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REASSIGNMENT OF STRUCTURES OF THE DIHYDRO-*v*-TETRAZINES[1]

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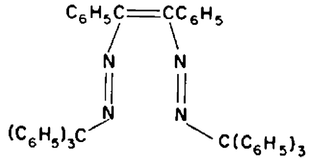
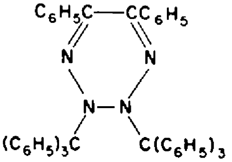
Abstract—The white crystalline product III from the oxidation of biacetyl *bis*-benzoylhydrazone, previously believed to be a dibenzoyldihydro-*v*-tetrazine has now been shown by its N.M.R. and infrared spectrum as well as its ready hydrolysis with acid and the reduction of one benzoyl group to benzyl alcohol to be not a tetrazine but instead the enol benzoate IIIB of 1-benzoylamino-4,5-dimethyl-1,2,3-triazole, an imino anhydride. The previously observed rearrangement of this substance on heating with the formation of 1-[N,N,-dibenzoylamino]-4,5-dimethyl-1,2,3-triazole is then reinterpreted as a 1,3-benzoyl migration from oxygen to nitrogen.

Similarly the oxidation product of benzil *bis*-benzoylhydrazone is, instead of a dihydrotetrazine, the enol benzoate (XII) of 1-benzoylamino-4,5-diphenyl-1,2,3-triazole and the oxidation product from the *bis*-benzoylhydrazone of pyruvaldehyde is the enol benzoate VIII of 1-benzoylamino-5-methyl-1,2,3-triazole. It seems unlikely that any reported examples of diacyldihydro-*v*-tetrazines analogous to III are authentic.

A PREVIOUS study[2] of the red product obtained from the reaction of the silver salt of phenylnitroacetonitrile with triphenylmethyl chloride led to the assignment of the *bis*-azoethylene structure I. Structural ambiguity introduced by the possibility of a tautomeric equilibrium of I with the dihydro-*v*-tetrazine structure II has prompted a further investigation of such systems.[3]



I



II

As a model compound with the ring system of II, was chosen the white crystalline substance III, m.p. 140°, which had been prepared[4,5] by oxidation of biacetyl *bis*-benzoylhydrazone (IV) and for which structure IIIA had seemed reasonably well established.[3]

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[1] This work was supported by a grant (G-14, 480) from the National Science Foundation, for which we express our appreciation.

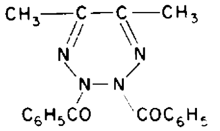
[2] D. Y. Curtin, R. J. Crawford and D. K. Wedegaertner, *J. Org. Chem.*, **27**, 4300 (1962).

[3] For reviews of the earlier work see J. G. Erickson, P. F. Wiley and V. P. Wystrach, *The Chemistry of Heterocyclic Compounds*, Interscience, New York (1956), Chapter III; E. Hoggorth, *Chemistry of Carbon Compounds*, Vol. IV C (E. H. Rodd Editor), Elsevier, Amsterdam, 1960, p. 1576 ff.; J. Doeuvre, *Traité de Chimie Organique*, Vol. XXI, Edited by V. Grignard, G. Dupont and R. Locquin, Masson et Cie, Paris 1953, p. 1087 ff.

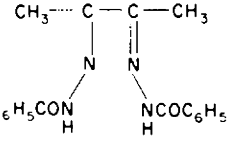
[4] H. v. Pechmann and W. Bauer, *Chem. Ber.* **33**, 644 (1900).

[5] H. v. Pechmann and W. Bauer, *Chem. Ber.* **42**, 659 (1909).

The N.M.R. spectrum (Fig. 1) suggested however, that the structural assignment IIIA was incorrect. In particular the two methyl groups which are equivalent in the structure IIIA showed absorption at different positions—at 7·75 and 7·65 τ, respectively. The same separation persisted in spectra measured at higher (60°) and lower (−28°) temperatures. Furthermore the infrared spectrum showed a strong absorption at 1750 cm^{-1} which it was not easy to reconcile with structure IIIA. The hydrazone IV had carbonyl absorption in the infrared at 1655 cm^{-1}.



