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HETEROTRIPTYCENES FROM A FIVE-MEMBERED HETEROCYCLIC DIAZONIUM CARBOXYLATE

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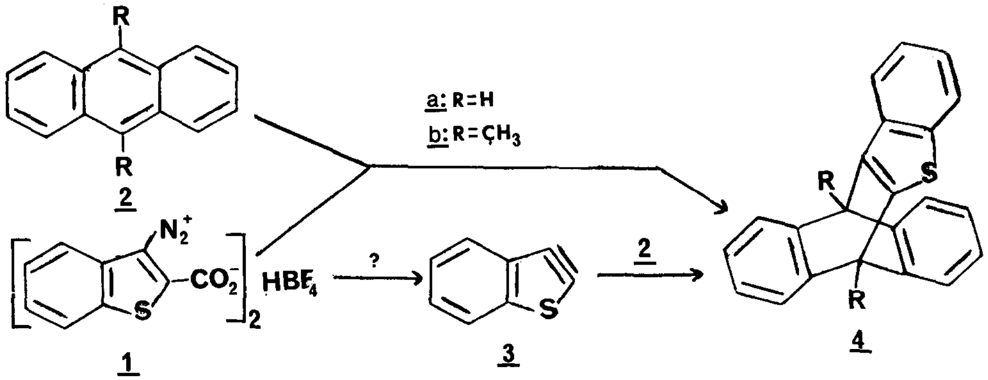
Summary: Heterotriptycenes (4) are formed when the benzo[b]thiophene diazonium carboxylate (1) is decomposed in the presence of anthracenes (2).

The thermolysis of arenediazonium carboxylates and their salts constitutes one of the most efficient methods of generating benzynes[1] and six-membered hetarynes[2]. Previous attempts[3-6] to employ this method for the generation of five-membered hetarynes failed, however, leading to extensive decomposition and low yields of arylation[4,6], nitration,[4,5,6] and diazo-coupling products.[3,6]

In support of the existence of a five-membered hetaryne, 2,3-didehydrothiophene[7], this communication describes the actual isolation of heterotriptycenes (4), the primary Diels-Alder adducts of a five-membered hetaryne (3) and anthracenes (2), from a potential hetaryne precursor, the diazonium carboxylate (1).



The diazonium carboxylate ·1/2HBF$_4$ salt (1), m.p. 148-150° dec., was prepared in 68% yield from 3-amino benzo[b] thiophene-2-carboxylic acid[8] by diazotization with isoamyl nitrite in HCl-dioxane followed by treatment of the resulting diazonium chloride with fluoroboric acid. Although satisfactory elemental analysis could not be obtained for (1), the data for C, H, S and N averaged closer to the formula of the half (± 0.7%) rather than the full salt (± 1.9%). This formulation is supported by analogy to the benzene series[9] and the infrared spectrum of (1) [3440(OH), 2210(N_2^+), 1705(C=O), 1655(COO$^-$), 1055Cm^{-1}BF$_4$)] .

A slurry of (1) in chlorobenzene was slowly added to a solution of two equivalents of anthracene (2a) or (2b) in chlorobenzene at 100°-110°C. After an additional hour of heating, the reaction mixture was separated by TLC to give, among several products, the heterotriptycenes (4a)[20%, m.p. 218-220°] and (4b) [52%, m.p. 244-245°], respectively, identified by their analytical[10] and spectra data. Compound (4a): ^{1}H NMR($CDCl_3$TMS, internal standard) δ6.80-7.85(12H) δ5.50(1H), δ5.70(1H); Mass spectrum (M/e, relative intensity), 310(M^+,92%), 309(M^+-R,100), 308(M^+-2R,48), U.V.-longest λ max at 306nm, Compound (4b); ^{1}H NMR δ6.60-7.85(12H), δ2.34(3H), δ2.68(3H), Mass spectrum, 338(M^+, 60%), 323(M^+-R, 100), 308(M^+-2R,93), U.V. - longest λ max at 307nm. Particularly significant are the characteristic[11,12] nmr absorptions of the nonequivalent bridgehead substituents, the prominent M,M-R, and M-2R ions in the mass spectra,[11-13] and the expected[14] absence of an anthracene - like chromophore in the ultraviolet spectra.

This isolation of the heterotriptycenes (4) not only provides the desired supporting evidence for the existence of the five-membered hetaryne intermediate (3), but also represents a more efficient synthesis of these interesting molecules,[12,14] and the first from potential precursors of five[5]-or six-membered[18] hetarynes or five-membered carbocyclic arynes.[15] Although the most straightforward rationale for the formation of the heterotriptycene (4) would be a Diel-Alder cycloaddition of the anthracenes (2) to the aryne, 2,3-didehydrobenzo [b] thiophene (3) other mechanisms are possible.[16-18] With the availability of this procedure, it should now be possible to apply the competition method[19] to determine if a truly "free" aryne (3) is involved.

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