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The Chemistry of Polyazanes. V. The Mechanism of the Oxidation of Benzalphenylhydrazone

By Hiroshi MINATO, Hiroo TATENO* and Hiroshi YOKOKAWA*

Department of Chemistry, International Christian University, Mitaka, Tokyo

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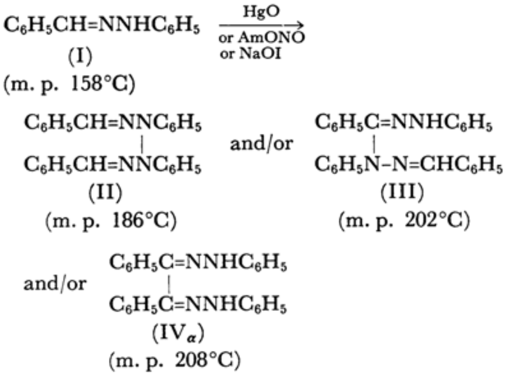
Benzalphenylhydrazone was oxidized with amyl nitrite and with sodium hypoiodite, and the products of the oxidation were analyzed. The products identified were dibenzaldiphenyltetrazone, α-benzilosazone and unoxidized benzalphenylhydrazone. The mechanism of the oxidation was discussed.

The oxidation of benzalphenylhydrazone (I) was investigated by several chemists many years ago, but the mechanisms proposed were not convincing, nor were the products of the oxidation quantitatively studied.

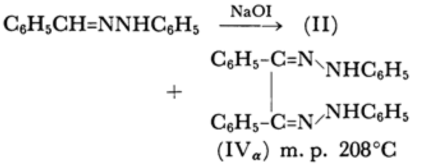
Minunni[1] oxidized the benzalphenylhydrazone with mercuric oxide, and obtained the compound II, dibenzaldiphenyltetrazone.



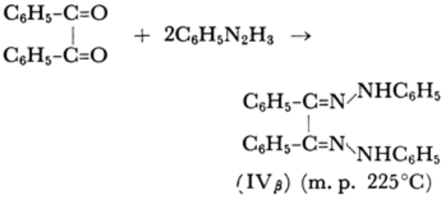
$$\underset{\text{(m. p. 158°C)}}{\underset{\text{(I)}}{C_6H_5CH{=}NNHC_6H_5}} \xrightarrow[\substack{\text{or AmONO}\\ \text{or NaOI}}]{\text{HgO}} \underset{\text{(m. p. 186°C)}}{\underset{\text{(II)}}{\begin{array}{c}C_6H_5CH{=}NNC_6H_5\\ |\\ C_6H_5CH{=}NNC_6H_5\end{array}}} \text{ and/or } \underset{\text{(m. p. 202°C)}}{\underset{\text{(III)}}{\begin{array}{c}C_6H_5C{=}NNHC_6H_5\\ |\\ C_6H_5N{-}N{=}CHC_6H_5\end{array}}} \text{ and/or } \underset{\text{(m. p. 208°C)}}{\underset{(IV_\alpha)}{\begin{array}{c}C_6H_5C{=}NNHC_6H_5\\ |\\ C_6H_5C{=}NNHC_6H_5\end{array}}}$$

Pechmann[2] oxidized the benzalphenylhydrazone with amyl nitrite and also obtained compound II.

Ingle and Mann[3] repeated Pechmann's experiment and obtained a compound melting at 202°C as well as the compound II melting at 186°C. Ingle and Mann assigned the structure III to this new compound. Then Ingle and Mann, using sodium hypoiodite as a new oxidizing agent, obtained a compound melting at 208°C as well as the compound II. They assigned the structure IV, benzilosazone, to this compound. However, the benzilosazone formed by mixing benzil and phenylhydrazine melts at 225°C. Therefore, they named the oxidation product (m. p. 208°C) as α-benzilosazone, and called the osazone (m. p. 225°C) formed from benzil and phenylhydrazone β-benzilosazone.