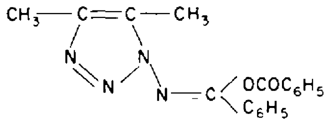
IIIA



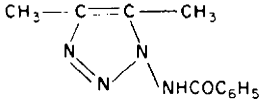
IV

Fig. 1. N.M.R. spectrum of a 10% solution in deuterochloroform of the benzoylaminotriazole enol benzoate III.

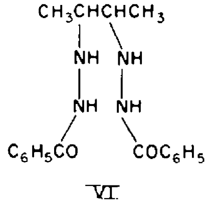
The spectral and chemical evidence to be discussed lead to the assignment to III of the amidotriazole enol ester (or imino anhydride) structure IIIB.



IIIB



V



VI

It will be seen that the spectral data cited are readily reconciled with the new structure IIIB. The explanation of the non-equivalence of the methyl absorptions in the N.M.R. follows immediately.

The carbonyl absorption frequency of an enol benzoate is expected to be at about 1750 cm^{-1} as was observed.[6] The chemical behavior of III confirms the structure IIIB. The ready hydrolysis[7] of one of the two benzoyl groups of III with the formation of

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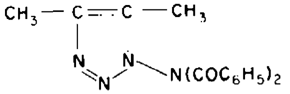
[6] D. Y. Curtin and M. L. Poutsma, *J. Amer. Chem. Soc.*, **84**, 4887 (1962).

[7] This reaction had been reported previously[5,8] to give a 90% yield of V with an unspecified m.p. and after an unspecified time.

the 1-benzoylaminotriazole V was confirmed. Hydrolysis occurred so readily that a 60% yield of V was obtained after treatment of III with concentrated hydrochloric acid for 5 min at room temperature. Reduction of III with lithium aluminum hydride gave benzyl alcohol and the benzamide V, behavior to be expected of the enol benzoate IIIB, and not consistent with the benzoyltetrazine structure IIIA. By way of comparison, the reduction of the dibenzoylhydrazone IV gave no cleavage of the benzoyl groups to benzyl alcohol but instead a product with four hydrogen atoms more than the starting material IV, probably one of the diastereoisomeric dibenzoylhydrazines VI formed by a simple reduction of the two carbon–nitrogen double bonds.[9,10] The infrared absorption (carbonyl absorption, 1640 cm^{-1}, N–H absorption at 3380 cm^{-1}) and the N.M.R. (methyl protons, doublet at 8·9τ, J6 c/s, C–H, multiplet at 6·75τ; phenyl protons multiplets at 2·5 and 2·1τ; and NH, multiplet at 1·2τ) support the structure VI.

The isomerization[8,11] of III at 150° to the 1-[N,N-dibenzoylamino]-triazole VII is of particular interest in view of the structural reassignment IIIB. It will be seen that this reaction is a 1,3-benzoyl migration (in this case from oxygen to nitrogen) which appears to be closely related to a number of such 1,3-migrations which have been found in other systems.[12] The structure assigned[8] previously to the dibenzoylamino compound VII was confirmed by the ultraviolet spectrum (Fig. 2) similar to spectra of other aminotriazole derivatives, by the infrared carbonyl absorption at 1715 cm^{-1} and by the N.M.R. which showed the methyl absorption as an incompletely resolved doublet with the peaks separated by 0·1 p.p.m.



VII

Reduction of the dibenzoylaminotriazole VII with lithium aluminum hydride was found to give benzyl alcohol. Such a reductive cleavage has been reported with other N-acyl heterocyclic compounds.[9b]

The "dibenzoyltetrazine" obtained by Stollé[8] from the *bis*-benzoyl-hydrazone of pyruvaldehyde must also be assigned a new structure, and has now been shown to be the aminotriazole derivative VIII, analogous to IIIB. The supporting evidence includes a characteristic infrared absorption at 1750 cm^{-1} and an ultraviolet spectrum similar to that of III. There is the more subtle problem in this case of deciding between structure VIII and the isomeric structure IX. Although it was reported by

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[8] See R. Stollé, *Chem. Ber.*, **59**, 1743 (1926) for earlier structural revisions.

[9] N. G. Gaylord, *Reduction with Complex Hydrides*, Interscience, New York, 1955, (a) p. 793 ff. (b) p. 544 ff.

