

electrochemical-chemical-electrochemical (ECE) mechanism,¹⁹ was nearly the same for each compound. This would make a relative correlation of $E_{1/2}$'s to MO energies possible. Adsorption effects were ruled out on the grounds that the diffusion plateaus were linear and undistorted if concentrations were kept below $5 \times 10^{-4} M$.

As a further test, cyclic voltammetry (CV) at a spherical platinum bead electrode (spe) was conducted on strained and strain-free molecules VII and VIII, respectively. The results are listed in Table VIII.

Table VIII. E_p Values from CV on Compounds VII and VIII

Compd	E_p^a	Scan rate ^b
VII	1.56	0.5
	1.58	1.0
VIII	1.63	0.5
	1.65	1.0

^a E_p is the peak potential *vs.* sce. ^b Scan rate given in volts/second.

In the CV experiment an E_p difference of 70 mV was observed, while an increase in scan rate showed a 20-mV shift for both compounds. Again, the wave shapes showed no distortion and steady-state cyclics retained the same E_p as the first-scan cyclic with no evidence of a reduction peak.

These two experiments indicate that although there are chemical kinetic effects (no reductive wave, E_p shifts with scan rate), the relative order of the oxidation potentials seem to be nearly the same for both experiments. There appears to be no detectable adsorption effects

which would cause the E_p to shift. Therefore, one should be able to make a semiquantitative correlation of the oxidative $E_{1/2}$'s with the MO energy of the highest filled MO. This correlation seems to be borne out in the significant anodic E_p shift on going from an unstrained (VII) to a strained (VIII) naphthalene compound.

Conclusions

Changes in reduction and oxidation potentials with ring strain have been observed. In the case of the naphthoquinones, this effect is rather dramatic. These observations indicate that ring strain effects cannot be ignored when one is determining oxidation or reduction potentials.

The changes in reduction and oxidation potentials with ring strain can be correlated within the Hückel framework using Streitwieser's "hybridization effect model." The fact that the same Hückel parameters which were found to correlate the epr data of these compounds also correlate the observed $E_{1/2}$ values is strong support for these parameters as a reasonable working model. It appears that a purely hyperconjugative model can be ruled out. Finally, though the oxidation results are to be considered very suspiciously, they are in the right direction as predicted by this simple model.

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Bridged Polycyclic Compounds. LXV. Electrophilic Addition of Hydrogen Chloride, Acetic Acid, and Their Deuterated Analogs to Benzonorbornadiene¹

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Contribution from the Departments of Chemistry, University of Colorado, Boulder, Colorado 80302, and Eastern Michigan University, Ypsilanti, Michigan 48197. Received July 6, 1970

Abstract: Addition of hydrogen chloride in acetic acid to benzonorbornadiene (**1**) leads to mixtures containing 94% benzonorbornenyl chloride (**8-Cl**) and 6% benzonorbornenyl acetate (**8-OAc**), with the composition invariant over a 90-fold variation in hydrogen chloride concentration. Addition of deuterated species leads to complete scrambling of deuterium between the positions randomized by Wagner-Meerwein rearrangements (**2-Cl** and **3-Cl**) in the chlorides, but less than complete scrambling in the acetate (more **2-OAc** than **3-OAc**). The data are consistent with competing mechanisms, one involving a nonclassical carbonium ion, and the other a syn-concerted "molecular" addition, and are not consistent with any process in which it is necessary to assume that reaction of a carbonium ion with chloride ion is slower than that with acetic acid.

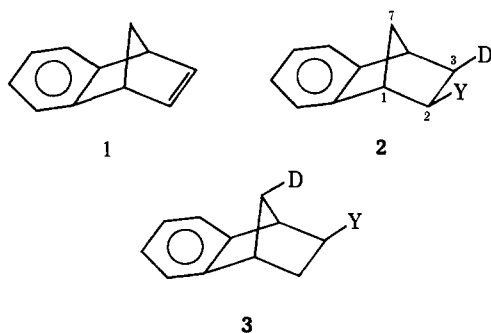
Electrophilic addition of deuterium chloride in deuterium oxide and in methylene chloride to benzonorbornadiene (**1**) has been shown² to lead exclusively to monodeuterio-*exo*-5-benzonorbornen-2-yl

chloride, with the deuterium mixed equally between the *exo*-C-3 (**2**) and *syn*-C-7 (**3**) positions. On the other hand,² addition of deuterioacetic acid under a variety of conditions led to mixtures of **2-OAc** and **3-OAc** in which **2** always predominated. With mineral acid present, the amount of **3-OAc** approached that of **2-OAc**, while, in the absence of acid catalysts and in

