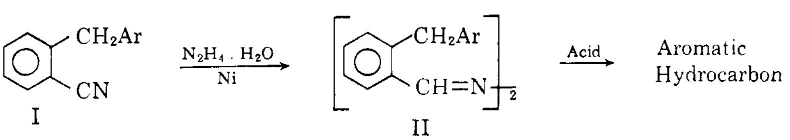

Nitrile		Azine		% Yield	Hydrocarbon	% Yield
Ia.	Ar = C_6H_5[a]	IIa.	Ar = C_6H_5	90	Anthracene	95
Ib.	Ar = $2,3\text{-}(CH_3)_2C_6H_3$[b]	IIb.	Ar = $2,3\text{-}(CH_3)_2C_6H_3$	88	1,2-Dimethylanthracene	90
Ic.	Ar = $1\text{-}C_{10}H_7$[c]	IIc.	Ar = $1\text{-}C_{10}H_7$	92	Benz[*a*]anthracene	98
Id.	Ar = $2\text{-}C_{10}H_7$[c]	IId.	Ar = $2\text{-}C_{10}H_7$	91	Benz[*a*]anthracene	95

[a] See C. Bradsher, *J. Am. Chem. Soc.*, **62**, 486 (1940). [b] See S. G. Quo, Ph.D. thesis, Virginia Polytechnic Institute, Blacksburg, Virginia. [c] See F. Vingiello and A. Borkovec, *J. Am. Chem. Soc.*, **77**, 3413 (1953).

unrelated investigation on the mechanism of the acid-catalyzed aromatic cyclodehydration reaction, Bradsher and Vingiello[4] have shown that the rate of formation of anthracene from 2-benzylbenzaldehyde is extremely rapid. These observations made it seem likely that properly substituted aromatic nitriles could be converted to the corresponding polynuclear aromatic hydrocarbons. When applied to 2-(arylmethyl)benzonitriles, this should lead to a general synthesis of anthracenes and the benzo derivatives of anthracene. The validity of this assumption was established by the synthesis of anthracene by the partial reduction of 2-benzylbenzonitrile (Ia. Ar = phenyl) with hydrazine hydrate and Raney nickel followed by the acid cyclization of the resulting 2-benzylbenzaldazine (IIa. Ar = phenyl). The synthesis of 1,2-dimethylanthracene was also effected. Benz[*a*]anthracene was prepared by the acid hydrolysis of 2-(1-naphthylmethyl)benzaldazine (IIc. Ar = 1-naphthyl) and also by the acid hydrolysis of 2-(2-naphthylmethyl)benzaldazine (IId. Ar = 2-naphthyl). The azines IIb, IIc, and IId were also prepared in very good yields from the corresponding nitriles Ib, Ic, and Id by the reaction with hydrazine hydrate and Raney nickel. From this preliminary investigation it appears that the preceding method of synthesis of polynuclear aromatic hydrocarbons has general application.

Experimental

General Procedure.—One gram of nitrile, 0.5 g. of Raney nickel,[5] 10 ml. of 85% hydrazine hydrate, and 50 ml. of 95% ethanol were heated at 50–55° until the evolution of ammonia ceased. The nickel catalyst was removed by filtration and the ethanolic solution was concentrated until the azine precipitated. The collected azine (see Table I) was heated under reflux with 50% sulfuric acid (or 10 ml. of 48% hydrobromic acid and 20 ml. of glacial acetic acid). The hydrocarbon was isolated by extraction with benzene and concentration of the benzene extracts.

TABLE I

2-(ARYLMETHYL)BENZALDAZINES (II)[a]

			Calcd.			Found[c]			
	M.p.[b]	Formula	C	H	N	C	H	N	(C = N)[d]
IIa	142–143	$C_{28}H_{24}N_2$	86.56	6.23	7.21	86.74	6.20	7.19	6.20 μ
IIb	196–197	$C_{32}H_{32}N_2$	86.44	7.26	6.30	86.74	7.08	6.20	6.20 μ
IIc	171–172	$C_{36}H_{28}N_2$	88.49	5.78	5.73	87.80	6.40	6.02	6.19 μ
IId	169–170	$C_{36}H_{28}N_2$	88.49	5.78	5.73	87.84	6.20	6.00	6.19 μ

[a] Recrystallized from benzene–ethanol as yellow needles. [b] Uncorrected; determined on Thomas-Hoover melting point apparatus. [c] Geller Laboratories, Bardonia, New York. [d] Infrared spectra obtained on a Perkin-Elmer Model 21, 0.5% in KBr.

