Tetrahedron Letters No.10, pp. 1205-1208, 1968. Pergamon Press. Printed in Great Britain.

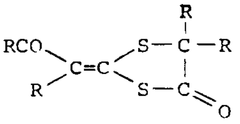
THE STRUCTURE OF THE PRODUCT FROM AZIBENZIL AND CARBON DISULFIDE

Peter Yates* and L. L. Williams

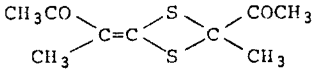
Contribution from the Departments of Chemistry,
Harvard University and the University of Toronto

(Received in USA 10 November 1967)

The product, $C_{29}H_{20}O_2S_2$, formed by reaction of 2-diazo-2-phenylacetophenone (azibenzil) with boiling carbon disulfide[1] has been assigned structure I[2] by Yates and Christensen[3] on the basis of spectroscopic and degradative evidence. Subsequently, a product, $C_9H_{12}O_2S_2$, formed by reaction of 3-diazo-2-butanone with carbon disulfide was assigned structure II[2] by Kirby[4] on the basis of analogy, in spite of n.m.r. spectral evidence to the contrary.[4] However, Kapecki, Baldwin, and Paul[5] have recently shown by an X-ray crystallographic study that the latter product has in fact the structure III. We wish to report here further evidence substantiating the assignment of structure I to the product from azibenzil, which is thus of different type from that given by 3-diazo-2-butanone.



I, R = C_6H_5
II, R = CH_3



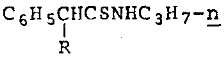
III

The presence of the grouping $-S-C(C_6H_5)_2-CO-$ in the azibenzil product has been confirmed by degradation under much more mildly basic conditions than those employed earlier.[3] Treatment of the product in chloroform solution with propylamine at room temperature for 6 hours gave

---

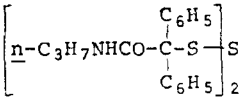
* To whom enquiries should be addressed at the Lash Miller Chemical Laboratories, University of Toronto, Toronto 5, Ontario, Canada.

compounds IV and V .[6] Compound IV, fluffy white needles, m.p. 67°, showed $\lambda_{max}(CCl_4)$ 2.95(sh), 3.01, 5.98, 6.26, 6.57 μ, λ_{max}^{MeOH} 249 (log ε 4.20), 265 (infl., 4.09) mμ, $\lambda_{max}^{MeOH-MeONa}$ 273(3.89), 340(4.18) mμ, δ($CDCl_3$) 0.90 (t), 1.55 (m), 3.42 (m), 6.30 (s), 7.33 (m), 8.05 (m), 9.30 (br m). Treatment of IV with dilute aqueous sodium hydroxide at room temperature gave benzoic acid and 2-phenyl-N-propylthioacetamide (VI), m.p. 55.5-57°, identified by mixed m.p. and spectral comparison with an authentic sample, m.p. 55.5-56.5°, prepared by reaction of propyl isothiocyanate with benzylmagnesium chloride. Compound V, fine white needles, m.p. 167-168°, showed $\lambda_{max}^{CHCl_3}$ 2.91, 2.94(sh), 6.01, 6.27 μ, and strong ultraviolet end absorption (log ε_{235} 4.40). Reduction of V with Raney nickel in ethanol or with zinc and acetic acid gave 2,2-diphenyl-N-propylacetamide, m.p. 94.5-95°, identified by mixed m.p. and spectral comparison with an authentic sample, m.p. 95-95.5°, prepared by reaction of diphenylacetyl chloride with propylamine. The formation of the trisulfide[7] rather than the corresponding disulfide[3] is unexpected, but readily interpretable in terms of reaction of the latter with hydrosulfide ion followed by oxidative recoupling: the presence of hydrosulfide ions in the reaction mixture is indicated by the observation that hydrogen sulfide is formed during the reaction. The formation of a product with the grouping $-S-C(C_6H_5)_2-CO-$ under such mild conditions confirms the presence of this grouping in the compound, $C_{29}H_{20}O_2S_2$, as in I.



$C_6H_5\underset{R}{C}HCSNHC_3H_7\text{-}\underline{n}$

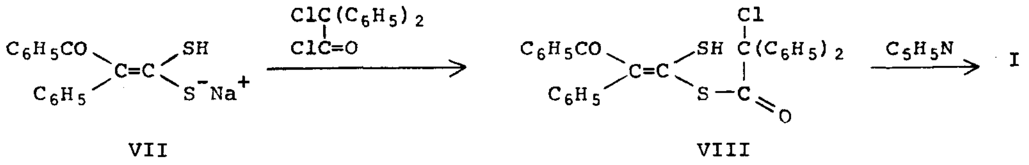
IV, R = COC_6H_5
VI, R = H



$\left[\underline{n}\text{-}C_3H_7NHCO\text{-}\overset{C_6H_5}{\underset{C_6H_5}{C}}\text{-}S\text{-}\right]_2 S$

V

An alternative synthesis of I, albeit in low yield, also corroborates this structural assignment. Treatment of deoxybenzoin with one molar equivalent of sodium amide in benzene at reflux followed by reaction with one molar equivalent of carbon disulfide at room temperature gave the red sodium salt of phenylbenzoyldithioacetic acid (VII). Addition of α-chlorodiphenylacetyl chloride in benzene rapidly discharged the red color to give an intermediate considered to be VIII: pyridine was then added and the mixture was heated under reflux. From the benzene-soluble fraction of the reaction mixture compound I was isolated in 4% yield as yellow prisms, m.p. 153-155°, shown to be identical with the product from azibenzil, m.p. 154-155°, by infrared spectral comparison and mixed m.p.



It is thus clear that the product obtained from the reaction of carbon disulfide with azibenzil differs from that formed with 3-diazo-2-butanone in that one of the RCOCR moieties has undergone rearrangement of Wolff type. The exceptional facility of such rearrangement when R = C_6H_5 finds analogy in earlier observations. A question which remains unanswered by the present degradative and synthetic results concerns the possibility of bonding between the oxygen atom of the ketonic carbonyl group of I and a sulfur atom; such a modification of structure I has previously been considered because of the abnormally weak intensity of the infrared stretching band assigned to this carbonyl group.[8] However, recent X-ray crystallographic studies of related compounds have shown that although the corresponding sulfur-oxygen distance is considerably less than the sum of the van der Waals radii of sulfur and oxygen, it is not sufficiently short to suggest significant covalent bonding between these atoms.[5,9,10]

REFERENCES

1. J. Meyer, Helv. Chim. Acta, **8**, 38 (1925).
2. Structures I and II do not connote assignment of stereochemistry.

3. P. Yates and B. G. Christensen, *Chem. Ind. (London)*, 1441 (1958).

4. A. J. Kirby, *Tetrahedron*, **22**, 3001 (1966).

5. J. A. Kapecki, J. E. Baldwin, and I. C. Paul, *Tetrahedron Letters*, in press; we thank Professor Baldwin for providing us with a preprint of this paper.

6. Satisfactory elemental analytical data have been obtained for all new compounds characterized by m.p.

7. The alternative, branched trisulfide structure for this product is considered unlikely, but has not been vigorously excluded.

8. L. L. Williams, Ph.D. Thesis, Harvard University, 1961.

9. T. R. Lynch, I. P. Mellor, S. C. Nyburg, and P. Yates, *Tetrahedron Letters*, 373 (1967); I. P. Mellor and S. C. Nyburg, private communication.

10. W. H. Schmidt and A. Tulinsky, *Tetrahedron Letters*, in press; we thank Professor Tulinsky for providing us with a preprint of this paper.