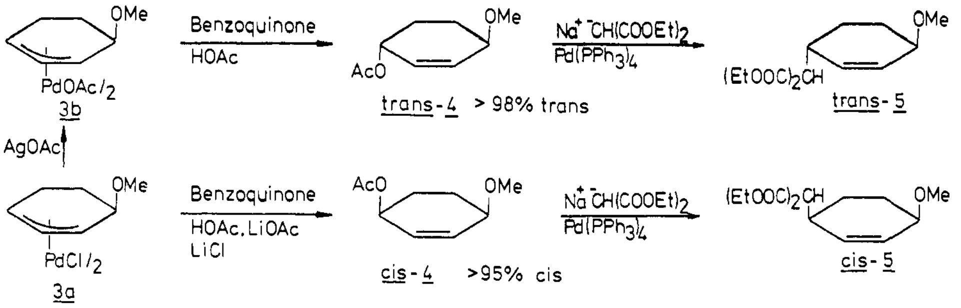
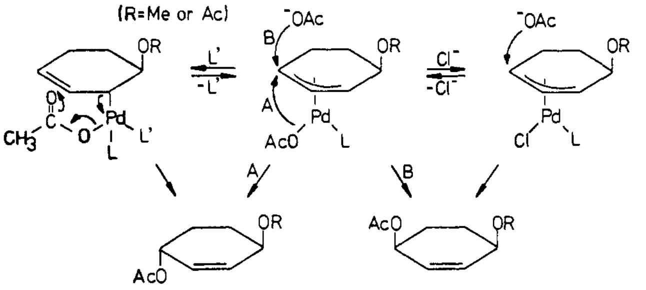
Scheme II



Scheme III



trans-**4** as the sole product (>98% trans). Performing the same reaction with **3b** in the presence of lithium acetate and lithium chloride changed the steric course of the nucleophilic attack and gave *trans*-**4** and *cis*-**4** in a 1:1 ratio. A clean trans attack by acetate to give pure *cis*-**4** was obtained with the chloro complex **3a**. Thus treatment of **3a** with benzoquinone in acetic acid in the presence of lithium chloride and lithium acetate gave pure *cis*-**4** with high stereoselectivity (>95% cis).[17]

A likely mechanism, which accounts for the results (Scheme III), is that chloride ions effectively block the coordination of acetate to palladium and hence hinder the cis-migration path. In the presence of chloride ligands mainly external trans attack on the π-allylpalladium complex takes place; in the absence of chloride ligands both cis and trans attack can occur depending on the acetate concentration.[18]

Since allylic acetates are versatile starting materials and can readily be stereospecifically substituted (retention) by a number of nucleophiles using a palladium(0) catalyst (eq 1),[1b,19,20] the

(eq 1)

stereocontrolled reactions reported here open a way of forming a new carbon–carbon bond or carbon–nitrogen bond with desired stereochemistry in a π-allylpalladium complex or a diene. We have demonstrated this by transforming the π-allylpalladium complex **3** into either *cis*-**5** or *trans*-**5**[21] in good yield via the corresponding acetates **4** (Scheme II).

Acknowledgment. We are grateful to the Swedish Natural Science Research Council and "Stiftelsen Bengt Lundqvists minne" for financial support and Dr. H. E. Högberg for helpful discussions.

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(17) *cis*- and *trans*-**4** had different ^1H NMR spectra ($CDCl_3$, 200 MHz), and the cis compound was characterized with an authentic sample (cf. ref 3).

(18) Trost et al.[2] proposed a similar mechanism to explain the effect of phosphine in decreasing the Pd-catalyzed isomerization of allylic acetates.

(19) Trost, B. M.; Genêt, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 8516.

(20) (a) Atkins, K. E.; Walker, W. E.; Manyik, R. M. *Tetrahedron Lett.* **1970**, 3821. (b) Takahashi, K.; Miyake, A.; Hata, G. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 230.