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[4] C. Bradsher and F. Vingiello, *J. Am. Chem. Soc.*, **71**, 1434 (1949).

[5] L. Covert and H. Adkins, *ibid.*, **54**, 4116 (1932).

Hydrolysis of Simple Aromatic Esters and Carbonates

GLENN D. COOPER[1] AND BARRY WILLIAMS

General Electric Company Research Laboratory, Schenectady, New York

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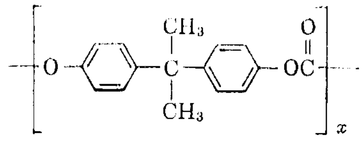
It has been reported[2] that aromatic polycarbonates derived from 2,2-bis(4-hydroxyphenyl)propane,



are much more resistant to hydrolytic degradation than aromatic polyesters obtained from condensation of *m*-hydroxybenzoic acid,

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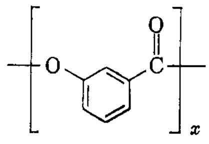
[1] Present address, Research Center, New Mexico State University, University Park, New Mexico. Inquiries should be directed to this address.

[2] R. Gilkey and J. R. Caldwell, *J. Appl. Polymer Sci.*, **2**, 198 (1959).



It is not known whether this is because of factors such as differences in degree of crystallinity, solubility of water in the polymers, etc., or whether it reflects an inherent difference in the ease of hydrolysis of the two types of ester groups. Although few reactions have been investigated as extensively as ester hydrolysis, little information is available on the hydrolysis of completely aromatic esters, $\mathrm{Ar}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OAr}$, or diaryl carbonates. Bunton[3] reported that phenyl benzoate hydrolyzes much faster than alkyl benzoates in basic soution and that the rate in acid solution is very slow and Tommila[4] measured the rate of reaction of phenyl benzoate with hydroxide ion in 56% acetone, but no measurements of the rates of hydrolysis of aryl carbonates appear to have been reported. We have therefore investigated the hydrolysis of phenyl benzoate and diphenyl carbonate, the simplest representatives of these two ester types, in acidic, basic, and "neutral" solution, *i.e.*, without added acid or base.[5] For purposes of comparison, a few measurements were also made on phenyl ethyl carbonate and ethyl benzoate. The solvent in all cases was prepared by mixing equal volumes of 1,4-dioxane and water.

Acid and Neutral Solution.—Phenyl benzoate and diphenyl carbonate hydrolyze slowly but at a conveniently measurable rate in 0.1 *N* perchloric acid at 100°, the carbonate being approximately three times the more reactive. Rates were measured at several acid concentrations from 0 to 0.1 *M*, with the result shown in Fig. 1. The hydrolysis of phenyl benzoate is first order in both ester and acid, with a negligible rate in the absence of added acid. Diphenyl carbonate, however, hydrolyzes at an appreciable rate without added acid, (about 40% of the rate in 0.1 *N* perchloric acid),[6] and the observed rate in acid solution may be separated into two terms, a "water reaction," and an acid-catalyzed reaction: $k_{\mathrm{obs}} = k_{\mathrm{H_2O}} + k'\,[\mathrm{H^+}]$. The water reaction presumably is of the type designated as $\mathrm{B_{Ac}2}$ in the notation of Ingold,[7] involving attack by a water molecule on the carbonyl group of the neutral ester:

