CHEMISTRY LETTERS, pp. 1149-1152, 1977. Published by the Chemical Society of Japan

THE DIELS-ALDER REACTION OF 2,4-DIPHENYLTHIOPHENE AND 2,5-DIPHENYL-1,4-DITHIIN WITH DIMETHYL ACETYLENEDICARBOXYLATE. NOVEL FORMATIONS OF THE NAPHTHO[2,1-b] AND [1,2-b]THIOPHENES

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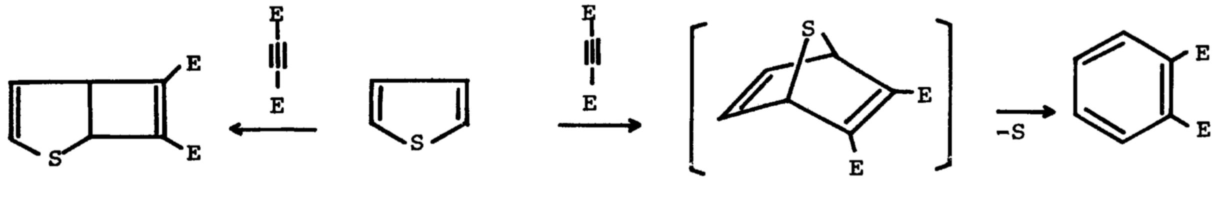
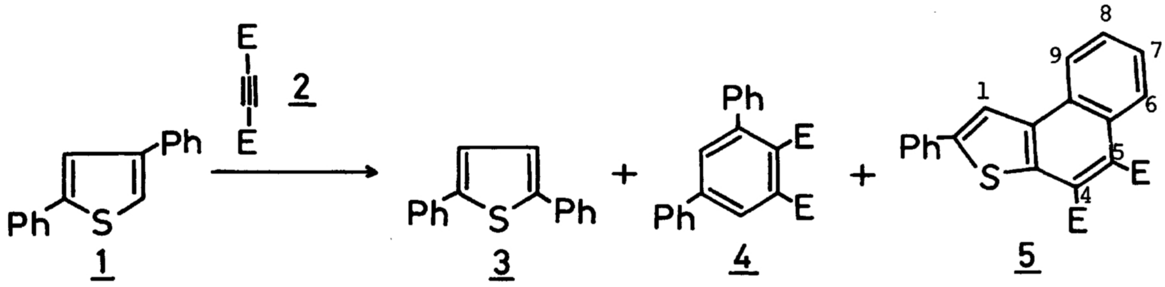
The naphtho[2,1-b]thiophene 5 was obtained by the reactions of dimethyl acetylenedicarboxylate (2) with 2,4-diphenylthiophene (1) and with 2,5-diphenyl-1,4-dithiin (6) as well, whereas the reaction of 6 with 2 under the mild conditions yielded the naphtho[1,2-b]thiophene 8.

In spite of the higher "resonance stabilization" as compared to other hetero five-membered dienes, thiophene derivatives can react with acetylenic dienophiles to give the 1,4-cycloadducts which eliminate sulfur spontaneously and produce substituted benzene derivatives.1) The thermal [2+2]-cycloaddition leading to 2-thiabicyclo[3.2.0]hepta-3,6-diene system has also been observed.2) In this communication we wish to report another new type of the Diels-Alder reaction of a thiophene derivative as well as the novel selective formation of the isomeric naphthothiophenes.



