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ELECTROPHILIC SUBSTITUTION IN CYCLOPENTA[C]THIAPYRAN

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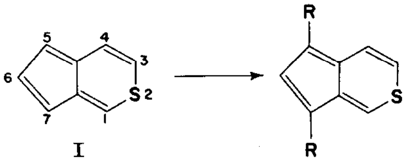
THE synthesis of cyclopenta[c]thiapyran (I) was announced in a recent communication[1] from this laboratory. The aromatic character of I, previously indicated by its thermal stability and the similarity of its ultraviolet and visible spectra to those of azulene, has now been demonstrated by successful electrophilic disubstitution. Further, strong evidence for the structures of the products has been obtained.



I

II, R = Cl
III, R = SCN
IV, R = Br
V, R = $COCH_3$

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[1] A. G. Anderson Jr., W. F. Harrison, R. G. Anderson and A. G. Osborne, J. Amer. Chem. Soc. 81, 1255 (1959).

Reaction of I with N-chlorosuccinimide in benzene gave a dichloro substitution derivative (II), m.p. 86-87°. (Found for $C_8H_4Cl_2S$: C, 47.04; H, 1.96; Cl, 34.87) Treatment of I with thiocyanogen in carbon tetrachloride produced a dithiocyano product (III), m.p. 152-154°. (Found for $C_{10}H_4N_2S_3$: C, 48.11; H, 1.28) The dibromo compound (IV), m.p. 84-86° dec. (Found for $C_8H_4Br_2S$: C, 32.95; H, 1.62) was formed by reaction of I with N-bromosuccinimide in benzene. Acetylation of I with excess acetic anhydride in the presence of stannic chloride gave a diacetyl derivative (V), m.p. 183-184.5°. (Found for $C_{12}H_{10}O_2S$: C, 66.14; H, 4.54). Reaction of I with tetranitromethane afforded only a mononitro substitution product, m.p. 147.5-150°. (Found for $C_8H_5NO_2S$: C, 53.38; H, 2.88).

Evidence for the structures of II, III, IV and V was obtained by analysis and comparison of the NMR spectra of I, II and III (Fig. 1). Our interpretation of the spectrum of I is as follows: The triplet of unit intensity at $\tau = 2.58$[2] is assigned to the proton in the 6-position. The weakly split doublet of unit intensity at $\tau = 1.65$ is due to the proton in the 1-position and the spin-spin splitting observed is thought to arise through interaction with the proton in the 3-position.[3] The doublet of unit intensity at $\tau = 2.02$ shows no splitting from interaction with the 1-proton and is therefore assigned to the proton in the 4-position. The absorptions due to the protons in the 3-, 5- and 7- positions all lie near $\tau = 3.15$ and insofar as the spectrum can be resolved the spin-spin couplings in this region are consistent with this assignment (see Fig. 1).[4]

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[2] $\tau = 10.00 - \delta^{\text{int.}}_{\text{Me}_4\text{Si}}$

[3] Spin-spin coupling across a sulfur atom in an aromatic system has also been reported for 3-methylthiophene; I. Weinberg, Monthly Ecumenical Letters from Laboratories of NMR No. 12, 6 (1959).

No gross difference in the electronic distribution in the ground states of I and II would be expected[5] and, thus, no large differences in

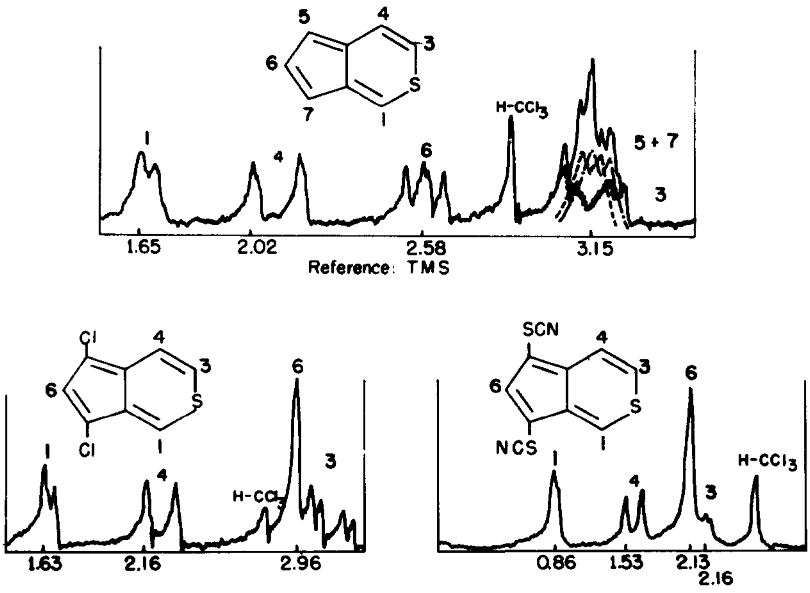

FIG. 1. NMR spectra of cyclopenta [c] thiapyran, 5,7-dichloro- and 5,7-dithiocyanocyclopenta [c]-thiapyran.

the values for the protons common to both. In the spectrum of II the doublet for the 4-proton, the doublet for the 1-proton, and the quadruplet

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[4] The relative chemical shifts of the protons in I suggest a charge displacement in the ground state of I with a dipole vector in the direction of the five-membered ring.

[5] The ultraviolet spectra of I and II are very similar.

for the 3-proton all are found within 0.15τ of the locations in the spectrum of I. Further, the triplet assigned to the 6-proton in I is replaced by a singlet of unit intensity (τ = 2.96) in the spectrum of II.[6] Therefore II almost certainly has the structure given.[7]

The spectrum of III is also strongly in accord with the proposed 5,7-disubstituted structure. The shift of the absorption downfield could arise through inductive[8] or ring current perturbations caused by the thiocyano groups.

By analogy, the structures shown (IV and V) are the most probable ones for these disubstitution compounds. It is not yet known whether the mononitro product is the 5- or the 7-substituted derivative, or a mixture of these. Further work is in progress.

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[6] The shift upfield of the absorption due to the 5-proton in II relative to I is also observed for the 2-proton in 1,3-dihaloazulenes as compared to azulene; A. G. Anderson, Jr. and L. L. Replogle, unpublished results.

[7] This conclusion is also supported by a study of the NMR spectrum of the cyclopenta [c] thiapyrillium ion in sulfuric acid and in deuterosulfuric acid wherein it was shown that equilibrium protonation of I occurs at the 5- and 7-positions; A. G. Anderson, Jr. and W. F. Harrison, unpublished results.

[8] The electron-withdrawing nature of the thiocyano group is reflected in its σp value of +0.60; F. G. Bordwell and P. J. Bontan, J. Amer. Chem. Soc. 78, 854 (1956).