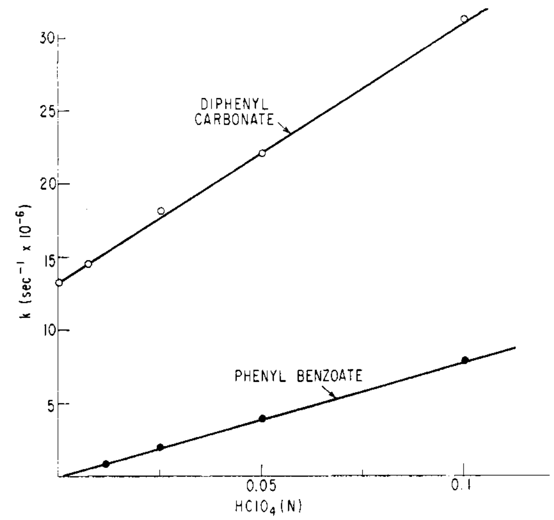
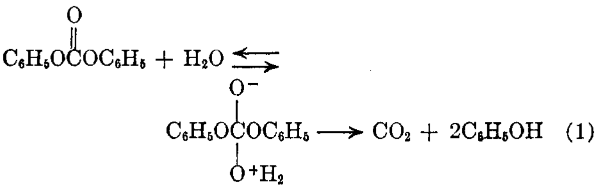


Fig. 1.—Effect of acid concentration on rate of hydrolysis in 1:1 dioxane–water at 100°.



$$\mathrm{C_6H_5O}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OC_6H_5} + \mathrm{H_2O} \rightleftarrows \mathrm{C_6H_5O}\underset{\underset{\mathrm{O^+H_2}}{|}}{\overset{\overset{\mathrm{O^-}}{|}}{\mathrm{C}}}\mathrm{OC_6H_5} \longrightarrow \mathrm{CO_2} + 2\mathrm{C_6H_5OH} \quad (1)$$

The possibility that the "neutral" reaction is due to hydroxide ion (from the Pyrex ampoules or from the autionization of water) is excluded. There was no trend in the calculated first-order rate constants with increasing extent of reaction in any of the experiments, although the products of the reaction, phenol and carbon dioxide, are weak acids whose formation would be expected to reduce the hydroxide ion concentration appreciably. The observed dependence of the rate on added acid concentration is also inconsistent with this explanation.

Basic Solution.—The reaction of diphenyl carbonate with hydroxide ion is too fast to be followed conveniently by ordinary sampling methods, so the rates were determined by following spectrophotometrically the rate of appearance of phenoxide ion in very dilute solutions of the carbonate in a sufficiently large excess of sodium hydroxide so that the reaction could be treated as pseudo first order. The reaction of alkyl carbonates with hydroxide ion has been shown to be a two-stage process in which the initial second-order reaction is followed by a slow first-order reaction[8,9]:

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(3) C. A. Bunton and D. N. Spatcher, *J. Chem. Soc.*, 1079 (1956).

(4) E. Tommila *Ann. Acad. Sci. Fennicae*, **A59**, No. 3, 3 (1942).

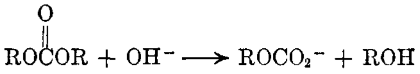
(5) The terms "neutral" solution and "neutral" reaction are used throughout this paper to describe the spontaneous reaction in the absence of added acid or base and do not imply reaction at controlled pH.

(6) The increase in rate observed on addition of acid is so small that it might conceivably be attributed to a salt effect on the water reaction rather than to acid catalysis, but this possibility is eliminated by the observation that the rate of the neutral reaction is not significantly affected by the addition of sodium chloride ($k_{110°}$ in dioxane–water = 2.17×10^{-1} sec.$^{-1}$; $k_{110°}$ in dioxane–water–0.11 *M* NaCl = 2.14×10^{-5} sec.$^{-1}$.

(7) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York, 1953, p. 752.

(8) N. F. Miller and L. O. Case, *J. Am. Chem. Soc.*, **57**, 810 (1935).

(9) I. Noring, A. Jensen, and C. Faurholt, *Acta Chem. Scand.*, **6**, 404 (1952).



$$\mathrm{RO\overset{\overset{O}{\|}}{C}OR + OH^- \longrightarrow ROCO_2^- + ROH} \qquad (2)$$

$$\mathrm{ROCO_2^- \longrightarrow RO^- + CO_.} \qquad (3)$$

The reaction of the diaryl carbonates presumably follows the same course, but the decomposition of the intermediate monophenyl carbonate anion is extremely fast, so that the over-all rate is that of the first step. In Fig. 2 the appearance of phenoxide ion from the reaction of diphenyl carbonate (7.5 × 10^{-5} M) with hydroxide ion (10^{-2} M) is shown as a pseudo-first-order reaction. The plot of log ($A_\infty - A$) is linear with time over the entire range, and the absorbance at $t = \infty$ corresponds to two phenoxide ions for each molecule of the carbonate. The second-order character of the reaction was confirmed by the identity of rate constants in reactions at varying concentrations of carbonate and hydroxide ion.