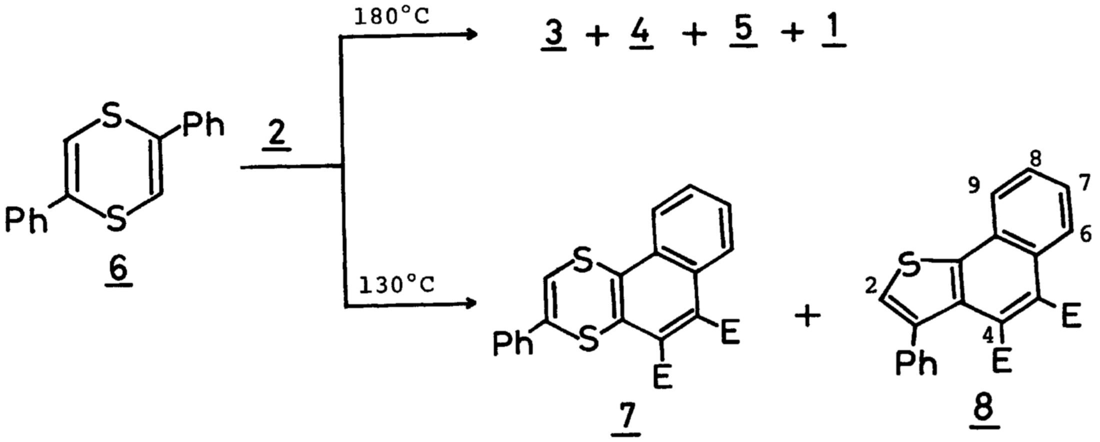
A mixture of 2,4-diphenylthiophene (1) and an excess of dimethyl acetylenedicarboxylate (2) was refluxed in o-dichlorobenzene for 10 hr. Column chromatography on silica gel gave 2,5-diphenylthiophene (3), the phthalate 4, and dimethyl 2-phenylnaphtho[2,1-b]thiophene-4,5-dicarboxylate (5) in 27, 12, and 6 % yields, respectively, along with 36 % of recovered 1. The major product 3 was identified through an authentic sample of 2,5-diphenylthiophene. The structure of 4 and 5 was deduced from the spectroscopic properties including ^{13}C-nmr spectra. For 4: oil; NMR($CDCl_3$) δ 3.73(3H, s), 3.96(3H, s), 7.4-7.7(10H, m), 7.80(1H, d, J=2 Hz), 8.25(1H, d, J=2 Hz); IR(neat) 1730, 1735, 765, 745, 700 cm^{-1}; MS m/e 346(M^+), 315 (M^+-CH_3O). For 5: m.p. 154-155 °C; NMR($CDCl_3$) δ 4.08(3H, s), 4.12(3H, s), 7.2-7.95(8H, m), 8.07(1H, s, H-1), 8.26(1H, broad d, J=8 Hz, H-9); IR(nujol) 1726, 1710 cm^{-1}; MS m/e 376(M^+), 375(M^+-H), 344(M^+-S). The characteristic low-field signals of δ 8.07 and 8.26 in the nmr spectrum of 5 are attributable to H-1 and H-9 of a naphtho[2,1-b]thiophene system,[3] which should be deshielded by the opposed ring. Addition of incremental amounts of Eu(fod)$_3$ caused only a small shift for these two signals but induced marked downfield shifts for a slightly broad doublet (J=9 Hz) with a meta coupling. The magnitude of the induced shift of this doublet was nearly the same as that of one of the ester Me's (ca. 3.5 ppm/mol. equiv.). These facts can be best interpreted in terms of the preferential complexation at the 5-ester carbonyl, which should cause that highly induced shift for H-6 because of its spatial closeness to the 5-ester Me. Irradiation of the broad doublets of H-9 and H-6, independently, in the presence of the shift reagent revealed the partial structure of C_6-C_7-C_8-C_9.



E = CO_2CH_3

The cycloaddition of 2 to the thiophene ring and subsequent loss of sulfur accounts for the formation of 4, as has already been reported,[1] whereas the competitive formation of 5 involves the unusual Diels-Alder addition to the diene comprised of one unsaturated bond of the thiophene system and one "Kekulé-bond" of a phenyl substituent.[4] The initial Diels-Alder adduct would readily undergo dehydrogenation to afford the aromatic system of 5.

