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The Chemistry of Polyazanes. VI. The Oxidation of ω, ω′-Dibenzoylcarbohydrazide

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ω, ω′-Dibenzoylcarbohydrazide (DBC) was oxidized with sodium hypochlorite in an aqueous ethanolic solution at -70°C. At first the solution had a deep red color, but it gradually faded away. The products of the reaction isolated were benzoic acid, ethyl benzoate, carbon dioxide, 2-phenyl-1, 3, 4-oxadiazol-5-one, and *N, N′*-dibenzoylhydrazine. Then, DBC was oxidized with hypochlorous acid, the products of this reaction were not very different from those obtained with sodium hypochlorite. A plausible mechanism was presented, which assumed the formation of bis(benzoylimino)urea, which was then decomposed heterolytically by the nucleophilic attack of ethanol and water molecules.

Compounds containing a chain of several nitrogen atoms have been investigated in our laboratories

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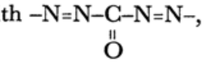
in the last few years.[1-5] In relation to these compounds, our attention has been drawn to a compound in which a chain of four nitrogen atoms is intercepted by a carbonyl group, namely, bis-(benzoylimino)urea (BIU). In BIU, two benzoyl radicals are connected with  $-N{=}N-\underset{\underset{O}{\|}}{C}-N{=}N-$, which may change spontaneously into gaseous nitrogen molecules and a carbon monoxide molecule. If BIU is prepared and if it then decomposes at very low temperatures into two benzoyl radicals, two nitrogen molecules and one carbon monoxide molecule, BIU might be used as an initiator of polymerization at very low temperatures.

Stollé and Krauch[6] observed that the oxidation of ω, ω'-dibenzoylcarbohydrazide (DBC) with an aqueous sodium hypochlorite solution gave a yellow-red color, and that the color immediately disappeared with evolution of gas. They did not, however, elucidate the structure and the nature of the compound possessing the yellow-red color.

The oxidation of DBC with an aqueous sodium hypochlorite solution and with a hypochlorous acid solution has now been investigated in detail and will be described in this paper.

Experimental

ω, ω'-Dibenzoylcarbohydrazide (DBC).—DBC was prepared according to the method of Stollé and Krauch.[6] Seventy grams of carbohydrazide (0.716 mol.) was dissolved in 750 ml. of a 1.6 N sodium hydroxide solution. To this solution, 202 g. of benzoyl chloride (1.423 mol.) was stirred, drop by drop, with cooling. After the mixture had been allowed to stand for 12 hr., the precipitates were filtered off, and washed with water and ether. The yield of crude DBC was 200 g. (0.672 mol.). It was recrystallized from ethanol. M. p. 204.5°C (lit.: 205°C).

The Oxidation of DBC with a Sodium Hypochlorite Solution.—First, a blank test was run in order to check whether ethanol, used as an antifreeze solvent, is oxidized with sodium hypochlorite. One milliliter of a 6.965% aqueous sodium hypochlorite solution and 3.0 ml. of water were mixed at 0°C. To this solution 25.0 ml. of ethanol was added, and the mixture was immediately cooled to -70°C. Then 1.5 g. of potassium iodide, 3 ml. of glacial acetic acid, and 15 ml. of ethanol were added. After it had been warmed to room temperature, the solution was titrated with a 0.1037 N sodium thiosulfate solution. The titer was 9.70 ml. In the absence of ethanol, the titer was 9.75 ml.

Run 1.—Fifteen milliliters of a 6.965% aqueous sodium hypochlorite solution (13.41 mmol.) and 45 ml. of water were mixed at 0°C. Three-hundred-seventy-five milliliters of cooled ethanol was added to this solution, and this mixture was immediately cooled to -70°C. Then this cooled mixture was added to a solution of 2.091 g. of DBC (6.67 mmol.) in 300 ml. of ethanol which had been cooled to -70°C. The mixed solution had a deep red color at -70°C. After about 3 min., the color turned orange and gradually faded away. The solution was stirred for about 2 more hr. at -70°C, and then warmed to room temperature.