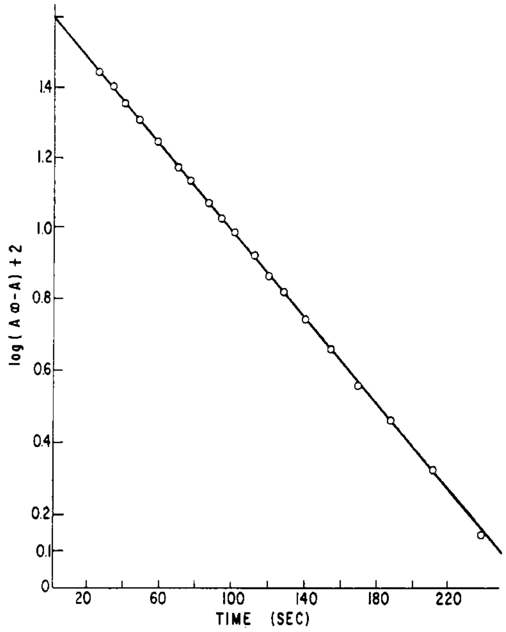


Fig. 2.—Reaction of diphenyl carbonate (7.5 × 10^{-5} M) with hydroxide ion (10^{-2} M) in 1:1 dioxane–water at 25°.

Comparison of Rates.—The rates of hydrolysis under acidic, basic, and "neutral" conditions of the esters investigated are compared in Table I. The second-order rate constant listed for the acid-catalyzed hydrolysis of diphenyl carbonate was obtained by subtracting the neutral rate from the observed rate in 0.1 N perchloric acid solution. The least variation between the rates for the different esters was observed in the acid-catalyzed reactions, and the greatest variation in the "neutral" reactions, but under all conditions diphenyl carbonate was more rapidly hydrolyzed than phenyl benzoate, the difference being a factor of at least one thousandfold in neutral solution. It is apparent that the greater resistance to hydrolysis of aromatic polycarbonates compared to aromatic polyesters[1] can not be attributed to an inherently greater reactivity of the latter type of ester group, but must be due to other factors which control the rate of hydrolysis of the bulk polymers.[10]

Table I

Rates of Hydrolysis of Esters

Ester	Reaction	k
Diphenyl carbonate	E + H_2O(100°)	1.31 × 10^{-5} sec.$^{-1}$
Phenyl benzoate	E + H_2O(100°)	$<10^{-8}$ sec.$^{-1}$
Ethyl benzoate	E + H_2O(100°)	$\sim10^{-7}$ sec.$^{-1}$
Phenyl ethyl carbonate	E + H_2O(100°)	1.3 × 10^{-7} sec.$^{-1}$
Diphenyl carbonate	E + H^+(100°)	2.33 × 10^{-4} l. mole^{-1} sec.$^{-1}$
Phenyl benzoate	E + H^+(100°)	9.3 × 10^{-5} l. mole^{-1} sec.$^{-1}$
Ethyl benzoate	E + H^+(100°)	1.7 × 10^{-4} l. mole^{-1} sec.$^{-1}$
Phenyl ethyl carbonate	E + H^+(100°)	1.7 × 10^{-4} l. mole^{-1} sec.$^{-1}$
Diphenyl carbonate	E + OH^-(20°)	8.4 × 10^{-1} l. mole^{-1} sec.$^{-1}$
Phenyl benzoate	E + OH^-(20°)	4.2 × 10^{-2} l. mole^{-1} sec.$^{-1}$
Ethyl benzoate	E + OH^-(20°)	2.5 × 10^{-3} l. mole^{-1} sec.$^{-1}$
Phenyl ethyl carbonate	E + OH^-(20°)	9.6 × 10^{-2} l. mole^{-1} sec.$^{-1}$

