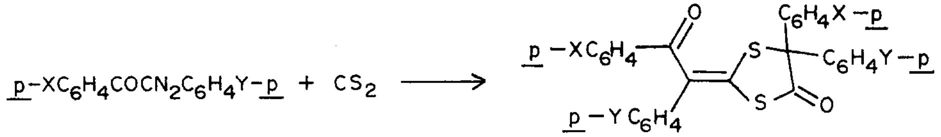
Tetrahedron Letters No. 39, pp. 3649 - 3652, 1971. Pergamon Press. Printed in Great Britain.

THE REACTION OF CARBON DISULFIDE WITH α-DIAZO KETONES. THE STRUCTURE AND STEREOCHEMISTRY OF THE RACEMIC PRODUCT FROM 2-(p-BROMOPHENYL)-2-DIAZOACETOPHENONE

K. Dichmann, D. Bichan, S.C. Nyburg and Peter Yates
Lash Miller Chemical Laboratories, University of Toronto
Toronto 5, Ontario, Canada

(Received in USA 29 June 1971. received in UK for publication 1 September 1971)

The product formed from 2-diazo-2-phenylacetophenone (I) and carbon disulfide (1) has been assigned structure II (stereochemistry undefined) as a result of spectroscopic and degradative studies (2). An analogous structure, IV, has been assigned to the major product from 2-diazo-4'-fluoro-2-(p-fluorophenyl)-acetophenone (III) and carbon disulfide on spectroscopic grounds (3). In contrast, the product from 3-diazo-2-butanone (V) and carbon disulfide (4) has been assigned structure VI as the result of an X-ray crystallographic study (5).



