charcoal and recrystallization from ethanol to m.p. 109–111°; lit.[8] m.p. 109–111.5°. Commercial peroxyacetic acid solutions, generously donated by BECCO, were used.

Preparation of *o*-Nitrosobenzamide.—To absolute ethanol (40 ml.), previously saturated with anhydrous sodium acetate, was added ~40% peroxyacetic acid (20 ml.). The mixture was centrifuged and the supernatant liquid cooled to 0°. To the cooled solution was added a solution of *o*-aminobenzamide (1.4 g.) in ethanol (20 ml.), and the reaction mixture was allowed to stand for about 1 hr. The solution was then evaporated at room temperature (reduced pressure) to lower volume (about 15 ml.); the precipitated solid was removed by filtration, and washed first with cold ethanol (—10°) and then with ether. The product (1.3 g., 85%) was a pale green solid, m.p. 220° dec. It was stored at −10° in the absence of light until used. Absorption (in ethanol): λ_{max} at 750 (1.40; 0.01 *M* solution), 310 (3.67), and 285 mμ (log ε 3.71). Selected infrared maxima (KBr): 6.7 and 7.9 μ.

Anal. Calcd. for $C_7H_6N_2O_2$: C, 56.00; H, 4.03; N, 18.66. Found: C, 56.51; H, 4.25; N, 18.36. The elemental analysis was done by Dr. S. M. Nagy at Massachusetts Institute of Technology.

Reaction of *o*-Nitrosobenzamide with Cyanide Ion.—*o*-Nitrosobenzamide (2.0 g.) was heated with an equivalent amount of potassium cyanide (or sodium hydroxide) in 60 ml. of 50% aqueous ethanol in a sealed tube at 140–160° for 1.25 hr. The resulting brownish solution was acidified with hydrochloric acid and repeatedly treated with decolorizing charcoal until colorless. The clear solution was then made basic, evaporated to near dryness, and acidified with hydrochloric acid, and the resulting precipitate was removed by filtration. This precipitate was then sublimed once and the yellowish sublimate recrystallized from water. The resulting benzoic acid melted at 122°. Its ultraviolet spectrum in aqueous medium was identical with that of an authentic sample of benzoic acid, and it did not depress the melting point of authentic benzoic acid. The yield of the isolated product was 20% with cyanide ion and 40% with hydroxide ion. The reaction was accompanied by the evolution of a gas, which was dried with liquid nitrogen and then shown to be nitrogen by mass spectral analysis.

Acknowledgment.—The authors wish to thank Professors J. F. Bunnett and J. O. Edwards for their kind interest in this work. Professor Bunnett directed our attention to ref. 4. This work was supported in part by the U. S. Atomic Energy Commission, Contract 1983. The gas analysis was performed at Harvard University through the courtesy of Dr. G. O. Dudek.

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[8] I. M. Heilbron, "Dictionary of Organic Compounds," Vol. I, Oxford University Press, New York, N. Y., 1934, p. 37.

Amines Derived from Dihalopropenes. V.[1a] Reaction of 2-Haloallylamines with Various Bases[1b]

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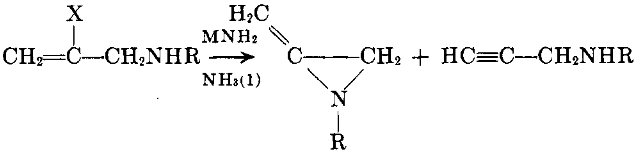
An N-alkylallenimine III is obtained as the main product from the reaction of an N-(2-bromoallyl)-alkylamine I with sodium amide in liquid ammonia,[2,3] but the only discernible product from the reaction of N-(2-chloroallyl)ethylamine (IIa, R = C_2H_5) with potassium amide in liquid ammonia was N-ethylpropargylamine (IVa, R = C_2H_5). In order to determine if the course of the reaction of an N-(2-haloallyl)alkylamine with amide in liquid ammonia was influenced by the alkyl metal cation,[4] we examined the reactions of the N-(2-haloallyl)ethylamines with the common alkali metal amides in liquid ammonia. Reactions were carried out on a small scale, and the yields and product compositions were determined by gas–liquid partition chromatography (g.l.p.c.).