A reaction of 2,5-diphenyl-1,4-dithiin (6) with 2 in o-dichlorobenzene at 130 °C for 30 hr led to the isolation of the naphthodithiin 7 (9 %) and dimethyl 3-phenylnaphtho[1,2-b]thiophene-4,5-dicarboxylate (8) (8 %). Traces of 1 were



also separated,$^{5)}$ while most of 6 was recovered. The structure of 7 and 8 was confirmed on the basis of their spectroscopic properties. For 7: m.p. 176 °C; NMR ($CDCl_3$) δ 3.82(3H, s), 3.84(3H, s), 7.4-7.8(10H, m); IR(nujol) 1730, 1710 cm^{-1}; MS m/e 408(M^+), 407(M^+-H), 376(M^+-S). For 8: m.p. 134-135 °C; NMR($CDCl_3$) δ 3.14(3H, s), 4.01(3H, s), 7.45(5H, m), 7.7(3H, m, H-2 and Ph-ortho), 8.2(2H, m, H-6 and H-9); IR(nujol) 1730, 1710 cm^{-1}; MS m/e 376(M^+), 375(M^+-H). The unusual high-field signal of the ester Me (δ 3.14) in 8 is interpreted as a result of the shielding effect due to the closely-spaced phenyl group and thus assigned to 4-ester Me. The shift reagent allowed the observation of each individual resonance of H-6(broad d), H-9(broad d), and H-2(s) as well as ortho protons(m) of the phenyl substituent.

The further conversion of 7 to 8 or 5 under the same conditions as those of the reaction of 6 has not been effected. Thus it seems likely that 7 and 8 were produced via independent pathways. The regioselective extrusion of sulfur is assumed to occur from an intermediate to 7, resulting in the formation of 8, and not 5.

When the reaction of 6 was carried out under the more vigorous conditions in refluxing o-dichlorobenzene for 10 hr, 3 (6 %), 4 (4 %), and 5 (35 %) were again isolated along with 1 (36 %). Probably 3, 4, and 5 would be formed via 1 which is derived from 6 by thermal extrusion of sulfur.$^{5)}$

The characteristic feature of the above reactions is that the orientation of desulfurization from 6 can be controlled depending on the reaction temperature. Despite the moderate yields, we believe these reactions provide a highly convenient route to an isomeric pair of naphtho[2,1-b] and [1,2-b]thiophenes. There seems to be a number of interesting features with regard to the reaction mechanisms. In particular, the novel phenyl migration found in the reaction of 1 with 2 is noteworthy. We are now extensively exploring the mechanism which accounts for the formation of all the products.

References and Notes

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(2) (a) H. Wynberg and R. Helder, Tetrahedron Lett., 3647 (1972); (b) D. N. Reinhoudt, H. C. Volger, C. G. Kouwenhoven, H. Wynberg, and R. Helder, Tetrahedron Lett., 5269 (1972); (c) D. N. Reinhoudt and C. G. Kouwenhoven, J. C. S. Chem. Comm., 1233 (1972).

(3) The nmr parameters derived by the second order analyses are available for parent naphtho[2,1-b] and [1,2-b]thiophenes: D. F. Ewing and R. M. Scrowston, Org. Magn. Resonance, 3, 405 (1971).

(4) The "Kekule-bond" of a phenyl substituent rarely enter into the Diels-Alder reaction as a diene component. A few examples are described in M. C. Kloetzel, Org. React., 4, 1 (1948); J. A. Norton, Chem. Rev., 31, 319 (1942).
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(5) It has been established(6) that 2,4-diphenyl-1,4-dithiin is thermally unstable and decomposes to give sulfur and 2,4-diphenylthiophene on heating above 190 °C. No effort was devoted to detecting sulfur in our reactions but the evolution of hydrogen sulfide was observed.

(6) W. E. Parham in "Organic Sulfur Compounds", Vol. 1, N. Kharasch, Ed., Pergamon Press, Inc., New York, N. Y., 1961, Chapter 22.

(7) Satisfactory elemental analyses have been obtained for all new compounds.

(Received August 11, 1977)