$$C_6H_5CH{=}NNHC_6H_5 \xrightarrow{\text{NaOI}} \text{(II)} + \underset{(IV_\alpha)\ \text{m. p. 208°C}}{\begin{array}{l}C_6H_5{-}C{=}N{\diagdown}NHC_6H_5\\ \quad\ \ |\\ C_6H_5{-}C{=}N{\diagup}NHC_6H_5\end{array}}$$



$$\begin{array}{l}C_6H_5{-}C{=}O\\ \quad\ \ |\\ C_6H_5{-}C{=}O\end{array} + 2C_6H_5N_2H_3 \rightarrow \underset{(IV_\beta)\ \text{(m. p. 225°C)}}{\begin{array}{l}C_6H_5{-}C{=}N{\diagup}NHC_6H_5\\ \quad\ \ |\\ C_6H_5{-}C{=}N{\diagdown}NHC_6H_5\end{array}}$$

However, they did not mention anything about the reason why IV_α, not IV_β, was produced by the oxidation of benzalphenylhydrazone.

This investigation was undertaken in order to find out: 1) the products of the oxidation of benzalphenylhydrazone by amyl nitrite and sodium hypoiodite; 2) whether or not compound III was present in the oxidized mixture, and 3) a plausible mechanism for the oxidation of benzalphenylhydrazone.

Experimental

Benzalphenylhydrazone (I).—By mixing phenylhydrazine and benzaldehyde in ethanol, yellow crystals of benzalphenylhydrazone were produced. After the recrystallization from ethanol, they melted at 155—156°C. (Literature: 156°C).

β-Benzilosazone (IV_β). — A hot ethanol solution containing 4.5 g. of phenylhydrazine hydrochloride (0.032 mol.) and 11.3 g. of sodium acetate (0.1486 mol.) was added to an ethanol solution containing 3 g. of benzil (0.0142 mol.). Bright yellow crystals were recrystallized from a 2 : 1 mixture of benzene and ethanol. M. p. 224—225°C (Literature: 225°C).

The Oxidation of Benzalphenylhydrazone (I) by Amyl Nitrite.—Five grams of benzalphenylhydrazone (I) (0.0255 mol.) was dissolved in 100 ml. of ether, and 6.0 ml. (0.0403 mol.) of amyl nitrite was

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* American Chemical Society-Petroleum Research Fund Scholar.

[1] G. Minunni, *Gazz.*, **22**, 228 (1892).

[2] H. von Pechmann, *Ber.*, **26**, 1045 (1893).

[3] H. Ingle and H. H. Mann, *J. Chem. Soc.*, **67**, 607 (1895).

added to this solution. The mixture was heated on a water-bath at 40—50°C for 6 hr. This solution was orange yellow at first, but on further heating it became darker, and yellow crystals precipitated. Brown nitrogen dioxide gas evolved for several hours.

The mixture was cooled, and the yellow crystals were filtered and washed with ethanol and ether; yield, 0.5690 g.; m. p. 184—186°C. This was identified as dibenzaldiphenyltetrazone (II) from its melting point and its infrared spectrum. The filtrate was evaporated to dryness to yield 5.114 g. of a yellowish-red residue. This residue was divided by repeated recrystallization from ether and ethanol into three fractions. The first fraction, weighing 0.0212 g., was identified as the benzalphenylhydrazone (I) by a study of its melting point and its infrared spectrum. The second fraction, weighing 3.990 g., was identified as α-benzilosazone, (IV_α) from a study of its melting point and its infrared spectrum. The third fraction, weighing 1.003 g., was an oily substance which was not identified.