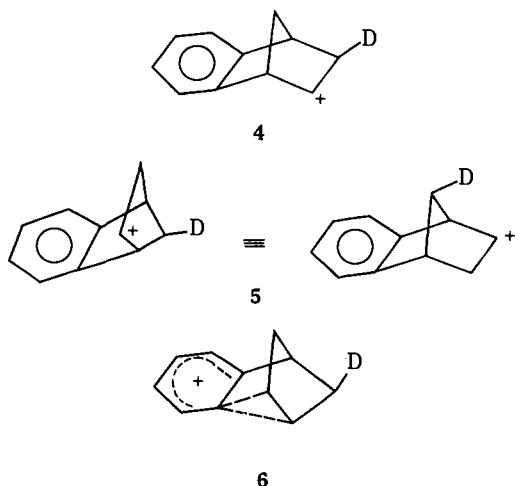
(1) Previous paper in series: LXIV. S. J. Cristol, A. R. Dahl, and W. Y. Lim, *J. Amer. Chem. Soc.*, **92**, 5670 (1970).

(2) S. J. Cristol and R. Caple, *J. Org. Chem.*, **31**, 2741 (1966).

media of lower polarity, 2-OAc was formed almost to the exclusion of 3-OAc. For example, a run containing 0.18 M D₂SO₄ and 4 mol % of 1 in CD₃CO₂D gave a mixture containing 2:3 in a 1.15:1.00 ratio, while one without sulfuric acid and containing 19 mol % of 1 and 37 mol % of cyclohexane in CD₃CO₂D gave 2:3 in an 11.0:1.0 ratio.

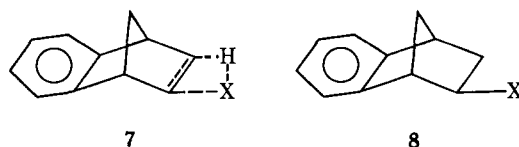


Two alternative rationalizations were offered² to interpret the stereochemical results and the amounts of deuterium scrambling. In the first of these consistent with the data then available, it was assumed that the reaction involved two classical ions, 4 and 5 (associated, of course, with gegenions or gegenmolecules), formed seriatim, 4 by deuteration of 1, and 5 by Wagner–Meerwein rearrangement of 4. As one limiting case, if 4 and 5 are not rapidly interconverted, compared with coordination with gegenion, gegenmolecule, or solvent, products 2 will be formed to the exclusion of products 3. In the other limit, if the 4 ⇌ 5 transformation is rapid compared with coordination with nucleophile, scrambling of deuterium between C-3 and C-7 will be complete, and equal amounts of 2 and 3 should result. Some consequences of these assumptions and of the data indicated above are (1) the rate of capture of the carbonium ion is greater by acetate ion than by acetic acid (more scrambling in latter case); (2) the rate of capture by acetate, compared with rearrangement, is greater in nonpolar solvents than in polar solvents (more scrambling in latter case); and (3) the rate of capture by acetic acid is greater than that by chloride ion (more scrambling in the latter case). The first two of these consequences seem reasonable; the third is tested in the work described in this manuscript.



The second “equally acceptable” hypothesis offered² assumed that two quite different routes are utilized in

these (and analogous) addition reactions. One, leading to complete mixing at C-3 and C-7, involves the nonclassical ion 6 (or a set of rapidly equilibrating cations, such as 4 and 5, which simulates 6) conjugate to a gegenion or gegenmolecule, which can collapse to equal amounts of 2 and 3. This process is responsible for the Wagner–Meerwein scrambling and its importance may be measured by twice the deuterium content at C-7. The alternate route, leading to the excess syn–exo addition over that involved in the Wagner–Meerwein equilibration, could be a single step molecular addition not involving a carbonium ion intermediate. An oversimplified model for the general reaction is shown as transition state 7 (solvent molecules, additional protons, and the attendant anions are omitted). The question of four- vs. six-membered ring was discussed earlier so that, with acetic acid, the X group may involve attack by either the ether oxygen (four-membered ring) or the carbonyl oxygen (six-membered ring). Our data do not discriminate among these possibilities.² The solvent effects which were observed could also be rationalized readily by these mechanisms. Compared with the uncatalyzed reactions, acid catalysis should favor proton transfer without coincident acetic acid coordination, *i.e.*, lead to more deuterium scrambling. The concerted addition process should be favored by reduced polarity of solvent, as the alternative process involves the formation of ions from neutral molecules.