I, X = Br
II, X = Cl

III

IV

We observed no significant difference in the yields or product compositions from reactions of N-(2-bromoallyl)ethylamine (Ia, R = C_2H_5) with lithium amide, sodium amide, and potassium amide. Using a constant amide–Ia mole ratio of 1.2, which Pollard and Parcell found gave optimum yields of allenimines from N-(2-bromoallyl)alkylamines,[2] initial Ia concentrations of 0.25 and 0.5 *M*, and reaction times of 4.5 to 5 hr., imine–amine mixtures consisting of 75–82% N-ethylallenimine (IIIa, R = C_2H_5) were obtained in yields of 48–62%. As the 2,3-dibromopropene used for the preparation of Ia and other N-(2-bromoallyl)alkylamines contained less than 1.5% of the isomeric 1,3-dibromopropenes,[5] we could estimate that the Ia contained less than 2% of the isomeric N-(3-bromoallyl) ethylamines, which yield only the propargylamine under the reaction conditions used for allenimine formation.[6] Thus, most of the IVa was formed from dehydrobromination of Ia.

The product compositions obtained from all reactions of N-(2-chloroallyl)ethylamine (IIa) with any of the three alkali metal amides were identical and consisted of <1% IIIa and >99% IVa. Under the same reaction conditions used for Ia, treatment of IIa at an initial concentration of 0.5 *M* with potassium amide gave yields of 50–56% based on IIa, while use of lithium amide or sodium amide gave yields of 20–29%. When the amide–IIa ratio was increased to more than 2, yields of IVa from reactions of potassium amide with IIa at an initial concentration of 0.4 *M* were increased to over 80%. Comparable yields were also obtained using sodium amide, but reaction times of 9–10 hr. were required instead of 5 hours.

Reactions of N-(2-bromoallyl)methylamine, N-(2-bromoallyl)isopropylamine, and N-(2-bromoallyl)-hexylamine were carried out on a preparative scale with 0.8–1.5 moles of the amine using sodium amide–I ratios of 1.2. These reactions gave 46–70% yields of mixtures of three to four parts of the corresponding

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[1] (a) Part IV: A. T. Bottini, V. Dev, and M. Stewart, *J. Org. Chem.*, **28**, 156 (1963); (b) acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research; (c) American Chemical Society Petroleum Research Fund Fellow, 1961.

[2] C. B. Pollard and R. F. Parrell, *J. Am. Chem. Soc.*, **73**, 2925 (1951).

[3] A. T. Bottini and J. D. Roberts, *ibid.*, **79**, 1462 (1957).

[4] See W. H. Puterbaugh and C. R. Hauser, *J. Org. Chem.*, **24**, 416 (1959).

[5] Treatment of the 2,3-dibromopropene with lithium aluminum hydride in ether gave a mixture of 1- and 2-bromopropenes that was 98.8% 2-bromopropene as determined by g.l.p.c. See L. F. Hatch, P. D. Gardner, and R. E. Gilberg, *J. Am. Chem. Soc.*, **81**, 5943 (1959), for an earlier application of a method similar to that used by us.

[6] A. T. Bottini, B. J. King, and J. M. Lucas, *J. Org. Chem.*, **27**, 3688 (1962).

TABLE I

PHYSICAL AND ANALYTICAL DATA OF 2-HALOALLYLAMINES AND ALLENIMINES

Compound	R	B.p., °C. (mm.)	$n^{25}D$	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
I	t-C_4H_9	103–105 (90)	1.4671	43.76	7.34	7.29	43.71	7.17	7.06
I	n-C_6H_{13}	122–124 (24)	1.4715	49.10	8.24	6.36	48.96	7.87	5.97
II	t-C_4H_9	61–62 (26)	1.4431	56.93	9.55	...	56.81	9.66	...
III	CH_3	52.2–52.6 (760)	1.4380	[a]	...	...	...	...	...
III	t-C_4H_9	113–115 (760)	1.4350	75.62	11.78	12.60	75.26	11.69	12.55

[a] Because of the volatility of this compound, a satisfactory elemental analysis was not obtained. A study of the n.m.r. spectrum of N-methylallenimine has been reported by A. Lowenstein, J. F. Neueer, and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 3599 (1960).