The Oxidation of Benzalphenylhydrazone (I) by Iodine and Sodium Ethoxide.—Ten grams of benzalphenylhydrazone (I) (0.0510 mol.) in 200 ml. of ether were added to a solution of 1.59 g. of sodium (0.0650 mol.) in 20 ml. of ethanol. Then an ethereal solution of 6.57 g. (0.0510 mol.) of iodine was gradually stirred into this mixture over a 1.5 hr. period at room temperature. Then the solution was shaken with 50 ml. of a saturated solution of sodium sulfite in order to remove the last trace of iodine. Upon the evaporation of the ether, 10.773 g. of a brownish-red, somewhat resinous residue was obtained. This residue was divided into four fractions by repeated recrystallizations from ethanol, ethyl acetate, and/or benzene. The first three fractions were identified, by a study of infrared spectra and their melting points, as 0.296 g. of dibenzaldiphenyltetrazone (II) (0.71 mmol.), 4.943 g. of α-benzilosazone (IV_α) (12.67 mmol.), and 1.256 g. of benzalphenylhydrazone (I) (6.41 mmol.). It was not possible to identify the fourth fraction, which was viscous and resin-like.

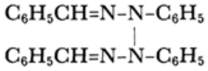
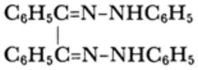
An Attempt to Oxidize α-Methylphenylhydrazone of Benzaldehyde.—A solution of 1.008 g. of the α-methylphenylhydrazone of benzaldehyde (0.0048 mol.) in 12 ml. of diethyl ether and a solution of 0.15 g. of sodium (0.0066 mol.) in 2 ml. of ethanol was mixed; a solution of 1.67 g. of iodine (0.0066 mol.) in 10 ml. of ether was then stirred, drop by drop, into this mixture. The solution thus prepared was treated in a manner similar to that described above for the oxidation of benzalphenylhydrazone. The white crystals obtained was recrystallized from ethanol; yield, 0.892 g. The melting point (105—107°C) and the infrared spectrum of these crystals were identical with those of an authentic sample of the α-methylphenylhydrazone of benzaldehyde.

An Attempt to Reduce β-Benzilosazone.—To a mixture of 3.7 g. of β-benzilosazone (0.0095 mol.), 90 ml. of ethanol and 20 ml. of benzene, 82 g. of a 3% sodium amalgam (0.0107 mol.) was added, at one time, at 90°C, and in a carbon dioxide atmosphere; the mixture was then stirred for 9 hr. at 90°C. The yellow color of β-benzilosazone disappeared within 2 hr. of the stirring. After 9 hr., the reaction mixture became white and highly viscous. It was neutralized with a 10% hydrochloric acid solution to pH 7.2. The mercury was removed, and the solution was made strongly acid by the addition of concentrated hydrochloric acid. When the solution was concentrated by the evaporation of the solvents, a pale green solution was obtained. When diethyl ether was added to this solution, white crystals obtained; yield, 0.43 g.; m. p. 242—244°C. From the mother liquor, 0.30 g. of white crystals were obtained; m. p. 183—184°C. When the filtrate was further evaporated, a dark brown solution of a high viscosity remained.

Results and Discussion

The products of the oxidation of benzalphenylhydrazone (I) with amyl nitrite are summarized in Table I. Pechmann2) oxidized benzalphenylhydrazone with amyl nitrite; he identified only the dibenzaldiphenyltetrazone (II), which was very little soluble in ethanol and was easily isolated. When Ingle and Mann3) repeated Pechmann's experiment, they found a compound melting at 202°C as well as the tetrazone (II). They assigned the structure III to this compound, but the assignment was made without any convincing evidence. Our experiment did not indicate the presence of the compound III. Since our experiment did not account for 100% of the starting material, the production of the compound III was not completely excluded. However, our data seem to imply that the compound melting at 202°C was most likely an impure form of α-benzilosazone, which melted at 208°C.