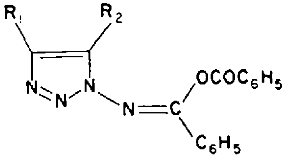
[10] It is of interest in this connection that an attempt[5] to reduce III with phenylhydrazine, a method which had been used successfully with structurally related azo compounds, led only to cleavage of a benzoyl group to give V.

[11] R. Stollé, *J. prakt. Chem.*, [2] **78**, 546 (1908).

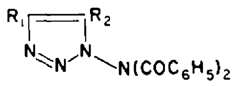
[12] See D. Y. Curtin and M. L. Poutsma, *J. Amer. Chem. Soc.*, **84**, 4892 (1962) for references to other examples. We are indebted to Dr. Michael Seidel for calling to our attention a possibly related 1,4-benzoyl migration[13] implicit in the formation of N,N′-dibenzoylhydrazine from 2,5-diphenyltetrazole and benzoic acid at 180°.

[13] R. Huisgen, J. Sauer and M. Seidel, *Chem. Ber.*, **94**, 2503 (1961).

Stollé[8] that the substance VIII, when heated at 140° underwent rearrangement to the 4-methyl compound XI, it has not been possible to repeat this experiment. Instead we have found the rearrangement leads to the 5-methyl compound X. This is in agreement with the observation by Stollé[8] that vigorous hydrolysis of VIII led to 1-amino-5-methyltriazole. The analogous diphenyl "dibenzoyltetrazine"[8,11] also must be reassigned the structure of an aminotriazole derivative XII since it, like III and VIII, has the carbonyl absorption at 1750 cm^{-1} and undergoes analogous reactions on heating or hydrolysis. It appears then that no authentic 2,3-dibenzoyldihydro-1,2,3,4-tetrazine is known at present.



VIII: $R_1 = H; R_2 = CH_3$
IX: $R_1 = CH_3; R_2 = H$
XII: $R_1 = R_2 = C_6H_5$



X: $R_1 = H; R_2 = CH_3$
XI: $R_1 = CH_3; R_2 = H$

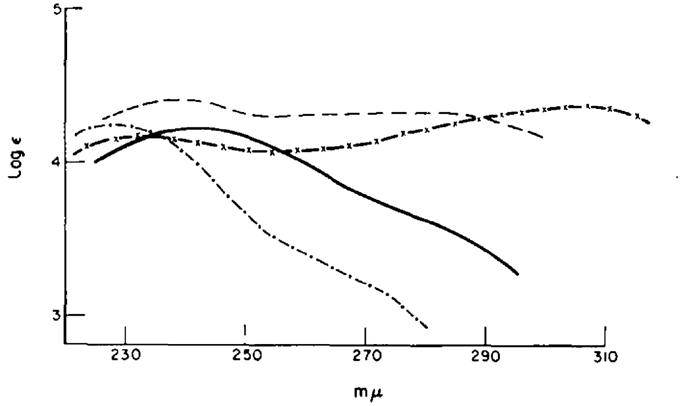
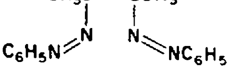


FIG. 2. Ultraviolet spectra in absolute ethanol of (– – – –) III; (—x—x) biacetyl-*bis* benzoyl-hydrazone (IV); (— · — ·) 1-benzoylamino-4,5-dimethyltriazole (V); (——) 1-dibenzoyl-amino-4,5-dimethyltriazole (VII).

In contrast to the benzoylhydrazones discussed above the *bis*-benzeneazo compound XIII, prepared by the method previously employed by von Pechmann,[14] showed a single absorption at 7·4τ when the N.M.R. spectrum was measured in deuterochloroform. The U.V. visible spectrum showed absorption maxima at 490 mμ



XIII

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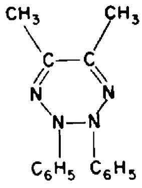
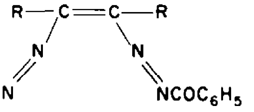
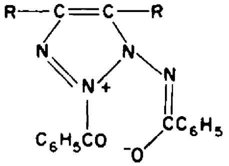
[14] H. von Pechmann, *Chem. Ber.*, **21**, 2751 (1888).