Experimental

Rates in Neutral and Acid Solution.—The solvent was freshly prepared for each experiment by mixing dioxane with an equal volume of water or aqueous acid solution and the acid concentration was determined by titration with standard base. The ester was weighed into a volumetric flask, dissolved, and diluted to the mark. In most cases the diphenyl carbonate solutions were 0.03 M and phenyl benzoate solutions 0.04 M. Five-milliliter portions of these solutions were transferred under nitrogen to Pyrex ampoules which were then sealed under nitrogen and placed in a constant-temperature bath. At suitable intervals ampoules were removed and immersed in liquid nitrogen to quench the reaction. The progress of the reaction was followed by bromometric titration of the phenol produced.[11,12] Each reaction was followed for a period of at least ten half-lives, and the rate constants were determined graphically in the usual manner; the results of a typical experiment are shown in Fig. 3. Rates were measured at 80, 90, 100, and 110° in neutral solution and in 0.1 N perchloric acid and activation energies were determined for the acid-catalyzed hydrolysis of phenyl benzoate and for the neutral and the acid-catalyzed hydrolysis of diphenyl carbonate. For diphenyl carbonate ΔH^* is 14.1 kcal. for the neutral reaction and 19.1 kcal. for the acid-catalyzed portion of the reaction. For the acid-catalyzed hydrolysis of phenyl benzoate ΔH^* is 20.4 kcal.

Rates of Reaction with Hydroxide Ion.—The rates of reaction of phenyl benzoate and diphenyl carbonate with hydroxide ion were measured by mixing dilute solutions of the ester and sodium hydroxide and following the rate of appearance of phenoxide ion. A high ratio of hydroxide

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[10] For example, the hydrolysis of polyethylene terephthalate has been shown to take place only in the amorphous portions of the polymer and is usually limited by the rate of diffusion of water into the polymer [R. C. Golike and S. W. Lasoski, Jr., *J. Phys. Chem.*, **64**, 895 (1960)].

[11] S. Siggia, "Quantitative Organic Analysis via Functional Groups," John Wiley and Sons, New York, N. Y., 1949, p. 111.

[12] The hydrolysis of ethyl benzoate was followed by titration of the benzoic acid.

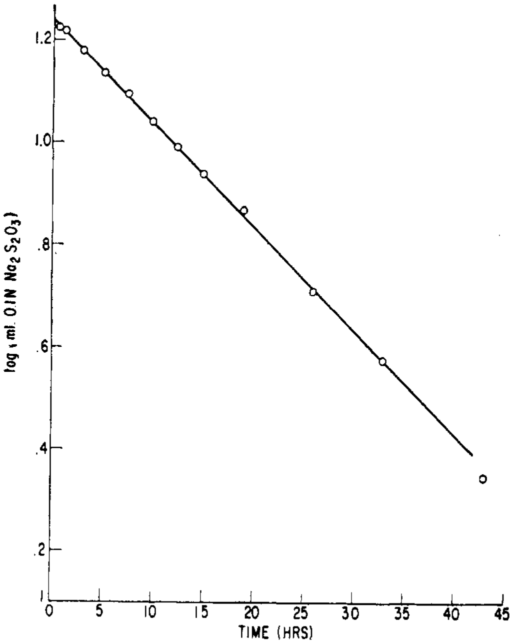

Fig. 3.—Hydrolysis of diphenyl carbonate in 1:1 dioxane–water at 100°.

ion to ester was used, so that the reaction could be treated as pseudo first order. In a typical experiment a solution of diphenyl carbonate (1.5×10^{-4} M) in 1:1 dioxane–water and a solution of sodium hydroxide (2×10^{-2} M) in the same solvent were immersed in a constant-temperature bath at 20°. After 30 min. equal volumes of the two solutions were mixed and the resulting solution was quickly transferred to a quartz cell in a Beckman Model DU spectrophotometer equipped with a jacket through which water was circulated from the constant temperature bath. The absorbance was measured at 291 μ. By using fast-draining pipets for the transfers the first measurement could be made within 30 seconds after the solutions were mixed. Subsequent measurements were made as fast as the instrument could be balanced (approximately every 10 sec.) until there was no further change in absorbance. Second-order rate constants were determined by dividing the pseudo-first-order rate constants (determined graphically from a plot of log ($A_\infty - A$) against time by hydroxide ion concentration. The calculated second-order constants for reaction of diphenyl carbonate were not affected by changes in the initial concentration of the two reagents:

