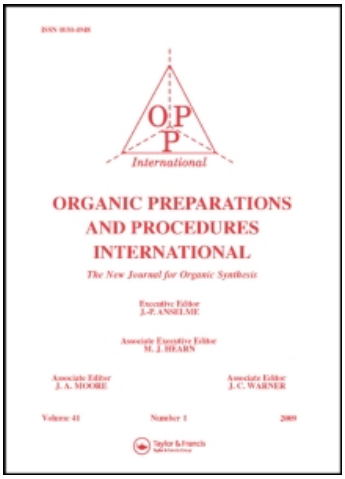

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[2-CARBOXY-2'-CHLORO-4,4', 5.5'-TETRA(BENZYLOXY)] AZOBENZENE FROM THE BENZYNE DECOMPOSITION OF 2-CARBOXY-4, 5-DIBENZYLOXYBENZENEDIAZONIUM CHLORIDE

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stirring and then the excess bromine[3] was removed by distillation until a temperature of 100° was reached. The aqueous slurry was filtered by suction and the solid collected was washed twice with water and dried at 110° to give 120.1 g (96%) of 4-bromomethyl-2,3,5,6-tetrabromophenol, mp. 181-182°, lit.[2,4] 183-184°, 182°.

^{1}H NMR: δ 4.75 (s, 2H, CH_2), 6.25 (s, 1H, OH).

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[2-CARBOXY-2'-CHLORO-4,4',5,5'-TETRA(BENZYLOXY)]AZOBENZENE FROM THE BENZYNE DECOMPOSITION OF 2-CARBOXY-4,5-DIBENZYLOXYBENZENEDIAZONIUM CHLORIDE†

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(04/07/86)

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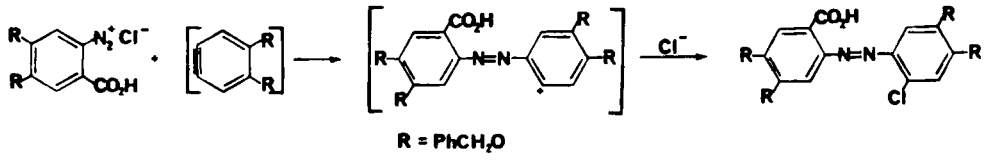
Of the many by-products reported from reactions involving benzynes generated from anthranilic acids via o-carboxybenzenediazonium salts, few

have retained both nitrogen atoms from the diazonium group.[1] The expected Diels-Alder adducts[2,3] from 4,5-dibenzyloxybenzyne (2) and 1-alkyl-2-pyridones[2] were accompanied by a bright orange solid (4), which is also formed when 2-carboxy-4,5-dibenzyloxybenzenediazonium chloride (1) is refluxed in tetrahydrofuran without 2-pyridones. The structure of 4 was elucidated by NMR (see Experimental Section). The low yield notwithstanding, this reaction provides a convenient route to this azo compound which might otherwise be difficult to obtain.

A plausible pathway to 4 involves the decomposition of 1 to the corresponding benzyne (2), followed by addition of 1 to 2 to generate initially 3, which leads to 4.



1 2 3 4

EXPERIMENTAL SECTION

^{1}H and ^{13}C NMR spectra were determined in $CDCl_3$ on a Nicolet NIC-360 spectrometer operating at 360 and 90.8 MHz for ^{1}H and ^{13}C, respectively. For the NOE experiments, subsaturating irradiation power was used to achieve frequency selectivity. Larger NOE (up to 20%) are obtained with higher powers. The COSY spectrum was obtained on a Varian XL-400 spectrometer at 400 MHz.

[2-Carboxy-2'-chloro-4,4',5,5'-tetra(benzyloxy)]azobenzene (4).- A mixture of 2-carboxy-4,5-dibenzyloxybenzenediazonium chloride[2] (1.62 g, 4.1 mmol), propylene oxide (1.0 mL, 15 mmol) in 1,2-dichloroethane (20 mL) was refluxed for 3 hrs. The reaction mixture was evaporated to dryness in vacuo, and flash chromatographed on silica gel.[2] Elution with chloroform provided fluffy (and highly electrostatic) orange crystals of 4 (0.14 g,

5%), which were recrystallized from chloroform, mp. 238-239°.

Anal. Calcd for $C_{41}H_{33}ClN_2O_6$: C, 71.87; H, 4.85; N, 4.09; Cl, 5.17

Found: C, 71.71; H, 4.75; N, 4.24; Cl, 5.35

The solid is insoluble in aqueous base, but dissolves in dilute aqueous alcoholic sodium hydroxide. IR (Nujol): 1733 (C=O), 1590 (N=N) cm^{-1}; ^{13}C NMR: δ 166.24 ($\underline{C}O_2H$), 135.78, 135.75, 135.64, 135.40 (*i*-C's of 4 Ph's), 128.64, 128.38, 128.19, 127.38, 127.18 (12 overlapping signals, *o*-, *m*-, *p*-C's of 4 Ph's), 71.28, 71.00, 70.95, 70.90 (4 $\underline{C}H_2O$), 153.72, 152.64, 152.27, 148.28, 144.92, 140.77, 131.84, 120.74, 115.13, 114.84, 101.35, 100.30 (12 remaining aromatic C's); MS (70 eV): m/e (rel intensity) 648 (M^+, 0.6), 258 (1), 181 (2), 105 (1), 91 (100), 83 (2), 77 (1), 73 (1), 65 (12), 44 (12). The ^1H NMR spectrum of 4 exhibited four singlets (2H, each) at 5.10, 5.27, 5.30, 5.32 ppm which are attributed to the methylene protons of four benzyloxy groups. In addition to a complex multiplet at 7.22-7.53 (20 H), there are four singlets (1H, each) at 7.09, 7.11, 7.63, 7.91 ppm which indicate the presence of two pairs of para-hydrogens in two different tetrasubstituted benzene rings. Each of these four protons was shown to be ortho to one benzyloxy group by NOE difference spectroscopy. Irradiation of each of the signals at 5.19, 5.27, 5.30, and 5.32 ppm enhanced just one of the singlets at 7.09, 7.11, 7.63 and 7.91 ppm, in this order, by 13-15%. Furthermore, long-range coupling (through 5 bonds)[4] between each of these hydrogens and the benzyloxy methylene groups could be detected by two-dimensional homonuclear shift correlated spectroscopy (COSY),[5] which further substantiates the orientations of these groups.

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THREE NEW PRODUCTS FROM METHYL 3,4-DIPHENYL-5-NITRO-2-FUROATE BY CATALYTIC REDUCTION

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All biological effects of 5-nitrofurans[1,2] seem to require the reduction of the 5-nitro group to a metabolically reactive intermediate.[3] In the case of the carcinogenic 5-nitrofurylthiazoles, the postulated reduction products 5-nitroso and 5-hydroxylamino derivatives have not been conclusively identified since authentic samples have not yet been synthesized, partly because of the extreme lability of these intermediates. Even the 2-aminofurans are generally unstable and undergo fission of the