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THE STRUCTURE OF THE ADDUCT FROM N-[p-BROMOBENZYL]-ISOQUINOLINIUM BROMIDE AND CARBON DISULFIDE[1]

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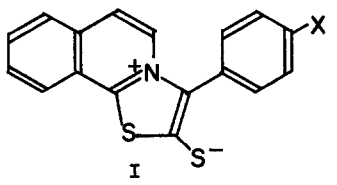
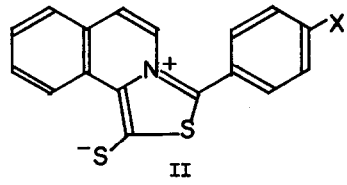
N-[Benzyl]isoquinolinium halides and carbon disulfide heated in strongly basic aqueous dioxane give adducts which have been assigned structure I (2). The available evidence (2) is equally consistent with the alternative formulation II. For an analogous base-catalyzed reaction between an N-[benzyl]-3,4-dihydroisoquinolinium halide and carbon disulfide, the structural ambiguity in the adduct as to the direction of addition on the CS double bond was clearly recognized (3).



I



II

The distinction between I and II has now been made through a complete x-ray crystallographic structure determination.

N-[p-Bromobenzyl]isoquinolinium bromide and carbon disulfide in base gave an adduct $C_{17}H_{10}BrNS_2$, m.p. 299-300° (4), which crystallizes as reddish-brown needles belonging to the monoclinic system with a = 21.95 ± 0.03Å., b = 7.19 ± 0.02Å., c = 19.62 ± 0.03Å., and β = 103° 30' ± 15', as determined on a precession camera, using MoK_α radiation (λ = 0.7107Å.). There are eight molecules of $C_{17}H_{10}BrNS_2$ in the unit cell (ρ meas. = 1.63 g./cm.^{3}, ρ calc. = 1.64 g./cm.^{3}), and systematic absences indicate that the space group is either C2/c or Cc, the former being established by the results of the analysis. A total of 1259 independent structure amplitudes was recorded on equi-inclination Weissenberg photographs and estimated visually (CuK_α radiation, λ = 1.5418Å.). The signs of the structure amplitudes were determined by the heavy atom method (5) and the structure I (X = Br) was readily deduced. Refinement by Fourier and least squares methods has given a final crystallographic R-factor of 0.09. A perspective drawing of the molecule projected down the c-axis is shown in Fig. 1.

Now that the structure of the adduct is secure, the mechanism through which adducts of this class originate is being investigated.

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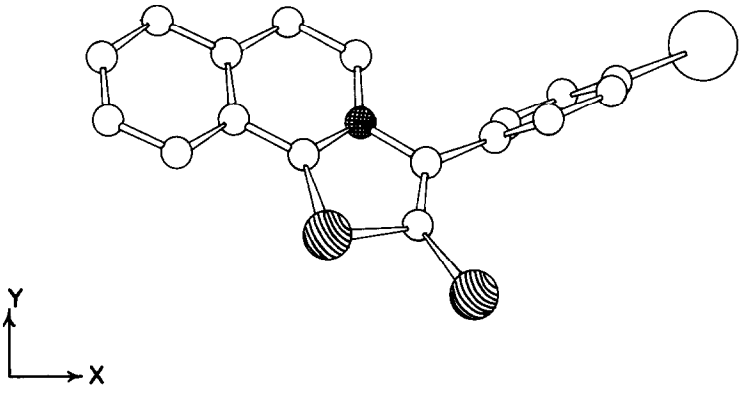

FIG. 1

Perspective drawing of molecule I (X = Br) projected down the c-axis.

REFERENCES

1. Cycloadditions. XI. Paper VIII, J. E. Baldwin, J. A. Kapecki, M. G. Newton, and I. C. Paul, Chem. Comm., in press; Paper IX, J. E. Baldwin, J. Org. Chem., 31, in press.

2. F. Kröhnke and H. H. Steuernagel, Angew. Chem., 73, 26 (1961); Chem. Ber., 97, 1118 (1964).

3. R. Huisgen, R. Grashey, and E. Steingruber, Tetrahedron Letters, No. 22, 1441 (1963).

4. Calcd. for $C_{17}H_{10}BrNS_2$: C, 54.84; H, 2.71; Br, 21.46. Found: C, 54.88; H, 2.72; Br, 21.26.

5. J. M. Robertson and I. Woodward, J. Chem. Soc., 219 (1937).