After it had been allowed to stand for a day, the mixture was distilled by the use of a 30-cm. Vigreux column. The ethanol was then distilled off, and a small amount of a brown residue remained. Sixty milliliters of ether was added to this residue, and the ethereal solution was dried with anhydrous sodium sulfate. After the evaporation of ether under reduced pressure, reddish-brown solids, weighing 1.40 g., remained. This solid material was divided into a petroleum ether-soluble fraction and a petroleum ether-insoluble fraction. The infrared spectrum of the petroleum ether-soluble fraction indicated the presence of benzoic acid and ethyl benzoate. It was found, by the use of the absorption of benzoic acid at 1415 cm^{-1} and that of ethyl benzoate at 1110 cm^{-1}, that 0.689 g. of benzoic acid (5.65 mmol.) and 0.164 g. of ethyl benzoate (1.09 mmol.) were present in this fraction.

The petroleum ether-insoluble fraction consisted of crystals weighing 0.261 g. and melting at 135°C. After they had been recrystallized three times from water, the crystals melted at 138—139°C. The crystals were identified as 2-phenyl-1, 3, 4-oxadiazol-5-one from the infrared spectrum and from the melting point of the mixture with an authentic sample (m. p. 139°C).[7]

Run 2.—Run 2 was different from Run 1 with respect to the work-up; after the reaction was over, the solution was acidified and the amount of carbon dioxide was analyzed.

Twenty milliliters of a 0.765 M aqueous sodium hypochlorite solution (15.30 mmol.) and 40 ml. of water were mixed at 0°C. Three-hundred-seventy-five milliliters of cooled ethanol was then added to this solution, and the mixture was immediately cooled to -70°C. Then this cooled mixture was added to a solution of 2.270 g. of DBC (7.61 mmol.) in 300 ml. of ethanol which had been cooled to -70°C in a one-liter, four-necked flask equipped with a mercury-sealed stirrer and with an outlet leading to an apparatus for the measurement of carbon dioxide. The mixed solution had a deep red color at -70°C. After about two minutes, however, the color turned orange. The mixed solution was stirred for two hours at -70°C. Then it was warmed to room temperature, and 13.81 ml. of 1.108 M hydrochloric acid (15.30 mmol.) was added. In order to determine the amount of carbon dioxide present, the solution was swept by a stream of a CO_2-free air, which was then led to a tube containing soda-lime. The increase in the weight of the soda-lime tube

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[1] H. Minato and M. Oku, This Bulletin, **38**, 1529 (1965).

[2] H. Minato and T. Fujisawa, ibid., **39**, 1054 (1966).

[3] H. Minato, M. Oku and S. Chan, ibid., **39**, 1049 (1966).

[4] H. Minato, M. Ibata and H. Iwai, *J. Chem. Soc. Japan, Ind. Chem. Sect. (Kogyo Kagaku Zasshi)*, **69**, 184 (1966).

[5] H. Minato, H. Tateno and H. Yokokawa, This Bulletin, in press.

[6] R. Stollé and K. Krauch, *Ber.*, **47**, 727 (1914).

[7] A. Dornow and K. Bruncken, ibid., **82**, 121 (1949).

was 0.1575 g. after the carbon dioxide had been completely absorbed. The pH of the mixed solution was 3.0.

After it had then been allowed to stand for a day, the solution was distilled by the use of water bath kept at 85°C. When about 10 ml. of the residual liquid was present in the flask, the distillation was stopped. Then the distillate was carefully redistilled unitl about 100 ml. remained in the flask, and the residual liquid was gas-chromatographed by the use of a Shimadzu GC-2B gas chromatograph; the presence of ethyl benzoate was detected and 2.33 mmol. of ethyl benzoate was found by the use of diphenyl ether as the internal standard.

To the 10-ml. residue of the first distillation, 300 ml. of ether was added. White precipitates were filtered off and found to be sodium chloride. When the ethereal solution was distilled, the residue was a mixture of white precipitates and a brown pasty oil. The white solids were filtered off, washed, and recrystallized from ethanol; m. p. 235—240°C. The infrared spectrum was exactly the same as that of authentic *N*, *N'*-dibenzoylhydrazine (m. p. 234—238°C).[8]

When the filtrate and washings were evaporated, a brown, pasty residue weighing 2.052 g. was obtained. This was found to be a mixture of benzoic acid and ethyl benzoate by a study of its infrared spectrum. 5.39 mmol. of benzoic acid and 2.22 mmol. of ethyl benzoate were found to be present.