I, $X = Y = H$

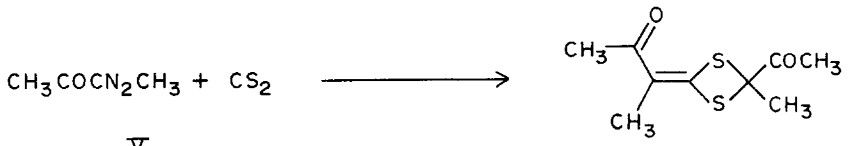
III, $X = Y = F$

VII, $X = H$, $Y = Br$

II, $X = Y = H$

IV, $X = Y = F$

VIII, $X = H$, $Y = Br$



V

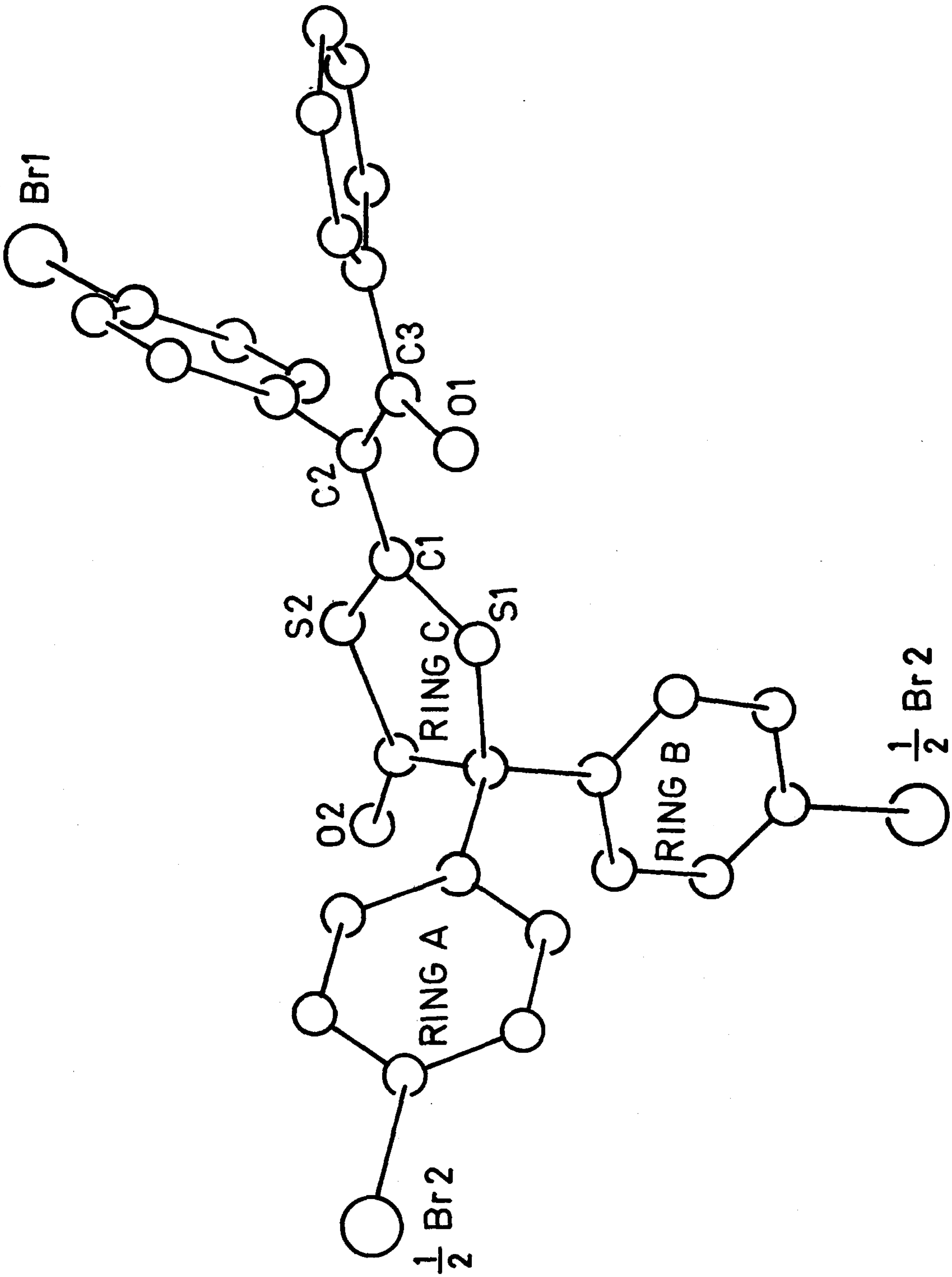
VI

This striking divergence of reaction pathway between the aromatic and aliphatic series has led us to determine the structure of a member of the former series by X-ray crystallography. Reaction of 2-(p-bromophenyl)-2-diazoacetophenone (VII) (6) with carbon disulfide gave a pale yellow crystalline product (69%), m.p. 156-158°, whose composition (Anal. Calcd. for $C_{29}H_{18}Br_2O_2S_2$: C, 56.00; H, 2.90; Br, 25.75; S, 10.30. Found: C, 56.17; H, 3.05; Br, 25.46; S, 10.09 and spectra [$\lambda_{max}^{CHCl_3}$ 5.86, 6.00 (w), 6.17 (m) μ; 256 (ε 15,100), 351 mμ (ε 10,600); m/e 620, 622, 624] showed it to be an analog of the products from I and III.

The crystals, $C_{29}H_{18}O_2Br_2S_2$ (M.W. = 622.4 g/mole) are triclinic, space group $P\bar{1}$; a = 13.336 (3), b = 10.220 (3), c = 9.655 (4) Å, α = 99.15 (4), β = 89.51 (4), γ = 96.00 (4)°; V = 1291.3 $Å^3$; D_m = 1.60, D_x = 1.61 (Z = 2) g/cc. The intensities were measured on an automated four-circle diffractometer in the 2θ-θ scan mode, at a scan rate of 2°/minute. CuKα radiation was used and of the 3735 independent reflections examined in the range $0 \leq \sin\theta \leq 0.88$, 2940 were observable. No corrections were made for absorption ($\mu = 60.4\ cm^{-1}$) or extinction.

The distribution of normalized structure factors clearly indicated a centric space group. The structure was solved using the symbolic addition procedure (7). Initial phasing sets (7) of six reflections (consisting of three signs and three symbols) did not lead to intelligible E-maps. Accordingly several more initiating sets of normalized structure factors with $E \geq 1.73$ were chosen for phase generation and refinement by the tangent formula. All such groups of generated phases (300 each) had some hkℓ indices in common and the symbolic phases for these reflections were either consistent from group to group or not. One phasing set from the self-consistent group was chosen and yielded an E-map which clearly showed one Br, two S and fifteen C atoms.

Refinement showed that the structure is analogous to the structures assigned on chemical grounds to the products from I and III, and that its stereochemistry is that represented by VIII. However an unusual type of disorder is present in the crystal. Rings A and B (see figure) both showed p-bromine atoms (Br2) whose occupancies refined to 0.510 and 0.498 respectively to a conventional R factor 0.083. A molecule having the Br2 atom on ring A is enantiomorphously related to a molecule with the Br2 atom on ring B. This shows that the crystal, which is a racemate, has + and - molecules occupying the molecular


Br1
C3
O1
C2
C1
S2
S1
RING C
O2
RING B
½ Br 2
RING A
½ Br 2

sites at random.

If two adjacent molecules are at x,y,z and x,1+y,1+z then a Br2 atom on ring A has a close intermolecular contact (3.56 Å) with a Br2 atom on ring B of the second molecule. Atom Br1 (x,y,z) has a close contact (3.47 Å) with Br1 on the adjacent molecule at -x,1-y,-z. There are no other short contacts.

Ring C is nearly planar with an expected short S1 -- O1 distance (2.55 Å). Other bond lengths and angles are normal.

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