TABLE I. PRODUCTS OF OXIDATION OF BENZALPHENYLHYDRAZONE WITH AMYL NITRITE*

Product	g.	mmol.	mol./mol. I
$C_6H_5CH{=}NNHC_6H_5$	0.0212	0.108	0.004
 $C_6H_5CH{=}N{-}N{-}C_6H_5$ $C_6H_5CH{=}N{-}N{-}C_6H_5$	0.569	1.46	0.057
 $C_6H_5C{=}N{-}NHC_6H_5$ $C_6H_5C{=}N{-}NHC_6H_5$	3.990	10.2	0.400
	% Accounted for		92.8% of I

* Five grams of benzalphenylhydrazone (25.5 mmol.) was mixed with 40.3 mmol. of amyl nitrite in ethanol.

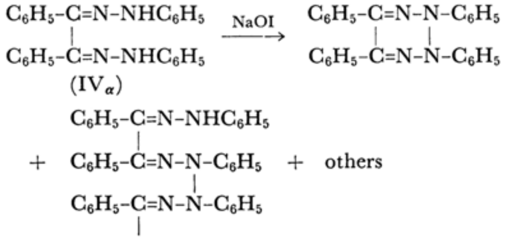
The products of the oxidation of benzalphenylhydrazone with sodium hypoiodite are summarized in Table II. Ingle and Mann3) did the same oxidation; they reported the formation of II and IV_α, but did not give any quantitative data. A comparison of Tables I and II reveals that, in the case of the oxidation with sodium hypoiodite, the smaller percent of the starting material was accounted for and about 13% of I remained unoxidized, even though a stoichiometric amount of the oxidant was present. The residue, which was unidentifiable, was resinous. These facts seem to indicate that a part of the sodium hypoiodite

TABLE II. PRODUCTS OF OXIDATION OF BENZALPHENYLHYDRAZONE WITH IODINE AND SODIUM ETHOXIDE*

Product	g.	mmol.	mol./ mol. I
$C_6H_5CH{=}NNHC_6H_5$	1.256	6.41	0.126
$C_6H_5CH{=}N{-}NC_6H_5$ $C_6H_5CH{=}N{-}NC_6H_5$	0.296	0.710	0.014
$C_6H_5C{=}NNHC_6H_5$ $C_6H_5C{=}NNHC_6H_5$	4.943	12.67	0.249
	% Accounted for		65.2% of I

* Ten grams of benzalphenylhydrazone (51.0 mmol.) in ether was mixed with an ethanolic solution of 1.59 g. of sodium (65.0 mmol.) and with an ethereal solution of 6.57 g. (51.0 mmol.) of iodine.

was used to oxidize some of the oxidation products to resinous substances. α-Benzilosazone possesses oxidizable hydrogens; a plausible scheme of this oxidation may be shown as follows:



$$\begin{array}{l}C_6H_5{-}C{=}N{-}NHC_6H_5\\ \quad|\\ C_6H_5{-}C{=}N{-}NHC_6H_5\\ (IV_\alpha)\end{array}\xrightarrow{NaOI}\begin{array}{l}C_6H_5{-}C{=}N{-}N{-}C_6H_5\\ \quad|\qquad\ \ |\\ C_6H_5{-}C{=}N{-}N{-}C_6H_5\end{array}$$

$$+\ \begin{array}{l}C_6H_5{-}C{=}N{-}NHC_6H_5\\ \quad|\\ C_6H_5{-}C{=}N{-}N{-}C_6H_5\\ \qquad\qquad|\\ C_6H_5{-}C{=}N{-}N{-}C_6H_5\\ \quad|\end{array}\ +\ \text{others}$$

As to the mechanism of the oxidation of benzalphenylhydrazone, neither Pechmann nor Ingle and Mann proposed anything. Minunni[1] proposed the following mechanism.

By the abstraction of a hydrogen atom attached to nitrogen, a radical, $C_6H_5CH{=}N\dot{N}C_6H_5$ (A), is formed. This free radical, with a divalent nitrogen-atom, is unstable and rearranges to $C_6H_5\dot{C}{=}NNHC_6H_5$ (B) with a trivalent carbon atom.

$$\underset{(I)}{C_6H_5CH{=}NNHC_6H_5} \rightarrow \underset{(A)}{C_6H_5CH{=}N\dot{N}C_6H_5} \rightarrow \underset{(B)}{C_6H_5\dot{C}{=}NNHC_6H_5}$$

The combination of A-A results in the tetrazone (II), while that of B-B results in the osazone (IV).