Carbon monoxide was found to be absent among the reaction products in a separate experiment using iodine pentoxide and potasssium iodide.

The Oxidation of DBC with Hypochlorous Acid.—First, a blank test was run in order to check whether or not ethanol was oxidized with hypochlorous acid. 2.003 g. of a 0.732 M aqueous hypochlorus acid solution was cooled to 0°C. To this solution 50 ml. of ethanol and 6 ml. of water were added, and the mixed solution was immediately cooled to −70°C. Then 2 g. of potassium iodide, 3 ml. of glacial acetic acid, and 30 ml. of ethanol were added to the solution. After it had been warmed to room temperature, the solution was titrated with a 0.1037 N sodium thiosulfate solution. The titer was 27.65 ml., which corresponded to a 0.728 M hypochlorous acid solution. This test showed that only 0.55% of the hypochlorous acid initially present was consumed by the reaction with ethanol.

21.60 ml. of a 0.640 M aqueous hypochlorous acid solution (13.82 mmol.) and 38.4 ml. of water were mixed at 0°C. After 375 ml. of cooled ethanol had then been added to this solution, the mixture was immediately cooled to −70°C. Then this cooled mixture was added to a solution of 2.052 g. of DBC (6.88 mmol.) in 300 ml. of ethanol which had been cooled to −70°C in a one-liter, four-necked flask equipped with a mercury-sealed stirrer and with an outlet leading to an apparatus for the determination of carbon dioxide. The mixture did not acquire a deep red color, but only a light yellow color. After it had been kept at −70°C for two hours, it was warmed to room temperature. The increase in the weight of the soda-lime tube was 0.1530 g., corresponding to the evolution of 3.47 mmol. of carbon dioxide. After it had then been allowed to stand at room temperature for a day, the mixed solution was distilled. 6.18 mmol. of ethyl benzoate was found to be present in the distillate by the use of a Shimadzu GC-2B gas chromatograph. The residue was washed with petroleum ether, and the white solids (m. p. 127°C) were found, by a study of the infrared spectrum, to be *N*-benzoyl-*N'*-ethoxycarbonylhydrazine (m. p. 127°C). The petroleum ether-washings were evaporated to yield an oil weighing 0.6154 g. Its infrared spectrum showed that it contained 0.671 mmol. of benzoic acid and 2.04 mmol. of ethyl benzoate.

The Oxidation of DBC with Sodium Hypochlorite and the Reduction of the Oxidation Product with Hydrogen Sulfide.—Ten milliliters of a 0.433 M aqueous sodium hypochlorite solution (4.33 mmol.) and 7.5 ml. of water were mixed at 0°C. One hundred milliliters of cooled ethanol was added to this solution, and this mixture was immediately cooled to −70°C. Then this cooled mixture was added to a solution of 0.642 g. of DBC (2.15 mmol.) in 90 ml. of ethanol which had been cooled to −70°C. When the mixed solution possessed a deep red color, 4.5 ml. of a 1.0 M hydrochloric acid solution was added, after which hydrogen sulfide was passed into this mixed solution for five minutes. Then it was warmed to room temperature.

After the mixture had been allowed to stand at room temperature for a day, it was distilled. Most of the liquid was distilled at about 79°C, but a yellowish residue remained. It was shaken with 20 ml. of water, and the precipitates were filtered; this treatment was repeated four times. Then the precipitates were shaken with 20 ml. of ether, and the solids were filtered; this procedure was repeated four times. The white solids obtained weighed 0.115 g. (0.385 mmol.), and melted at 199—203°C. The infrared spectrum was exactly the same as the infrared spectrum of the authentic DBC. After the ethereal washings had been evaporated, a yellowish-brown residue, weighing 0.309 g., remained. The infrared spectrum showed that the residue contained 0.034 mmol. of benzoic acid and 0.306 mmol. of ethyl benzoate.