While the data reviewed above are limited to the benzonorbornadiene case, similar data requiring multiple mechanistic paths are available in other systems and with a variety of addends, so that the question of multiple mechanisms is of general interest. These include, among others, addition of water,^{3,4} methanol,^{4,5} and acetic acid,⁵ or their deuterated analogs to *exo*- and *endo*-5,6-trimethylenenorbornene, addition of methanol,³ acetic acid,^{3,6,7} and acetic acid-*O-d*⁶ to norbornadiene, addition of aqueous hydrogen bromide and hydrogen chloride to 2,3-dideuterionorbornene,⁸ and addition of deuterium chloride,⁹ acetic acid-*d*₄,¹⁰ and trifluoroacetic acid-*d*¹⁰ to norbornene. While all of the results do not necessarily have to be covered by a single umbrella of explanations, it is clear that the problem outlined above is of general interest, tying in with the whole question of classical *vs.* nonclassical σ -bridged carbon cations. Our new results on the addition of hydrogen chloride and acetic acid to 1 do enable us to choose among the alternatives given above, for the benzonorbornadiene case at least.

(3) S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, *J. Amer. Chem. Soc.*, **84**, 3918 (1962).

(4) S. J. Cristol, L. K. Gaston, and D. W. Johnson, *Tetrahedron Lett.*, **4**, 185 (1963).

(5) S. J. Cristol and G. C. Fusco, *J. Org. Chem.*, **33**, 106 (1968).

(6) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *ibid.*, **31**, 2719, 2726, 2733, 2738 (1966).

(7) E. Vogelfänger, Ph.D. Thesis, University of California at Los Angeles, 1963.

(8) J. K. Stille, F. M. Sonnenberg, and T. H. Kinstle, *J. Amer. Chem. Soc.*, **88**, 4922 (1966).

(9) H. C. Brown and K.-T. Liu, *ibid.*, **89**, 3900 (1967).

(10) H. C. Brown, J. H. Kawakami, and K.-T. Liu, *ibid.*, **92**, 3816, 5536 (1970).

Table I. Addition of Hydrogen Chloride and Acetic Acid to Benzonorbornadiene (1)

[1], M	[HCl], M	[TMAC], ^a M	Mol % in product		% reaction ^b
			8-Cl	8-OAc	
1.3	2.3		95	5.5	96 ^c
0.70	1.3		94, 91, 93, 93	5.9, 9.5, 6.7, 7.5	98, 99, 61, 66
0.28	0.51		94, 95, 95	6.3, 5.4, 5.3	74, 69, 70
0.14	0.26		93, 95, 94, 93	7.2, 5.2, 6.1, 7.1	58, 61, 71, 59
0.028	0.051		94	5.8	62 ^d
0.014	0.026		93	7.1	32
0.70	1.3	0.08	94	5.6	96
0.70	1.3	0.5	94	6.2	98
0.14	0.26	0.25	94	6.4	85
0.028	0.051	0.040	93	6.7	56

^a Tetramethylammonium chloride. ^b The temperature was 22 ± 3° and, except where indicated, reaction proceeded for 20 hr. ^c Reaction time 17 hr. ^d Reaction time 66 hr.

Table I includes data upon the effect of variation of reactant concentrations upon the products of reaction of 1 with solutions of hydrogen chloride in glacial acetic acid, in some cases in the presence of tetramethylammonium chloride. Although the data show some scatter (and although it would be useful to have enough rate data to determine precise reaction order), certain conclusions may be reached from the data available in Table I and from those of the previous work.² These are as follows: (1) added tetramethylammonium chloride has no effect upon product composition; (2) the rate of formation of both 8-Cl and 8-OAc increases with increasing hydrogen chloride concentration; and (3) over a 90-fold variation in hydrogen chloride concentration (and an equivalent variation of concentration of 1), the product composition remains invariant, approximately 94% 8-Cl and 6% 8-OAc being formed.