allenimine and one part of the corresponding propargylamine. Treatment of N-(2-bromoallyl)-t-butylamine (Ib, R = t-C_4H_9) under conditions optimum for formation of other allenimines from other N-(2-bromoallyl)-alkylamines gave a 45% yield of a mixture containing 32% N-t-butylallenimine (IIIb, R = t-C_4H_9) and 68% N-t-butylpropargylamine (IVb, R = t-C_4H_9). A number of small scale reactions were carried out using Ib at an initial concentration of 0.4 M and sodium amide–IIb mole ratios ranging from 1.4 to 2.0. An amide–IIb mole ratio of 1.6 to 1.8 appeared to be optimum, and three preparative scale reactions using a mole ratio of 1.7 gave 62–68% yields of products consisting of 35–45% IIIb and 55–65% IVb.

N-Isopropylpropargylamine[7a] and N-t-butylpropargylamine (IVb)[7b] were isolated in yields of 82% and 87%, respectively, from reactions of 0.55 mole of N-(2-chloroallyl)-isopropylamine[7a] and 0.8 mole of N-(2-chloroallyl)-t-butylamine with 2.1 equivalents of sodium amide. Products from these reactions contained less than 1% of the allenimine as estimated by g.l.p.c.

Several observations incidental to this work should also be noted. Treatment of either I or II with sodium amide, lithium aluminum hydride, and methylmagnesium bromide in ether at 35° proved to be unsatisfactory methods of preparation for either III or IV. Surprisingly, Ia was found to undergo significant dehydrobromination to IVa in liquid ammonia when treated with coarsely powdered sodium hydroxide.

Experimental[8]

Preparation of N-(2-Haloallyl)alkylamines, N-Alkylallenimines, and N-Alkylpropargylamines.—Appropriate modifications of the procedure described for the preparation of N-(2-bromoallyl)-n-propylamine,[9] which is a slight modification of the procedure of Pollard and Parcell[2] for the preparation of N-(2-bromoallyl)-alkylamines from water-soluble primary amines, were used for the preparation of the N-(2-haloallyl)alkylamines except N-(2-bromoallyl)methylamine and N-(2-bromoallyl)-n-hexylamine. Yields ranged from 68–84%.

N-(2-Bromoallyl)-n-hexylamine (283 g.) was obtained in 66% yield by use of a modification of Pollard and Parcell's procedure[2] for the preparation of N-(2-bromoallyl)alkylamines from water-insoluble primary amines. Isopropyl ether was used as solvent in place of ethyl ether, and the reaction mixture was stirred mechanically.

Addition with stirring over a period of 220 min. of 600 g. (3.0 moles) of 2,3-dibromopropene to 2000 g. of 40% by weight aqueous methylamine (25.8 moles) in a 5-l. flask equipped with a Dry Ice condenser charged with an ice–salt mixture gave 283 g. (63%) of N-(2-bromoallyl)methylamine, b.p. 66–68° (90 mm.), $n^{25}D$ 1.4858, lit.[10] b.p. 135°, and 54 g. (13%) of methyl bis(2-bromoallyl)amine, b.p. 93–95° (7 mm.), $n^{25}D$ 1.5236, lit.[10] b.p. 100–102° (14 mm.).

With the exception that commercial sodium amide was usually used in place of freshly prepared sodium amide, Pollard and Parcell's procedure[2] was used for the preparation of allenimines from N-(2-bromoallyl)alkylamines. The use of toluene in place of ether was found to simplify the isolation of N-methylallenimine. Allenimines that were >99.5% pure as indicated by g.l.p.c. were obtained from distillations through a 1000 × 13 mm. column packed with glass helices and equipped with a total reflux head.

Preparations of N-alkylpropargylamines from N-(2-chloroallyl)alkylamines were carried out in the same manner as preparations of N-alkylallenimines from N-(2-bromoallyl)alkylamines except reaction times were 10 hr. or longer and the sodium amide–N-(2-chloroallyl)alkylamine mole ratio was 2.1. Initial sodium amide concentrations were 0.8 M.

Boiling points, refractive indices, and elemental analyses of new compounds are given in Table I.