Results and Discussion

ω, *ω'*-Dibenzoylcarbohydrazide (DBC) was oxidized with sodium hypochlorite at −70°C in a mixture of water and ethanol; the latter was used as the anti-freeze. When DBC and the

Table I. Products of oxidation of DBC

Product (mol./mol. DBC)	Oxidant		
	NaOCl		HOCl
	Run 1	Run 2	
Benzoic acid	0.847	0.708	0.098
Ethyl benzoate	0.163	0.598	1.195
2-Phenyl-1, 3, 4-oxadiazol-5-one	0.241	—	—
N, *N'*-Dibenzoylhydrazine	—	0.075	—
N-Benzoyl-*N'*-ethoxycarbonylhydrazine	—	—	0.194
Carbon dioxide	(not determined)	0.468	0.505
% C_6H_5 accounted for	62.6	72.8	74.4
% CO accounted for	49.7	64.1	72.9

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8) H. H. Hatt, "Organic Syntheses," Coll. Vol. II., 208 (1943).

oxidant were mixed, the mixed solution had a deep red color, but this gradually faded away. The results of an analysis of the products of the reaction are shown in Table I.

The products of the decomposition of bis(benzoylimino)urea (BIU), which was supposed to be the oxidation product of DBC, indicate that BIU did not decompose homolytically with the production of free radicals. The products of the reaction are best described by the nucleophilic attack of ethanol or water molecules or ethoxide or hydroxide ions upon benzoyl carbon atoms of BIU, as is shown in Fig. 1. When sodium hypochlorite was used as the oxidizing agent, the medium was alkaline, the ethoxide ions and hydroxide ions present may be supposed to be far more nucleophilic than the ethanol and water molecules.

If DBC was oxidized in a non-alkaline condition, BIU formed might decompose homolytically to yield free radicals. In order to check this possibility, DBC was oxidized with hypochlorous acid. The products of the decomposition of BIU in an acid medium, shown in Table I, indicate that the BIU formed was attacked by ethanol and water molecules and decomposed heterolytically rather than homolytically. The products of decomposition were not very different from those formed in an alkaline condition. 0.24 mol. of 2-phenyl-1, 3, 4-oxadiazol-5-one was produced from one mole of BIU in Run 1 with sodium hypochlorite. In the case of Run 2, hydrochloric acid was added to the reaction mixture after the reaction had been completed; this acidification must have decomposed 2-phenyl-1, 3, 4-oxadiazol-5-one. When hypochlorous acid was used as the oxidant, none of this heterocyclic compound was detected.

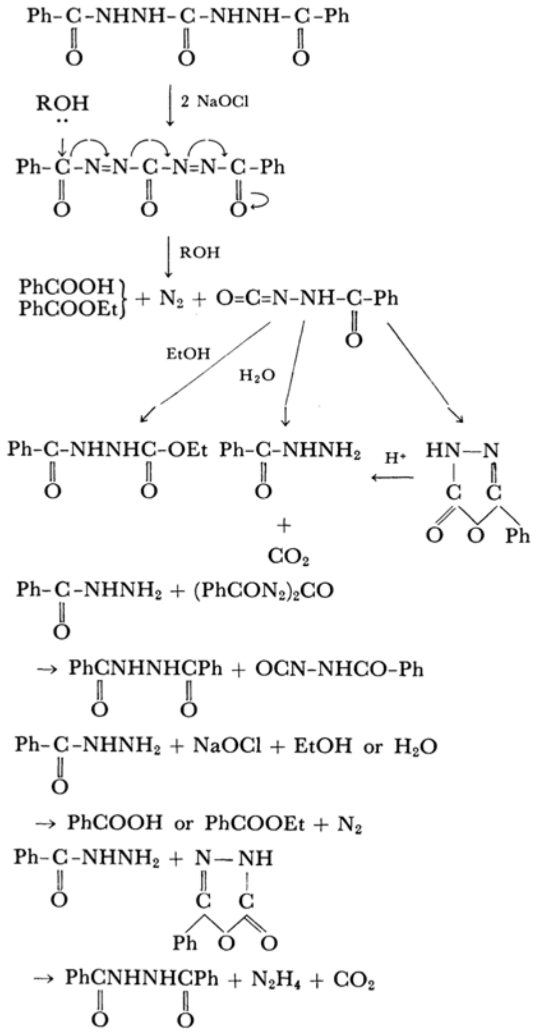
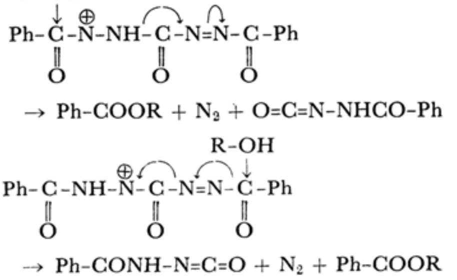