(ϵ 1780), 390 mμ (ϵ 75,500) and at 375 mμ (ϵ 76,500) and a point of inflexion at 240 mμ (ϵ 7,150). While this evidence does not rigorously exclude the possibility that a tautomeric equilibrium exists in solution between the *bis*-azoethylene XIII and the tetrazine XIV it certainly makes such an equilibrium seem improbable.


XIV

The mechanism of formation of enol benzoate III and its relatives by the oxidation of *bis*-hydrazones remains to be investigated. It is by no means impossible that the oxidation of the benzoyl derivatives proceeds initially to give an azo ethylene XV analogous to the diphenyl derivative XIII and that the difference in the two systems is due to the instability with respect to ring closure and benzoyl migration to form the enol benzoate which is possible with the dibenzoyl compound XV but not the phenyl analog. This point is under further investigation.[15]


XV


XVI

EXPERIMENTAL[16]

1-*Benzoylamino-4,5-dimethyl-1,2,3-triazole enol benzoate* (III)

The oxidation of biacetyl *bis*-benzoylhydrazone in ethanol was carried out with aqueous potassium ferricyanide at room temperature following the procedure of von Pechmann.[4,5] The substance after

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[15] A possible intermediate in this reaction sequence is a zwitterionic structure of which one resonance structure is XVI. Dr. A. R. Katritzky has informed us that he has experimental evidence suggesting that III and its relatives have zwitterionic structures rather than the enol benzoate structures such as IIIB as proposed here. While our evidence perhaps does not rule out this possibility completely it seems more compatible with the enol benzoate structures.

[16] All melting points are corrected. Microanalyses were obtained in the Microanalytical Laboratory at the University of Illinois under the direction of Mr. J. Nemeth. Infrared spectra were measured with a Perkin-Elmer Model 21 spectrophotometer and N.M.R. spectra reported in τ units [G. V. D. Tiers, *J. Phys. Chem.* **62**, 1151 (1958)] with a Varian Associates A-60 spectrophotometer at 60 Mc with tetramethylsilane as an internal standard. We are indebted to Mr. O. Norton and Mr. D. Johnson and their associates for these spectra. Ultraviolet spectra were obtained in ethanol with a Bausch and Lomb Spectronic 505 spectrophotometer using 1 cm quartz cells. Molecular weights were determined in benzene with a Mechrolab Vapor Pressure Osmometer, Model 301A, by Mr. J. Nemeth.

"Petroleum ether" refers to the hydrocarbon fraction, b.p. 30–60°.

[17] The high and low temperature spectra were measured with a Varian V-4300-2 spectrophotometer at 60 Mc with a Hewlett-Packard 200-CD Oscillator to calibrate the spectra. The sample was placed in a Varian V-4340 variable temperature probe fitted with a model V-4331 7HR Dewar insert.

recrystallization from ethanol had m.p. 139–140° (*lit.*[4,5] 140°). The ultraviolet spectrum had maxima at 241 mμ (ε 25,000) and 280 mμ (ε 21,400). The infrared spectrum of a 10% solution in chloroform showed strong absorption at 1750 and 1639 cm^{-1}. The N.M.R. spectrum of a 10% solution in deuterochloroform showed peaks at 7·75 and 7·65 (methyl groups) and at 2·4 and 1·9τ with relative areas of 2·9, 3·2, 6·2, 3·9. In the same solvent at —28° and at 60° the N.M.R. spectra[17] were similar to that at room temperature. The separations between the methyl peaks were 0·14 and 0·13 p.p.m., respectively, compared with the value of 0·10 p.p.m. at room temperature. (Found: C, 67·3; H, 5·0; N, 17·5, mol. wt. 316. $C_{18}H_{16}N_4O_2$ requires C, 67·5; H, 5·0; N, 17·5, mol. wt. 320). A somewhat better procedure is as follows.

Oxidation of 3·2 g of *bis*-hydrazone in 60 ml of dry ether with 6 g of yellow mercuric oxide, 0·6 g of magnesium oxide and 3 g of iodine gave 1·2 g of the same product III, m.p. 139–140°, obtained with potassium ferricyanide.

