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ON THE STRUCTURE OF MAX BERGMANN'S "BENZALDEHYDE PHENYLHYDRAZONE OXIDE"

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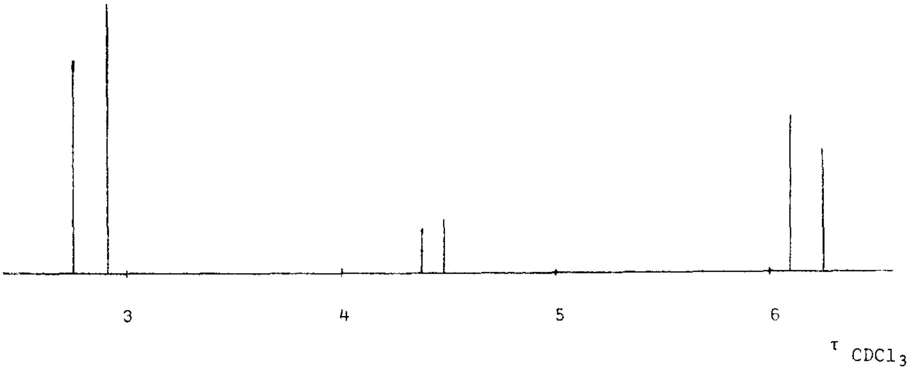
In 1923 Bergmann, Ulpts, and Witte(1) reported that the action of perbenzoic acid on benzaldehyde phenylhydrazone resulted in the formation of a new crystalline compound, m.p. 201°. This "benzaldehyde phenylhydrazone oxide" was so insoluble as to preclude for its characterization all but the most drastic degradation reactions; however, on the basis of elemental analysis Bergmann ascribed to it the structure 1.

Subsequently a number of workers(2-5) extended Bergmann's observation to a variety of aryl- and alkylhydrazones, thereby obtaining high-melting, insoluble compounds similar to that from benzaldehyde phenylhydrazone. In all of these cases the analytical data were reported in agreement with the simple addition of one atom of oxygen to the hydrazones. Infrared spectra of the compounds were devoid of O-H, N-H, and C=O absorption, but strong bands in the 6.7 - 7.0 μ region suggested the presence of an azoxy group.

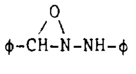
After several proposals of 2,(2,3) the structure which gained general acceptance(6) was Lythgoe's formulation 3.(4) Lythgoe had in hand compounds 4, m.p. 104°; and 5, m.p. 107°. The structures of both 4 and 5 rest on a reliable classical determination based on patterns of aromatic substitution. Lythgoe showed that 4 could be transformed by base into a compound, m.p. 186°, identical with that obtained in the Bergmann manner by the action of perbenzoic acid on *p*-chlorobenzaldehyde *p*-bromophenylhydrazone. Guided by similarities in the ultraviolet spectra, Lythgoe formulated the transformation as 6 → 7, a base catalyzed *trans* → *cis* change of configuration about the azoxy group. By analogy, the original Bergmann compound was then 3.

Figure I: Nmr Spectrum of "Benzaldehyde Methylhydrazone Oxide"



Consideration of the nmr spectra of the Bergmann compounds suggests a different solution to the problem. The spectrum of the compound(5) from benzaldehyde methylhydrazone and perbenzoic acid is reproduced schematically in Figure I. The pattern of peaks suggests a mixture of two very similar substances. Indeed, fractional crystallization yields two compounds from the mixture. Integration reveals that each compound contains phenyl protons, methyl protons, and methine protons in the ratios five to three to *one*. Analogous results are obtained with other Bergmann compounds and lead to the conclusion that the "hydrazone oxides" should be formulated as **8**. "Benzaldehyde methylhydrazone oxide" is then **8b**, the spectrum in Figure I being that of the mixture of *dl* and *meso* forms. Likewise, "benzaldehyde phenylhydrazone oxide" is **8a**, and Lythgoe's **7** is **8c**. It is apparent that the elemental analyses of previous workers were misleading. (We have obtained analyses in agreement with **8**.)