Analytical Method.—Solutions containing 19–78% N-ethylallenimine (IIIa) by weight were prepared using IIIa and N-ethylpropargylamine (IVa) that were >99.5% pure. Each of these solutions was diluted with ether to give a series of solutions containing 64.2–99.1% ether by weight, and g.l.p. chromatograms were taken of 5 μl. samples of all solutions at 120° with a helium flow rate of 90 ml./min. The retention times (t_r) in sec. measured from the air peak were 50, 215, and 330 for ether, IIIa, and IVa, respectively. A linear plot with a slope of unity was obtained when the weight fraction of IIIa was plotted against $\mathrm{H}_{\mathrm{IIIa}}/(H_{\mathrm{IIIA}} + H_{\mathrm{IVa}})$ where H_{IIIa} and H_{IVa} are the peak heights of the bands due to IIIa and IVa, respectively. Data obtained for all solutions (0–99.1% ether by weight) fitted the plot, and no value of $H_{\mathrm{IIIa}}/(H_{\mathrm{IIIa}} + H_{\mathrm{IVa}})$ was obtained that was different from the weight-fraction of IIIa by more than 2%. The accuracy of the analytical method was not affected by the addition to the solutions of N-(2-bromoallyl)ethylamine, t_r = 1550 sec., or N-(2-chloroallyl)ethylamine, t_r = 845 sec., or by variation of the sample size from 2 to 10 μl.[11] For solutions containing 90.8–99.1% ether by weight, the sum of the weight fractions of IIIa and IVa was equal to $(2.4 \pm 0.2)\ (H_{\mathrm{IIIa}} + H_{\mathrm{IVa}})/(H_{\mathrm{IIIa}} + H_{\mathrm{IVa}} + H_{\mathrm{e}})$, where H_{e} is the normalized height of the ether band.

Description of a typical small scale reaction and analysis follows. A slurry of potassium amide was prepared by the addition of 2.38 g. of potassium to 100 ml. of ammonia and 12 mg. of anhydrous ferric chloride contained in a 250-ml. flask equipped with a sealed mechanical stirrer and Dry Ice condenser protected with a tube containing soda lime. N-(2-Bromoallyl)ethylamine (Ia, 8.2 g.) was added to the stirred slurry from a syringe in 2 min. After 4.5 hr., the Dry Ice had been allowed to evaporate, and the condenser was charged with an ice–salt mixture. Ether (50 ml.) and water (50 ml.) were added cautiously in that order. The ammonia was allowed to evaporate, the phases were separated, and the aqueous solution was extracted with 30 ml. of ether. The ether extracts were combined and dried with sodium

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(7) These compounds are prepared more conveniently by the reaction of propargyl bromide with excess alkylamine: (a) J. J. D'Amico, M. W. Harman, and R. H. Cooper, *J. Am. Chem. Soc.*, **79**, 5270 (1957); (b) J. J. D'Amico, U. S. Patent 2.943,079 (June 28, 1960); *Chem. Abstr.*, **54**, 25,943 (1960).

(8) Boiling points are uncorrected. Infrared spectra were obtained with a Beckman IR-4 spectrophotometer. Gas–liquid partition chromatograms were obtained using a 2-m. column packed with nonyl phthalate on firebrick in a Model 1 Chromat-O-Flex, Loe Engineering Co., Pasadena, Calif. Microanalyses were performed by Mr. V. H. Tashinian, Berkeley, Calif., and Drs. Weiler and Strauss, Oxford, England.

(9) A. T. Bottini and R. E. Olsen, *J. Am. Chem. Soc.*, **84**, 195 (1962).

(10) J. V. Braun, M. Kühn, and J. Weismantel, *Ann.*, **449**, 249 (1926).