These results differ from those on the reaction of cyclohexene with hydrogen chloride in acetic acid,¹¹ where there is clearly a competition between mechanisms involving carbonium ion-chloride ion ion-pair collapse to give syn addition of hydrogen chloride, ion-pair reaction with solvent to give anti addition of acetic acid, and a termolecular reaction involving acid, olefin, and chloride ion to give anti addition of hydrogen chloride. They are, on the other hand, similar to those¹² with *tert*-butylethylene and styrene, in that there are no termolecular anti processes, and, most importantly, that the transition states for both hydrogen chloride and acetic acid additions have the same number of hydrogen chloride molecules. This fact makes it clear that it cannot be assumed that chloride ion is poorer than acetic acid at capturing a cation such as 4, as the ratio of 8-Cl to 8-OAc is approximately 15. One may conclude then that the first set of alternative mechanisms given above (classical ions 4 and 5 interconverting at a rate competitive with capture by acetic acid, or acetate, and more rapidly than capture by chloride ion) cannot be correct if, in this mixed system, like the experiments² in which HCl and acetic acid were used separately, the formation of alkyl chloride is attendant with complete Wagner-Meerwein scrambling, while that of acetate is not.

(11) (a) R. C. Fahey, M. W. Monahan, and C. A. McPherson, *J. Amer. Chem. Soc.*, **92**, 2810 (1970); (b) R. C. Fahey and M. W. Monahan, *ibid.*, **92**, 2816 (1970).

(12) R. C. Fahey and C. A. McPherson, *ibid.*, **91**, 3865 (1969).

Table II. Addition of Deuterium Chloride and Acetic Acid-*d*₄ to Benzonorbornadiene^a

Run no.	Chloride			Acetate		
	% D in parent ion	% D at C-7	% D at C-3	% D in parent ion	% D at C-7	% D at C-3
1	93.7	45.5	48.2	92.0	Not determined	
2	96.4	48.8	47.6	94.8	39.7	55.1
3	95.2	47.8	47.4	93.7	37.9	55.8
Av ^b	(100.0)	49.7	50.3	(100.0)	41.2	58.8

^a Initial concentrations in CD₃CO₂D: [1], 0.70 M (run 1), 0.47 M (runs 2 and 3); [DCl], 0.95 M (run 1), 0.63 M (runs 2 and 3). ^b Normalized to 100% D in parent ion.

The data in Table II show that this is the case. The chloride products had deuterium completely scrambled between C-3 and C-7, *i.e.*, equal amounts of 2-Cl and 3-Cl, while the acetate had 59% of the deuterium at C-3 (2-OAc) and only 41% at C-7 (3-OAc).

The results make it clear that carbonium ion processes in these additions to 1 must be assumed to lead to complete scrambling of deuterium (*i.e.*, equal amounts of 2 and 3), and that the excess of 2-OAc in acetic acid additions is the result of a competing concerted cyclic process. Although one can rationalize the results in the other systems mentioned above⁸⁻¹⁰ on the same basis, there are no data to support such an assertion. Indeed, a very strong, but perhaps not conclusive, case has been made¹⁰ against concerted processes in additions to 7,7-dimethylnorbornene.¹³ Experiments such as we are here reporting would give interesting data for these other systems.

Experimental Section

Reagents. Benzonorbornadiene (1) was prepared by the method of Wittig.¹⁴ Deuterium oxide (99.7%) was obtained from General Dynamics Corporation and acetic acid-*d*₄ and acetyl chloride-*d*₃ from Volk Radiochemical Co., Burbank, Calif. Solutions of hydrogen chloride in acetic acid or of deuterium chloride in acetic acid-*d*₄ were prepared by mixing appropriate amounts of acetyl chloride (or acetyl chloride-*d*₃) and water (or D₂O) in acetic acid (or CD₃CO₂D).

Reaction Conditions. Solutions of 1 and HCl (or DCl) in acetic acid (or CD₃CO₂D) were allowed to stand at room temperature, generally for 20 hr. The reactions were worked up by adding water, extracting with CCl₄, washing with 5% aqueous NaHCO₃ and with water, drying over MgSO₄, and concentrating for vpc analysis.