The mechanism proposed by Minunni seems to be unacceptable for two reasons. First, the radical B appears to be a more stable radical than the radical B. In the radical A, the odd electron is in resonance with the p-electrons of C=N and two benzene rings; hence, this radical is a rather well-stabilized radical. The radical B, on the other hand, is not so stable, since the odd electron is in resonance with the p-electrons of only one benzene ring. Therefore, it is unlikely that the radical A rearranges to the less stable radical B. Second, the combination of two B radicals should produce the thermodynamically more stable osazone, the β-form, not the α-form. In order, for the radical B to be stabilized, the p-orbital with the odd electron must be parallel with the p-orbitals of the benzene ring. When this rotation occurs, the radical becomes symmetrical, and the combination of B-B should yield the more stable β-osazone. For these two reasons, Minunni's mechanism seems to be unacceptable.

Sidgwick[4] explained this reaction by assuming the initial formation of two radicals; the radical A formed by the hydrogen-abstraction from the α-nitrogen of I, and the radical B formed by the hydrogen-abstraction from the α-carbon of I:

$$\underset{(A)}{C_6H_5CH{=}N{-}\dot{N}{-}C_6H_5} \leftarrow \underset{(I)}{C_6H_5CH{=}N{-}NHC_6H_5} \rightarrow \underset{(B)}{C_6H_5\dot{C}{=}NNHC_6H_5}$$

The combination of A-A will form II, while that of B-B will form IV. However, Sidgwick's explanation does not solve any of the difficulties mentioned above in connection with Minunni's mechanism. Since the radical A appears to be much more stable than the radical b, the hydrogen abstraction most likely will take place on the α-nitrogen, not on the α-carbon. The combination of two B radicals should yield the β-benzilosazone, but the osazone isolated by the experiment was the α-form.

We wish to propose and describe a plausible mechanism for the oxidation of benzalphenylhydrazone.

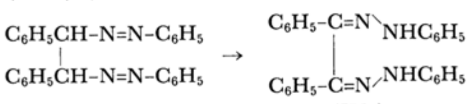
The abstraction of hydrogen takes place on the α-nitrogen atom of I and yields the radical A, which is stabilized by the resonance expressed by the limiting forms, A and C.

$$C_6H_5CH{=}NNHC_6H_5 \rightarrow$$

$$[\underset{(A)}{C_6H_5CH{=}N{-}\dot{N}{-}C_6H_5} \leftrightarrow \underset{(C)}{C_6H_5\dot{C}H{-}N{=}N{-}C_6H_5}]$$

The combination of A-A results in the formation of II. The combination of C-C will yield the compound IV′, which is then expected to tautomerize to IV_α:

(C) + (C) →



$$\underset{(IV')}{\begin{array}{l}C_6H_5CH{-}N{=}N{-}C_6H_5\\ \qquad|\\ C_6H_5CH{-}N{=}N{-}C_6H_5\end{array}} \rightarrow \underset{(IV_\alpha)}{\begin{array}{l}C_6H_5{-}C{=}N\diagdown NHC_6H_5\\ \qquad\ |\\ C_6H_5{-}C{=}N\diagup NHC_6H_5\end{array}}$$

(IV′) (IVα)

The combination of A-A is a combination of electronegative nitrogen atoms, which must be less favorable than the combination of C-C. In the actual experiments, the benzilosazone (IV) was

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[4] N. V. Sidgwick, "Organic Chemistry of Nitrogen," Clarendon Press, Oxford (1937), p. 464.

found in a much greater quantity than the tetrazone (II).

In order to defend this mechanism, the following three conditions must be satisfied:

(1) The trivalent carbon radical B, $C_6H_5\dot{C}=NNHC_6H_5$, is not formed from the oxidation of I.