Mild hydrolysis of the enol benzoate III. When 0·3 g of III was treated at room temperature for 5 min with 0·25 ml of concentrated aqueous hydrochloric acid the crystals dissolved and the odor of benzoyl chloride appeared. After neutralization of the acid with sodium bicarbonate to pH 7 there was obtained by filtration 0·13 g (60%) of the benzoylaminotriazole V, m.p. 89–91° [*lit.*[4] m.p. 95° (monohydrate)]. (Found, C, 56·0; H, 5·9; N, 23·7. $C_{11}H_{12}N_4O{\cdot}H_2O$ requires: C, 56·4; H, 6·0; N, 23·9.) The ultraviolet spectrum showed a maximum at 228 mμ (ε 18,000) and the infrared spectrum in chloroform a strong absorption at 1680 cm^{-1}. The N.M.R. in deuterochloroform showed only a single peak for the methyl groups at 7·85τ and aromatic absorption at 2·5 and 2·0τ. When hydrogen chloride was added to the solution the absorption at 7·85 became a doublet centered at 7·6τ and separated by about 0·07 p.p.m. (very weak absorption at 7·85τ due to the starting material remained). In addition there was aromatic absorption at 1·8 and 2·4τ and absorption due to the acidic protons at −3·4τ. The dibenzoylamide VII could be recovered unchanged from treatment with concentrated hydrochloric acid under the same conditions (as shown by the identity of its infrared spectrum with the original).

Reduction with lithium aluminum hydride of the enol benzoate III and the N,N-dibenzoylaminotriazole VII. To a suspension of 0·05 g of lithium aluminum hydride in 10 ml of dry ether was added 0·2 g of III in 20 ml of ether and the mixture heated under reflux for 8 hr. After addition of ice-water, extraction of the ether layer and drying over sodium sulfate, removal of the ether left an oil which was subjected to gas phase chromatography through an 8-ft column packed with silicone (QF-1)(20%) on chromosorb W at 100°. The retention time of 12·5 min. was identical with that of an authentic sample of benzyl alcohol. Neutralization of the reaction mixture (pH 7) and extraction with chloroform and ether gave the benzoylaminotriazole V, identified by a comparison of the infrared spectrum with that of the authentic material and by N.M.R. absorption at 7·85 (singlet), 2·5 and 2·0τ (both of the latter absorptions multiplets). A reduction of VII carried out in the same manner gave benzyl alcohol identified by its retention time in the gas phase chromatography.

Reduction of biacetyl bis-*benzoylhydrazone with lithium aluminum hydride.* Reduction of 0·40 g of the benzoylhydrazone[5] IV with 0·1 g of lithium aluminum hydride in 60 ml of dry ether was carried out for 8 hr with stirring after which addition of water and extraction of the ether layer gave when the ether was evaporated a white solid which was washed with ether–petroleum ether had m.p. 176–178°. (Found: C, 66·4; H, 6·7; N, 17·1. $C_{18}H_{22}N_4O_2$ requires C, 66·2; H, 6·8; N, 17·2.)

The infrared spectrum in chloroform showed maxima at 1640 cm^{-1} and 3380 cm^{-1}. The N.M.R. spectrum of a 7% solution in deuterochloroform showed absorption at 8·9τ (a doublet separated by 0·1 p.p.m. as well as multiplets at 6·8, 2·5, and 2·1 with areas of 5·9, 1·9. 6·0, 4·2. Absorption at about 1·2τ may be due to the NH protons.

Thermal rearrangement of the enol benzoate III to 1-(*N,N-dibenzoylamino*)-4,5-dimethyl-1,2,3-*triazole* (VII). When heated at 150° for 90 min with no solvent III (0·20 g) gave after recrystallization from ether–petroleum ether 0·17 g (85%) of the dibenzoylamino compound VII, m.p. 96–97° (*lit.*[5,8] needles, m.p. 115°; or prisms, m.p. 96°). The analytical sample had m.p. 94–96°. The I.R. spectrum in carbon tetrachloride showed strong absorption at 1715 cm^{-1}. The N.M.R. in deuterochloroform showed a doublet for the methyl groups centered at 7·86τ (area 6·1) with a separation of the peaks of 0·1 p.p.m. and two other multiplets at 2·55 and 2·2τ with relative areas of 6·0 and 3·8, respectively. (Found: C, 67·7; H, 5·1; N, 17·6. $C_{18}H_{16}N_4O_2$ requires C, 67·5; H, 5·0; N, 17·5).