Analysis Procedures. For quantitative analysis, the residues were dissolved in a small amount of CCl₄ and analyzed at 170° on a 7-m, 0.25-in. stainless steel column packed with 20% QF-1-0065 fluorosilicone on Anakrom ABS, 70-80 mesh, support. The retention times at a helium flow rate of 150 ml/min were: 1, 8.0 min; 8-Cl, 18.8 min; 8-OAc, 43.1 min; 8-Cl and 8-OAc gave peak areas proportional to weights of materials added, while the area for 1 had to be multiplied by a correction factor of 0.69 for computing (on a weight basis). For mass spectral analysis, samples were separated on a 7-m, 3/8-in. copper column using the same liquid phase and support.

Mass spectral analyses were carried out and computed as described earlier.² A sample of deuterio-*exo*-benzonorbornenyl chloride, purified by preparative gas chromatography, was prepared by the light-promoted sulfuryl chloride chlorination of *cis*-*exo*-5,6-dideuteriobenzonorbornene (2-D). The product, which

(13) It should, of course, be noted that, over the wide range of conditions used in the addition of acetic acid-*d* to benzonorbornadiene, partial scrambling of deuterium was observed. This suggests that, for this system and for norbornadiene,⁶ at least, where such data are available, and perhaps for other systems, carbonium ion and concerted cyclic processes occur at comparable rates. This means that data on 7,7-dimethylnorbornene,¹⁰ where a concerted process may be proscribed, are not necessarily pertinent to the unsubstituted norbornene case.

(14) G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958).

had 96.5% d_1 composition, was labeled 76.4% at C-3 (2-Cl) and 20.1% at C-7 (3-Cl).¹⁵ The composition of this mixture did not change substantially during two passes through the preparative gas chromatography separation procedures.

(15) The propensity of benzenorbornenyl radicals to rearrange has been noted previously.¹⁶

(16) S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, **32**, 3727 (1967).

Acknowledgments. J. M. S. is indebted to the National Science Foundation for financial support on a College Teachers Summer Research Program in 1967 and 1968 and on Academic Year Extension Grant GY-3825. The authors are indebted to Professor Robert C. Fahey for valuable discussions and suggestions.

The Synthesis of 1,2-Diethynylcyclohexene and Its Oxidation to a Tetradehydro[12]annulene Derivative¹

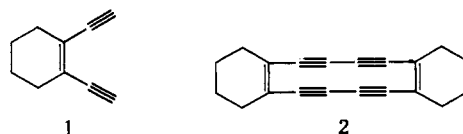
Gwenda M. Pilling and Franz Sondheimer*²

Contribution from the University Chemical Laboratory, Cambridge, England. Received August 10, 1970

Abstract: Two syntheses of 1,2-diethynylcyclohexene (**1**) are described. The first method involves the conversion of 1,2-cyclohexanedione (**3**) to 1,2-diethynyl-1,2-cyclohexanediol (**4**) by means of sodium acetylide, followed by reduction with diphosphorus tetraiodide. The second method, the preferred one, uses 2-isopropoxymethylene-cyclohexanone (**9**) as starting material; treatment with lithium acetylide and acid hydrolysis gave 2-ethynyl-1-cyclohexenecarboxaldehyde (**15**), which was converted to **1** by Wittig reaction with chloromethylenetriphenylphosphorane (**17**) and subsequent dehydrochlorination of the resulting chloromethylene compound (**18**, trans and cis isomers) with sodamide or potassium *tert*-butoxide. Oxidative coupling of **1** with cupric acetate in pyridine led to the corresponding cyclic "dimer" **2**, a tetraalkylated tetradehydro[12]annulene, in ~50% yield. The properties of **2** have been investigated, and there is some nmr evidence for the existence of a paramagnetic ring current. The oxidative coupling of **1** with oxygen, cuprous chloride, and ammonium chloride has also been studied, and it was found that this reaction gives rise to a variety of cyclic and "linear" chloro compounds.