(11) A standard curve for analysis of mixture of N-t-butylallenimine (IIIb, t_r = 465 sec.) and N-t-butylpropargylamine (IVb, t_r = 640 sec.) was also prepared from data obtained in a similar manner. The plot of weight fraction of IIIb *vs.* $H_{\mathrm{IIIb}}/(H_{\mathrm{IIIb}} + H_{\mathrm{IVb}})$ was also linear with a slope of unity.

hydroxide. The average values of $(H_{IIIa} + H_{IVa})/(H_{IIIa} + H_{IVa} + H_e)$ and $H_{IIIa}/(H_{IIIa} + H_{IVa})$ in 3 g.l.p. chromatograms of the ether solution, which weighed 54 g., were (1.84 ± 0.08) 10^{-2} and 0.77 ± 0.01, respectively, indicating that the conversion was 58% and that the product was 77% IIIa and 23% IVa.

Miscellaneous Reactions of N-(2-Haloallyl)ethylamines with Various Bases.—Treatment of 8.2 g. of N-(2-bromoallyl)ethylamine (Ia) with 2 g. of sodium amide in 100 ml. of ether at 25° for 5 hr. and room temperature for 24 hr., gave a 29% conversion to IVa. No IIIa was detected by means of g.l.p.c. A 6.0-g. sample of N-(2-chloroallyl)ethylamine (IIa) was treated in the same manner. No indication of the presence of IIIa or IVa in the ether solution was obtained by g.l.p.c.

Treatment of 36 g. of Ia with 300 ml. of *N*-methylmagnesium bromide in ether at reflux for 4 hr. and at room temperature for 16 hr., gave a 10% yield of a mixture of 24% IIIa and 76% IVa. Formation of IIIa and IVa was confirmed by means of infrared spectroscopy, and 29 g. (80%) of Ia was recovered. N-(2-Chloroallyl)isopropylamine (35 g.) was treated in the same manner. Traces of the corresponding III and IV (~90% IV), estimated as <0.5 g. (<2%), were detected by g.l.p.c.

Compound Ia (36.0 g.) was treated with 2.8 g. of lithium aluminum hydride in 300 ml. of ether at reflux for 2.5 hr. The mixture had darkened considerably after 1 hr. The mixture was allowed to stand overnight, and 10 ml. of water was added cautiously with stirring. After 1 hr., the ether solution was decanted from the dark precipitate and dried with sodium hydroxide. Presence of <0.6 g. (<4%) of IIIa and IVa consisting of more than 90% IIIa was detected by means of g.l.p.c. Only 18.5 g. (51%) of Ia was recovered. Compound IIa (18.0 g.) was also treated with 2.8 g. of lithium aluminum hydride in the same manner. No trace of either IIIa or IVa was detected in the concentrated ether solution from the reaction.

A mixture prepared from 4.0 g. of coarsely powdered sodium hydroxide, 8.2 g. of Ia, and 100 ml. of liquid ammonia was stirred at reflux for 10 hr. Ether (50 ml.) was added to the stirred mixture, and the ammonia was allowed to evaporate. Formation of 1.0 g. (24%) of IVa was detected by means of g.l.p.c.; formation of IVa was confirmed by means of infrared spectroscopy.

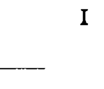
Dihalomalonaldehydes

S. TROFIMENKO

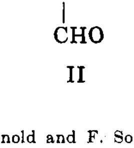
Contribution No. 879 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware

Received June 3, 1963

There are numerous examples of monosubstituted malonaldehydes,[1] depicted best by the "pseudoaromatic" structure I. By contrast, disubstituted malonaldehydes devoid of this "aromaticity" are little known. While acetals of dibromomalonaldehyde[2] and dimethylmalonaldehyde[3] have been reported, they were prepared indirectly and, until recently,[4] could not be converted to the free dialdehydes. This paper reports the first synthesis of negatively disubstituted malonaldehydes, dibromomalonaldehyde (II), and bromochloromalonaldehyde (III).

