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PREFERENTIAL DECARBOXYLATION OF DIAZONIUM CARBOXYLATES IN THE THIOPHENE SERIES. THE FIRST CONCLUSIVE EVIDENCE FOR THE COUPLING OF UNSUBSTITUTED THIOPHENEDIAZONIUM SALTS WITH β-NAPHTHOL

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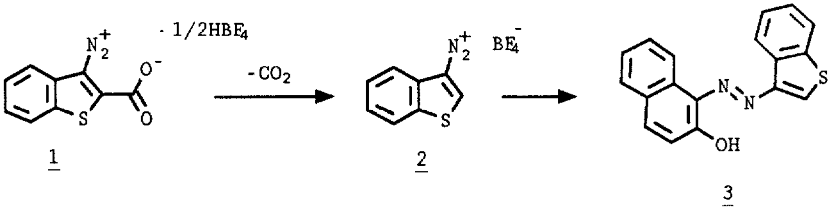
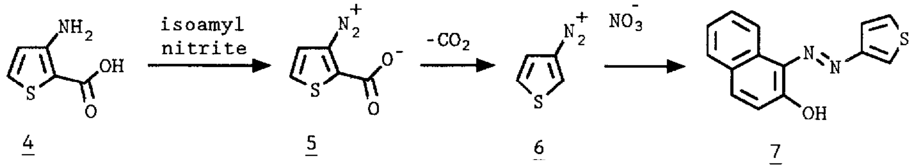
Summary: Preferential decarboxylation has been clearly established with the diazonium carboxylate 1, and evidence has been provided for the preliminary loss of CO_2 from the diazonium carboxylate 5. The resulting unsubstituted diazonium salts have been successfully coupled with β-naphthol.

It has been generally accepted[1-3] that the preliminary loss of CO_2 does not occur, during the decomposition of arenediazonium carboxylates to arynes, and other reactive intermediates. Although this possibility has been suggested on several occasions,[4-6] the wealth of existing evidence, in fact, strongly supports the loss of N_2, as being the first step in the decomposition process.[1-2]

This communication reports the isolation and coupling reaction of the diazonium salt 2 , which resulted from the preferential loss of CO_2 from the diazonium carboxylate[7] 1 ; and the isolation and coupling reaction of the diazonium salt 6, which presumably[8] resulted from the loss of CO_2 from the diazonium carboxylate intermediate 5. Although the diazonium salt 6 was first isolated in 1968, its structure was erroneously assigned[9-11] as the diazonium carboxylate 5. Unfortunately, no further studies, of this compound, have been reported, and the erroneous structure 5 has appeared in several extensive reviews.[2,3,12,13]





In view of earlier experiments,[2,3,10-13] conducted with the notion of decomposing the so-called diazonium carboxylate 5 as an aryne precursor, the findings presented, herein, have important implications. Specifically, such experiments, inadvertently, led to fallacious interpretations of results. Other reactions, such as the self-coupling of 2-carboxythiophene-3-diazonium chloride[14], which is accompanied by an unusual[15] decarboxylation, can now be readily explained.

Both diazonium salts 2 and 6 have been successfully coupled with β-naphthol, and represent the first conclusive evidence for such coupling reactions. The only claim for the coupling, of an unsubstituted thiophene diazonium salt, with β-naphthol,[16,17] was later refuted.[18] Recently, Porter[17] pointed out, that since no further work supports the initial claim, it must be regarded as suspect. The only example of an attempt to couple an unsubstituted benzo[b]thiophene diazonium salt (a 2-diazoniumbenzo[b]thiophene salt) with β-naphthol, failed.[19] It is especially noteworthy that both 2 and 6 also represent the first examples, of unsubstituted thiophene rings, bearing the diazonium moiety in the 3-position.

The diazonium salt 2 (50% yield) was isolated as a dark brown solid (dec. 190-193°), when the diazonium carboxylate 1/2HBF_4 salt 1[7,20,21] was decomposed in chlorobenzene at 100-110°. This salt was then coupled at 0-5° with β-naphthol in the presence of base (10% NaOH) to give an 85% yield of the desired product 3 (deep red solid). The diazonium salt 6, as previously described,[10-13] was isolated as a grey solid (exploded approx.115°) from the aprotic diazotization of 3-aminothiophene-2-carboxylic acid 4. Subsequent coupling of this salt with β-naphthol, in 10% NaOH, provided a 62% yield of the azo product 7 (reddish orange solid). Both azo products 3 and 7 were separated from the reaction mixtures by TLC, and recrystallized from either pet ether/ethyl ether (for 3) or MeOH/ water (for 7). The diazonium salts 2 and 6 were characterized by their infrared spectra, which were completely devoid of carbonyl absorption bands, and the positive identification of the corresponding coupled products 3 and 7, respectively. Diazonium salt 2 showed a strong diazonium absorption band at 2200 cm^{-1}, and a strong fluoroborate absorption at 1060 cm^{-1}; while diazonium salt 6 showed strong absorption bands at 2275 and 1385 cm^{-1} (NO_3^-)[22].

Spectra properties (UV,IR,^{1}H-NMR, and MS) were entirely consistent with the assigned structures for 3 and 7. Accurate mass measurements for both compounds were in excellent agreement with calculated values. Spectra data-Compound 3: UV(EtOH) λmax at 461, 433nm(sh); IR(KBr): 3400(broad), 3050,1610, 1590,1500-1380 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS, internal standard) δ 8.67-8.69 (d, 1H, J=8.4 Hz), 8.46-8.48 (d, 1H, J=8.0 Hz), 7.97-7.07 (m,10H); MS: m/z(rel.intensity) 306(6.9),305(21.1),304(100),276(5.8),275(13.6),271(13.4), 156(14.2),149(10.9),148(14.4),143(44.6),133(42.8),128(21.5),121(15),115(38.5) 114(11.7),89(30.2),77(10.8),63(10.5),45(12.4),28(12.6); calc for $C_{18}H_{12}N_2OS$: 304.067033; meas:304.067035. Compound 7: UV(EtOH) λmax at 445(sh), 410nm. IR (KBr): 3440 (broad),3100,1610,1590, 1460-1340 cm^{-1}; ^{1}H-NMR (400 MHz,$CDCl_3$, TMS,internal standard) δ 8.65-8.67 (d, 1H, J=8.4 Hz), 7.80-7.05(m,9H); MS:m/z (rel.intensity) 256(5.7),255(16.7),254(100),143(80.5),128(16.0),115(52.5),114 (10.7),111(24.6),101(11.0),83(31.8),45(13.2),39(26.3). calc for $C_{14}H_{10}N_2OS$: 254.051383; meas: 254.051385.

Presently, these unprecedented reactions (the preferential loss of CO_2 from diazonium carboxylates) are being viewed as the results of the unusual stability of the diazonium function, due to resonance provided by the S atom, and the reluctancy of the thiophene system to form five-membered hetarynes.

Efforts to determine if these reactions are characteristic of other five-membered ring systems, are now underway.

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