The fully conjugated macrocyclic polyenyne (dehydroannulenes) obtained by our group in recent years have been prepared from nonconjugated α,ω -diacetylenes by oxidative coupling to large-ring polyacetylenes, and subsequent formation of the conjugated systems.³ An attractive alternative involves the direct synthesis of dehydroannulenes by the coupling of conjugated α,ω -diacetylenes, but this approach had not been investigated by us before the presently described work was initiated in 1965 since no suitable starting materials (except for certain benz-fused derivatives⁴) were known.⁵ An appropriate conjugated diacetylene appeared to be 1,2-diethynylcyclohexene (**1**). The

fused cyclohexene ring in this substance ensures that the double bond is held in the required *cis* configuration, while its presence in the final conjugated systems should not seriously disturb the π -electron distributions. In this paper we describe the synthesis of **1** by two routes,⁸



and its oxidative coupling to the cyclic "dimer" **2**, a tetraalkylated tetradehydro[12]annulene. In the following paper⁹ the syntheses of 13-membered ring systems from **1** are reported.

Syntheses of 1,2-Diethynylcyclohexene (1). The starting material for the first synthesis of **1** was 1,2-cyclohexanedione (**3**), which was prepared most conveniently from cyclohexanone *via* 2-chlorocyclohexanone in 26% overall yield by the method of McEntee, *et al.*¹⁰ Treatment of **3** (which exists largely in the enolic form¹¹) with ~2.5 mol equiv of sodium acetylide in liquid ammonia for 24 hr gave 1,2-diethynyl-1,2-cyclohexanediol (**4**)¹² in 66% yield as a mixture of the *trans*

(1) Unsaturated Macrocyclic Compounds. LXXIII. [For part LXXII, see R. M. McQuilkin and F. Sondheimer, *J. Amer. Chem. Soc.*, **92**, 6341 (1970).] Taken from the Ph.D. Dissertation of G. M. Pilling, Cambridge University, Aug 1968.

(2) Author to whom inquiries should be addressed at the Chemistry Department, University College, London W.C.1, England.

(3) For reviews, see F. Sondheimer, *Pure Appl. Chem.*, **7**, 363 (1963); *Proc. Roy. Soc., Ser. A*, **297**, 173 (1967); *Proc. Robert A. Welch Found. Conf. Chem. Res.*, **12**, 125 (1968).

(4) (a) Synthesis and coupling of *o*-diethynylbenzene: O. M. Behr, G. Eglinton, A. R. Galbraith, and R. A. Raphael, *J. Chem. Soc.*, 3614 (1960); (b) synthesis and coupling of 1,8-diethynylanthracene: S. Akiyama, S. Misumi, and M. Nakagawa, *Bull. Chem. Soc. Jap.*, **33**, 1293 (1960); (c) synthesis and coupling of 1,8-diethynyl-naphthalene: R. H. Mitchell and F. Sondheimer, *Tetrahedron*, **24**, 1397 (1968); (d) synthesis and coupling of 2,2'-diethynylbiphenyl: H. A. Staab, H. Mack, and E. Wehinger, *Tetrahedron Lett.*, 1465 (1968).

(5) The synthesis and coupling of other suitable conjugated α,ω -diacetylenes (*cis*-3-hexene-1,5-diyne,⁶ *cis,cis*- and *cis,trans*-3,5-octadiene-1,7-diyne⁷) have now been carried out.

(6) W. H. Okamura and F. Sondheimer, *J. Amer. Chem. Soc.*, **89**, 5991 (1967).

(7) G. H. Mitchell and F. Sondheimer, *ibid.*, **91**, 7520 (1969); G. P. Cotterrell, G. H. Mitchell, and F. Sondheimer, unpublished experiments.

(8) Preliminary communication: G. M. Pilling and F. Sondheimer, *J. Amer. Chem. Soc.*, **90**, 5610 (1968).

(9) G. M. Pilling and F. Sondheimer, *ibid.*, **93**, 1977 (1971).

(10) M. E. McEntee, A. R. Pinder, H. Smith, and R. E. Thornton, *J. Chem. Soc.*, 4699 (1956).

(11) See G. Schwarzenbach and C. Wittwer, *Helv. Chim. Acta*, **30**, 663 (1947); G. Hesse and G. Krehbiel, *Justus Liebigs Ann. Chem.*, **593**, 35 (1955); R. Bakule and F. A. Long, *J. Amer. Chem. Soc.*, **85**, 2309, 2313 (1963).

(12) W. Ried and H. J. Schmidt, *Chem. Ber.*, **90**, 2499 (1957).