Diphenyl carbonate	Sodium hydroxide	k (l. mole^{-1} sec.$^{-1}$)
3.75×10^{-5}	10^{-2} M	0.87
7.5×10^{-5}	10^{-2} M	.84
1.5×10^{-4}	10^{-2} M	.88
7.5×10^{-5}	5×10^{-3} M	.84
1.5×10^{-4}	5×10^{-3} M	.85

Synthesis of 5-Ethyl-8-methoxycorydaldine

SANDOR KARADY[1]

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachsetts

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In connection with another problem it became necessary to synthesize 5-ethyl-8-methoxycorydaldine and some of its derivatives. Initial efforts to ethylate or acetylate 8-methoxycorydaldine[2] directly failed and consequently the ethyl group had to be introduced at an earlier stage. The synthetic sequence used is outlined in Chart I. Mescaline, the starting material of this synthesis, was prepared from gallic acid[3] and converted to the urethane I.[2] Acylation with acetic anhydride in polyphosphoric acid proceeded with excellent yield and the resulting ketone II exhibited infrared absorption at 1710 ($\text{—NH}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{—OC}_2\text{H}_5$) and 1680 cm.$^{-1}$ ($\text{—}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{CH}_3$). The nuclear magnetic resonance (n.m.r.) spectrum[4] exhibited singlets due to methyl groups at 6.14, 6.15, 6.21 (—OCH$_3$), and 7.6 τ ($\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{CH}_3$) as well as the usual signals for an ethyl group. The presence of a single aromatic proton was confirmed

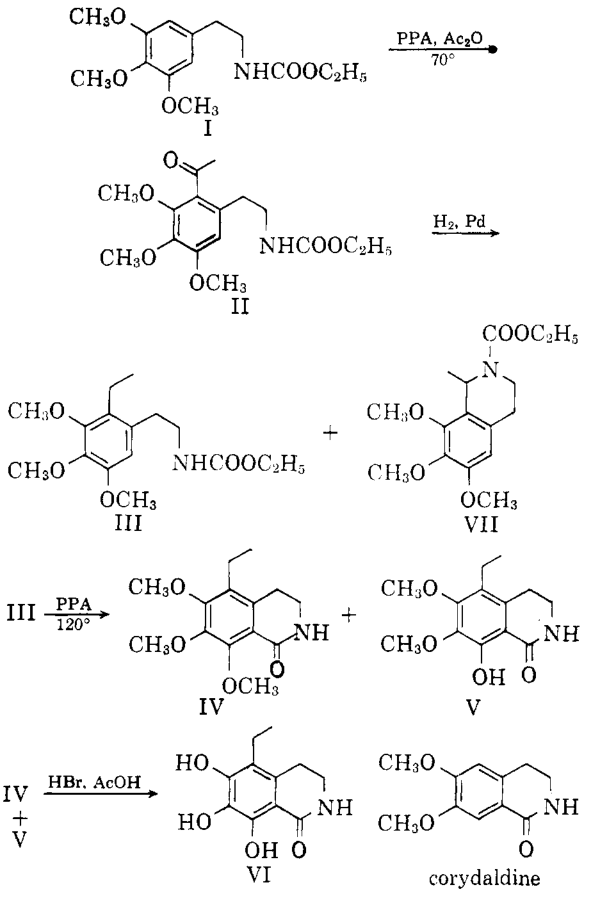

Chart I

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[1] National Institutes of Health Predoctoral Fellow, 1960–1961.

[2] R. H. F. Manske and H. L. Holmes, *J. Am. Chem. Soc.*, **67**, 95 (1945).

[3] F. Bennington, *ibid.*, **73**, 1353 (1951).

[4] All n.m.r. spectra were determined on a Varian A-60 spectrometer in carbon tetrachloride unless specified otherwise.