(2) The azo form IV′ should tautomerize to the hydrazone form IV under the experimental conditions.

(3) The tautomerism should yield the α-osazone, which is less stable than the β-osazone.

In an attempt to establish that the hydrogen atom of the α-carbon is not abstracted, the α-methylphenylhydrazone of benzaldehyde was prepared and was subjected to oxidation with sodium hypoiodite. After crystallization and washing, 90% of the α-methylphenylhydrazone was isolated as crystals; this fact indicates that the hydrogen atom on the α-carbon atom of the benzalphenylhydrazone will not be abstracted either.

The problem of the tautomerism from the azo form IV′ to the hydrazone form IV is rather complex. In 1961, Zollinger[5] wrote that "it has always been found that the hydrazone is the more stable species. Since the rate of rearrangement of the azo into the hydrazone form is in general very low, azo compounds can readily be isolated in spite of this. The reaction is favored by solvents able to provide protons and is catalyzed by acids and bases, but no exact investigations have yet been undertaken."

Brough et al.[6] prepared 1′-(*p*-chlorophenyl)-benzeneazomethane by the oxidation of the corresponding hydrazo-compound; they found that it was fairly stable at 0°C, but isomerized to the hydrazone in methanol at room temperature.

$$p\text{-Cl-}C_6H_4\text{-}CH_2\text{-}N=N\text{-}C_6H_5 \xrightarrow{CH_3OH} p\text{-Cl-}C_6H_5\text{-}CH=N\text{-}NH\text{-}C_6H_5$$

However, 1′, 1′-diphenylbenzeneazomethane, $C_6H_5\text{-}N=N\text{-}CH(C_6H_5)_2$, is rather stable and melts at 73—75°C. Perhaps the compound IV′ resembles 1′-(*p*-chlorophenyl)-benzeneazomethane rather than 1′, 1′-diphenylbenzeneazomethane, and perhaps the compound IV′ easily isomerizes to IV_α.

In order to ascertain what actually happens, an attempt was made to reduce IV_β so as to prepare IV′. When the β-benzilosazone IV_β was subjected to reduction with an excess amount of sodium amalgam or lithium aluminum hydride in an inert atmosphere, a mixture of several compounds always resulted, and it was not possible to prepare the compound IV′. Although the attempt to ascertain the easy isomerism from IV′ to IV_α failed, it seems likely that the isomerization proceeds under experimental conditions which are either basic (sodium hypoiodite) or acidic (amyl nitrite).

Now the problem of the tautomerism to the α-osazone, not to the β-osazone, should be dealt with. When the azo form IV′ tautomerizes to the osazone, two types of transition state seem possible, as is illustrated in Fig. 1. The IV′ form may tautomerize to IV either by way of the transition state of a four-membered ring, as is shown in Fig. 1 (a), or by way of the transition state of a five-membered ring, as is shown in Fig. 1(b). The transition state of Fig. 1(b) seems more favorable than that of Fig. 1(a), since the nitrogen atom and the hydrogen atom are more closely situated in Fig. 1(b) than in Fig. 1(a). If the compound IV′ tautomerizes to IV by way of the five-membered transition state, the osazone formed must be the α-osazone. When a compound like 1′, 1′-diphenylbenzeneazomethane is to tautomerize to a hydrazone, it must go through a four-membered transition state. It is highly likely that the rate of the tautomerization of IV′ to IV_α is much faster than that of 1′, 1′-diphenylbenzeneazomethane.

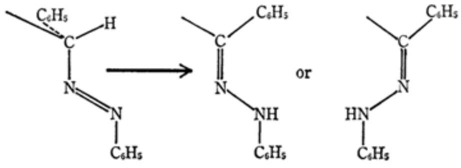

Fig. 1(a)

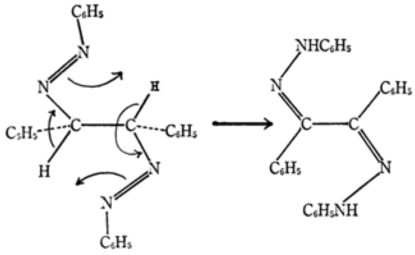

Fig. 1(b)

Thus, the mechanism proposed above as plausible seems to account for the available experimental data fairly well.