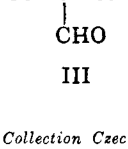


I



$$\mathrm{Br{-}\overset{\displaystyle CHO}{\underset{\displaystyle CHO}{C}}{-}Br}$$

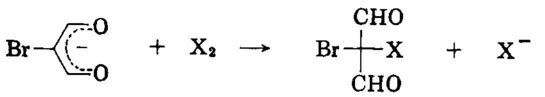
II



$$\mathrm{Br{-}\overset{\displaystyle CHO}{\underset{\displaystyle CHO}{C}}{-}Cl}$$

III

Both of these compounds were prepared by the action of the appropriate halogen on the sodium salt of bromomalonaldehyde, under scrupulously anhydrous conditions.[5]

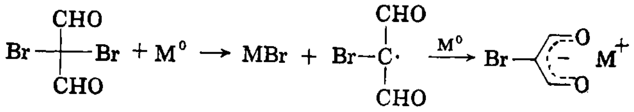


Dibromomalonaldehyde was obtained in better yields and was studied in more detail. It is readily soluble in common organic solvents; in water or aqueous tetrahydrofuran it dissolves with the formation of an isolable hydrate. Aqueous solutions of dibromomalonaldehyde can be titrated with base, the hydrate being cleaved to formic acid and dibromoacetaldehyde.

Dibromomalonaldehyde exhibits surprising thermal stability, remaining unchanged when refluxed at its boiling point (186°) for two hours. Even under such drastic conditions as passage over quartz chips at 390 and 450°, 50 and 40%, respectively, of the starting material is recovered.

In contrast to the thermal stability of dibromomalonaldehyde is its high sensitivity to radicals. When solutions of dibromomalonaldehyde (in benzene or carbon tetrachloride) are exposed to light or azo initiators, a rapid and complex reaction ensues; hydrogen bromide is evolved, and bromomalonaldehyde precipitates as an isolable product. When the reaction is allowed to proceed further, a complex mixture of acid bromides is obtained. It is noteworthy that bromomalonaldehyde by itself does not react under those conditions, nor does dibromomalonaldehyde in the absence of a solvent.

Dibromomalonaldehyde reacts with metals or metal carbonyls, presumably *via* two one-electron transfers, and yielded the metal salt of bromomalonaldehyde.



The bromomalonaldehyde radical gave no evidence of coupling in any of the preceding reactions; in fact, the most pronounced characteristic of dibromomalonaldehyde (or bromomalonaldehyde radical) is its tendency to revert to the aromaticity of bromomalonaldehyde anion, as a metal or proton chelate. In almost all reactions tried, including pyrolysis of anhydrous bromomalonaldehyde salts, bromomalonaldehyde could be sublimed out of the reaction mixture.

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(1) (a) Z = R or Ar [Z. Arnold and F. Sorm, *Collection Czech. Chem. Commun.*, **23**, 452 (1958)]; (b) Z = –CN [S. Trofimenko (unpublished results)]; (c) Z = –CHO [Z. Arnold and J. Zemlicka, *Collection Czech. Chem. Commun.*, **25**, 1318 (1958)]; (d) Z = –NO₂ [H. B. Hill, *Ber.*, **15**, 1906 (1882); *Am. Chem. J.*, **22**, 89 (1899)]; (e) Z = –COOR [L. Panizzi, *Gazz. chim. ital.*, **76**, 56 (1946)]; (f) Z = Br [M. J. Grard, *Compt. rend.*, **190**, 187 (1930); *Ann.*, **13**, 336 (1930)]; (g) Z = Cl [W. Diekmann, *Ber.*, **37**, 4638 (1904)]; (h) Z = OH (reductone) [T. Reichstein and R. Oppenauer, *Helv. Chim. Acta*, **16**, 988 (1933)]; (i) Z = –CRO [Z. Arnold and A. Holy, *Collection Czech. Chem. Commun.*, **28**, 869 (1963)].

(2) S. M. McElvain and L. R. Morris, *J. Am. Chem. Soc.*, **73**, 206 (1957).

(3) K. C. Brannock, *J. Org. Chem.*, **25**, 258 (1960).

(4) After this work has been completed, a report of the successful hydrolysis of dimethylmalonaldehyde tetraethyl acetal appeared: L. A. Yanovskaya, B. A. Rudenko, V. F. Kucherov, R. N. Stepanova, and J. A. Kogan, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2189 (1962).

(5) The question whether direct C-halogenation or O-halogenation, followed by some secondary process, takes place, remains open; only O-acylation has been reported for malonaldehydes [T. V. Protopopova and A. P. Skoldinov, *Zh. Obshch. Khim.*, **28**, 240 (1958); Z. Arnold and J. Zemlicka, *Collection Czech. Chem. Commun.*, **25**, 1318 (1960)].