Fig. 1. Plausible scheme of decomposition of BIU.

The behavior of the deep red substance can best be explained by assuming that bis(benzoylimino)-urea is produced by the oxidation of DBC. However, in order to confirm this, the deep red substance was reduced by hydrogen sulfide. Stollé oxidized *N, N'*-diacetylhydrazine and obtained diacetyldiimide, which was a deep red and unstable oil. He then reduced it with hydrogen sulfide and thus obtained *N, N'*-diacetylhydrazine again.

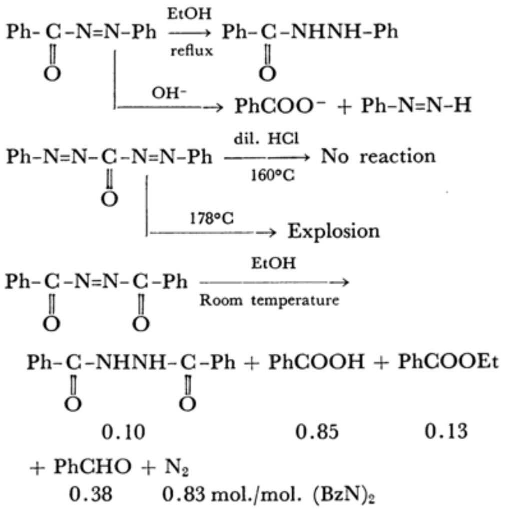
Soon after the DBC solution and sodium hypochlorite solution had been mixed and the deep red color produced, hydrogen sulfide gas was introduced in order to reduce the deep red substance. After the work-up, about 18% of the amount of DBC originally present was isolated. All the data, including those of this reduction experiment, can best be explained by assuming that the deep red substance produced by the oxidation of DBC is bis(benzoylimino)urea.

The nucleophilic attack of ethoxide and hydroxide ions upon BIU under alkaline conditions seems reasonable, but the equally fast attack of ethanol and water molecules on BIU under acid conditions seems somewhat surprising. Probably the azo double bonds are protonated, and this protonation induces the nucleophilic attack of ethanol and water molecules.



When DBC was oxidized under acid conditions, no deep red color was observed, even at the instant of mixing the reactants. This fact is reasonable, since the protonated BIU is not likely to have a deep color.

The structures of benzoylphenyldiimide,⁽⁹⁾ bis(phenylimino)urea,⁽¹⁰⁾ and dibenzoyldiimide⁽¹¹⁾ are somewhat related to the structure of BIU, and it is interesting to note their behavior in hydroxylic solvents:



$$\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}N{=}N{-}Ph \xrightarrow[\text{reflux}]{\text{EtOH}} Ph{-}\underset{\underset{O}{\|}}{C}{-}NHNH{-}Ph}$$

$$\xrightarrow{\mathrm{OH^-}} \mathrm{PhCOO^-} + \mathrm{Ph{-}N{=}N{-}H}$$

$$\mathrm{Ph{-}N{=}N{-}\underset{\underset{O}{\|}}{C}{-}N{=}N{-}Ph \xrightarrow[160^\circ C]{\text{dil. HCl}} \text{No reaction}}$$

$$\xrightarrow{178^\circ\mathrm{C}} \text{Explosion}$$

$$\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}N{=}N{-}\underset{\underset{O}{\|}}{C}{-}Ph \xrightarrow[\text{Room temperature}]{\text{EtOH}}}$$