Several points confirm our assignment: (a) Lythgoe's **4** is indeed converted by base to **8c**, even in the absence of oxygen. However, in keeping with a reaction which is not an isomerization but an oxidation, we find that 4,4'-dibromoazoxybenzene (a possible reduction product of **4**) is found in addition to **8c**. The conversion **4** → **8c** confirms the position of the oxygens in **8c**. (b) *Three* moles of perbenzoic acid are required in the oxidation of two moles of *p*-chlorobenzaldehyde *p*-bromophenylhydrazone to one mole of **8c**, in agreement with our formulation. (c) Oxidation of bis-azo compound **9a** with perbenzoic acid yields **8a**. (Compound **9a** is obtained from oxidation of benzaldehydephenylhydrazone with oxidizing agents such as mercuric oxide or amyl nitrite. Its structure rests securely on spectral data, elemental analysis, clean conversion to benzil osazone **10**,(7) and on its existence in *dl* and *meso* forms.)(8-10)



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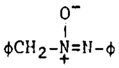
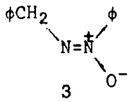


$\phi CH_2-\overset{O^-}{\underset{+}{N}}=N-\phi$

2



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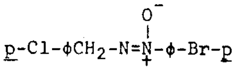
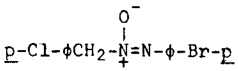


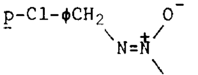
$p\text{-}Cl\text{-}\phi CH_2-N=\overset{O^-}{\underset{+}{N}}-\phi\text{-}Br\text{-}p$

4



$p\text{-}Cl\text{-}\phi CH_2-\overset{O^-}{\underset{+}{N}}=N-\phi\text{-}Br\text{-}p$

5



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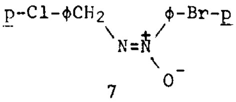

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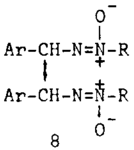

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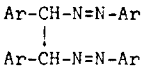


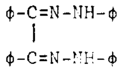
9

8a: Ar = ϕ, R = ϕ

9a: Ar = ϕ

8b: Ar = ϕ, R = CH_3

8c: Ar = p-Cl-ϕ, R = p-Br-ϕ



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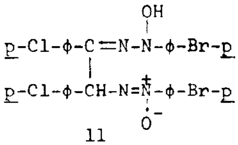

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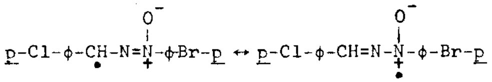
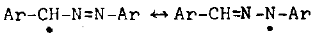


$p\text{-}Cl\text{-}\phi\text{-}\underset{\bullet}{CH}-N=\overset{O^-}{\underset{+}{N}}-\phi Br\text{-}p \leftrightarrow p\text{-}Cl\text{-}\phi\text{-}CH=N-\overset{O^-}{\underset{\overset{+}{\bullet}}{N}}-\phi\text{-}Br\text{-}p$

12



$Ar-\underset{\bullet}{CH}-N=N-Ar \leftrightarrow Ar-CH=N-\underset{\bullet}{N}-Ar$

13

Compound 8c was studied in some detail and proved to be of great interest. Its nmr spectrum shows the presence of two forms, *dl* and *meso*. The mixture can be enriched in one of the forms by rapid cooling of a carbon tetrachloride solution and subsequent filtration. However, the filtered solution, at first enriched in one isomer, reverts to a 50-50 mixture upon standing, the equilibration being accelerated by warming. The possibility that equilibration occurs via tautomer 11 is ruled out by the fact that deuterium exchange does not occur at the methine carbons. However, an electron spin resonance study(11) of the molecule in carbon tetrachloride solution reveals the presence of a radical whose concentration is reversibly temperature dependent. From this temperature dependence we have calculated that $\Delta H^{\ddagger}$ for the formation of the radical is approximately 14 kcal per mole. Equilibration is taking place via radical 12, an allylic nitroxide. Comparison may be made with compounds 9, which dissociate into hydrazonyl free radicals 13.(10) In these cases $\Delta H^{\ddagger}$ is approximately 27 kcal per mole.(12)

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(11) We thank Prof. August H. Maki for the esr investigation.

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