscopic analyses.
5. T.J. Batterham, "NMR Spectra of Simple Heterocyclies", John Wiley & Sons, Inc., New York, 1973, p. 375.
6. Hassner and Fowler[7] have demonstrated that cis-β-protons in vinyl azides are slightly shielded by the azide group. The fact that the H-2 and H-3 signals of benzofuran (in $CDCl_3$) appear at δ 7.54 and 6.86, respectively, precludes the possibility of 2-azidobenzofuran from consideration.
7. A. Hassner and F.W. Fowler, J. Org. Chem., 1968, **33**, 2686.
8. For example, the reaction of equimolar quantities of (1) and IN_3 resulted in the formation of a mixture of the diazides (2) and (3), and unreacted starting material.
9. T. Okuyama, K. Kunugiza, and T. Fueno, Bull. Chem. Soc. Jap., 1974, **47**, 1267.

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