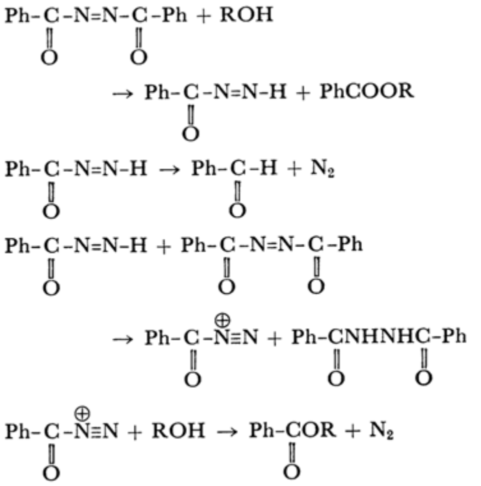
$$\underset{0.10}{\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}NHNH{-}\underset{\underset{O}{\|}}{C}{-}Ph}} + \underset{0.85}{\mathrm{PhCOOH}} + \underset{0.13}{\mathrm{PhCOOEt}}$$

$$+ \underset{0.38}{\mathrm{PhCHO}} + \underset{0.83\ \text{mol./mol.}\ (\mathrm{BzN})_2}{\mathrm{N_2}}$$

The decomposition of dibenzoyldiimide is especially interesting. Leffler and Bond⁽¹¹⁾ determined the rates of its decomposition and found that $k_1=7.33\times10^{-6}\ \mathrm{sec}^{-1}$ in benzene at 100°C (initial concentration (C_0)=0.03 M); $k_1=137\times10^{-6}\ \mathrm{sec}^{-1}$ in benzyl alcohol at 61.9°C (C_0=0.0051 M); $k_1=75.6\times10^{-6}\ \mathrm{sec}^{-1}$ (C_0=0.008 M), and $k_1=124\times10^{-6}\ \mathrm{sec}^{-1}$ (C_0=0.0135 M) in ethanol at 19.69°C.

Although both the products and the kinetics of the decomposition seem to suggest that the decomposition of the diimide in ethanol at 20°C is an ionic reaction initiated by the nucleophilic attack of ethanol on the benzoyl carbon, Leffler and Bond favored a free radical mechanism. Since they found acrylonitrile to polymerize in a benzene solution at 75°C, they thought the decomposition of the diimide in benzene at 75°C was likely to involve some homolytic decomposition. They argued that ethyl benzoate could be formed from the radical-ethanol complexes by the loss of hydrogen to another radical or to a molecule of dibenzoyldiimide, and that the second oxygen needed for the conversion of benzoyl radical to benzoic acid probably came from the solvent ethanol. These arguments seem unsatisfactory. They did not explain the formation of *N, N'*-dibenzoylhydrazine, either.

On the basis of the findings of the decomposition of bis(benzoylimino)urea, an ionic mechanism seems to be a better mechanism for the decomposition of dibenzoyldiimide, at least in ethanol near room temperature. The following reaction scheme seems to explain the reaction products:



$$\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}N{=}N{-}\underset{\underset{O}{\|}}{C}{-}Ph + ROH}$$

$$\rightarrow \mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}N{=}N{-}H + PhCOOR}$$

$$\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}N{=}N{-}H \rightarrow Ph{-}\underset{\underset{O}{\|}}{C}{-}H + N_2}$$

$$\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}N{=}N{-}H + Ph{-}\underset{\underset{O}{\|}}{C}{-}N{=}N{-}\underset{\underset{O}{\|}}{C}{-}Ph}$$

$$\rightarrow \mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}\overset{\oplus}{N}{\equiv}N + Ph{-}\underset{\underset{O}{\|}}{C}NHNH\underset{\underset{O}{\|}}{C}{-}Ph}$$

$$\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}\overset{\oplus}{N}{\equiv}N + ROH \rightarrow Ph{-}\underset{\underset{O}{\|}}{C}OR + N_2}$$

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9) G. Ponzio and G. Charrier, *Gazz. Chem. Ital.*, **39**, I, 598 (1909); S. G. Cohen and J. Nicholson, *J. Org. Chem.*, **30**, 1162 (1965).

10) E. Bamberger, *Ber.*, **44**, 3745 (1911).

11) J. E. Leffler and W. B. Bond, *J. Am. Chem. Soc.*, **78**, 336 (1956).