Oxidation of pyruvaldehyde bis-*benzoylhydrazone.* 1-*Benzoylamino-5-methyl*-1,2,3-*triazole enol benzoate* (*VIII*). The oxidation carried out by the method of Stollé[8] with mercuric oxide, magnesium oxide and iodine in ether gave the triazole VIII, m.p. 123–124° (*lit.*[8] 124°). (Found: C, 66·2; H, 4·6; N, 18·5. $C_{17}H_{14}N_4O_2$ requires C, 66·7; H, 4·6; N, 18·3.) The U.V. spectrum showed λ_{max} 240 mμ (ε 23,700)and 279 mμ (ε 20,900) and the infrared spectrum in carbon tetrachloride showed strong carbonyl absorption at 1750 and 1642 cm^{-1}. The N.M.R. spectrum in deuterochloroform showed a singlet at 7·55τ with multiplets at 2·4 and 1·8 (rel. areas 3·1, 6·8, and 4·3, respectively.)

Thermal rearrangement of the enol benzoate VIII. When VIII was heated at 140° for 2 hr it was converted to 1-dibenzoyl-amino-5-methyl-1,2,3-triazole, m.p. 132–134°, after recrystallization from ethanol, (*lit.*[8] m.p. 136°; m.p. of 1-dibenzoylamino-4-methyl-1,2,3-triazole, 152°). (Found: C, 66·7; H, 4·7; N, 18·5. $C_{17}H_{14}N_4O_2$ requires C, 66·7; H, 4·6; N, 18·3.) The N.M.R. in deuterochloroform showed absorption at 7·8τ (singlet) as well as multiplets at 2·5 and 2·2τ with relative areas of 3·1, 6·7 and 4·3.

Oxidation of benzil bis-*benzoylhydrazone.* 1-*Benzoylamino*-4,5-*diphenyl*-1,2,3-*triazole Enol benzoate* (XII). Oxidation of benzil *bis*-benzoylhydrazone[18] with alkaline potassium ferricyanide by the method previously reported[19] gave the enol ester XII which after recrystallization from chloroform had m.p. 188–189° (*lit.*[19] 189°). (Found: C, 74·7; H, 4·4; N, 12·6. $C_{28}H_{20}N_4O_2$ requires C, 75·7; H, 4·5; N, 12·6.) The U.V. spectrum showed a maximum at 242 mμ (ε 26,400) with a shoulder at 259 mμ (ε 24,200) and the infrared spectrum of a potassium bromide disk showed strong absorption at 1750 and 1640 cm^{-1}. The N.M.R. spectrum of a 2% solution in deuterochloroform showed only a complex multiplet centered at 2·5τ.

2,3-Bis-*benzeneazo*-2-*butene* (XIII)

Biacetyl *bis*-phenylhydrazone when oxidized with potassium dichromate in dilute acetic acid gave the azo olefin (XIII), dark red needles, m.p. 162° with decomposition (*lit.*[14] m.p. 169° with decomposition). (Found: C, 72.4; H, 6·1; N, 21·1. $C_{16}H_{16}N_4$ requires 72·7; H, 6·1; N, 21·2.) The U.V. spectrum had λ_{max} 375 mμ (ε 76,500), 390 mμ (ε 75,500) and 490 mμ (ε 1780) with a shoulder at 240 mμ (s 7,150). The infrared spectrum of a potassium bromide disk showed broad low absorption at 1615 cm^{-1}. The N.M.R. spectrum of a 10% solution in deuterochloroform showed a singlet at 7·4τ and two multiplets centered at 2·5 and 2·1τ with relative areas of 5·9, 6·1 and 4·1 respectively.

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[18] G. Struve, *J. prakt. Chem.* **50**, 295 (1894).

[19] R. Stollé, W. Münch and W. Kind, *J. prakt. Chem.* **70**, 433 (1904).