When Milligan and Minor[7] oxidized benzalphenylhydrazone with ammoniacal silver nitrate in dimethylformamide, they isolated two products, one melting at 201°C, and the other, at 187°C. They assigned the structure III to the former and the IV′ structure to the latter. Their assignment is surprising, especially in view of the existing experimental data.

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[5] H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, New York (1961), p. 327.

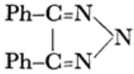
[6] J. N. Brough, B. Lytge and P. Waterhouse, *J. Chem. Soc.*, **1954**, 4069.

[7] T. W. Milligan and B. C. Minor, *J. Org. Chem.*, **27**, 4663 (1962).

The compound melting at 186°C was obtained from the oxidation of benzalphenylhydrazone with mercuric oxide,1) amyl nitrite,2,3) or sodium hypoiodite.3) Minunni,1) Pechmann,2) and Ingle and Mann3) assigned the structure II to this compound. Both Pechmann2) and Ingle and Mann3) reduced the compound melting at 186°C and obtained benzalphenylhydrazone, I. This fact is consistent with the structure II, but not with the structure IV′, which was suggested by Milligan and Minor.

The compound melting at 186°C is "very insoluble in almost all solvents, and dissolves but sparingly in hot benzene and chloroform."3) This solubility characteristic seems to go better with the structure II than with the structure IV′. Such azo compounds as $C_5H_5N{=}NCH(C_6H_5)_2$ and $(C_6H_5)_2CHN{=}NCH(C_6H_5)_2$ very readily dissolve in benzene and chloroform, and even in ligroin. It seems unlikely that the compound possessing the structure IV′ is very insoluble in almost all solvents.

The only data which seems to favor the structure IV′ is its NMR spectrum, which shows the aromatic multiplet at −436 c. p. s. and another signal at −343 c. p. s. (4.28 τ), the latter "corresponding in position and intensity to that expected for two protons on benzylic carbon atoms substituted by azo-unsaturation."7) However, the compound melting at 186°C was only sparingly soluble in hot chloroform, and the NMR spectrum measured in deuteriochloroform may not be too reliable. It was not possible to prepare a 0.001 M solution of the compound in chloroform due to its small solubility. The reduction with phenylhydrazine and the solubility of the compound melting at 186°C seem to be more persuasive than the NMR spectrum.

The compound melting at 208°C was converted to β-benzilosazone (IV_β) (m. p. 225°C) by heating it with phenylhydrazine, or by heating it with ethyl succinate.3) The compound yielded benzil and triphenylosotriazole,  upon reaction with sulfuric acid and water. β-Benzilsazone yielded only benzil and no triphenylosotriazole upon reaction with sulfuric acid and water. On the basis of these findings, Ingle and Mann3) assigned the structure IV_α to the compound melting at 208°C. Its infrared spectrum was very much similar to, but not superimposable upon, that of β-benzilosazone.

The compound melting at 202°C was assigned the structure III by Ingle and Mann3) and by Milligan and Minor7), but without any convincing evibence. Its ultraviolet spectrum ($\lambda_{max}^{CHCl_3}$ 298, 335 mμ: ε, 19400, 37000) and infrared spectrum (NH at 3330 cm^{-1} and ArC=N– at 1590, 1543, 1485 cm^{-1})7) were very similar to those of α-benzilosazone melting at 208°C ($\lambda_{max}^{CHCl_3}$ 295 (18300), 340 mμ (33200); 3330, 1590, 1543, 1485 cm^{-1}). It seems that the compound melting at 202°C may be the impure α-benzilosazone (m. p. 208°C).

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