(21) This compound partly isomerized to the corresponding vinyl ether on prolonged reaction time. No such isomerization was observed for *cis*-**5**, indicating that a pseudoaxial proton CH–O is required for isomerization to occur. A similar isomerization of analogous compounds has recently been observed by others: Åkermark, B.; Ljungqvist, A.; Panunzio, M. *Tetrahedron Lett.* **1981**, *22*, 1055.

The Binary Metal Hydrido Anion FeH_6^{4-}: An X-ray Structural Characterization

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Since the initial studies of Weichselfelder[1] in 1926, efforts to resolve the hydridic species produced by the reaction of excess Grignard with iron(III) chloride under an atmosphere of hydrogen have met with limited success. Apparently, a complex mixture of products ranging from tan precipitates to black tars can be obtained. The breadth of results lead to the diverse conclusions that the reaction mixture contained FeH_3,[2] FeH_6,[3] $Mg(FeH_4)_2$,[4] or a variety of other hydridic products not necessarily containing iron.[5] With one possible but not probable exception,[2a] no pure hydridic product was obtained prior to the isolation of $FeH_6Mg_4X_4(THF)_8$ (X is a mixture of bromide and chloride) by one of us.[6] An X-ray structural investigation of this material was undertaken and has now revealed the presence of an unusual polyhydrido complex. We report here the results of that study and the discovery of the hexahydridoiron(II) anion FeH_6^{4-}, a new member of the very rare class of anionic binary transition-metal hydrides.

The synthesis and isolation of $FeH_6Mg_4Br_{3.5}Cl_{0.5}(THF)_8$ has been reported elsewhere.[6] A yellow, air-sensitive crystal of dimensions 0.15 × 0.25 × 0.55 mm was selected for the X-ray analysis and sealed in a glass capillary under a nitrogen atmosphere. The compound crystallizes in the monoclinic space group $C2/c$ with $a = 20.427$ (4), $b = 11.623$ (2), $c = 21.661$ 21.661 (7) Å; $\beta = 109.39$ (2)°; $V = 4851$ (2) Å^3; $Z = 4$. Two quadrants of intensity data ($2\theta < 45°$) were collected at ambient temperature

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(1) Weichselfelder, T. *Liebigs Ann. Chem.* **1926**, *447*, 64–77.

(2) (a) Ray, R. C.; Sahai, R. B. N. *J. Indian Chem. Soc.* **1946**, *23*, 67–72. (b) Sarry, B. *Z. Anorg. Allg. Chem.* **1956**, *288*, 48–61.

(3) Tullis, J. European Scientific Notes, No. 7; Office of Naval Research: London, 1953.

(4) Takegami, Y.; Fujmaki, T. *Kogyo Kagaku Zasshi* **1961**, *64*, 287–291.

(5) Kost, M. E.; Mal'tseva, N. N.; Mikheeva, V. I. *Russ. J. Inorg. Chem.* **1964**, *9*, 576–579.

(6) Gibbins, S. G. *Inorg. Chem.* **1977**, *10*, 2571–2576.

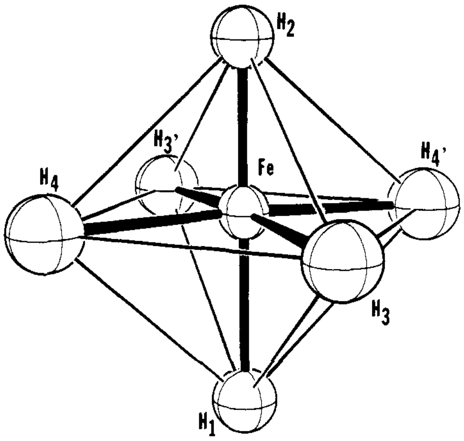

Figure 1. View of the FeH_6^{4-} core structure of $FeH_6Mg_4Br_{3.5}Cl_{0.5}(THF)_8$. Thermal ellipsoids in this and subsequent plots correspond to 20% probability.

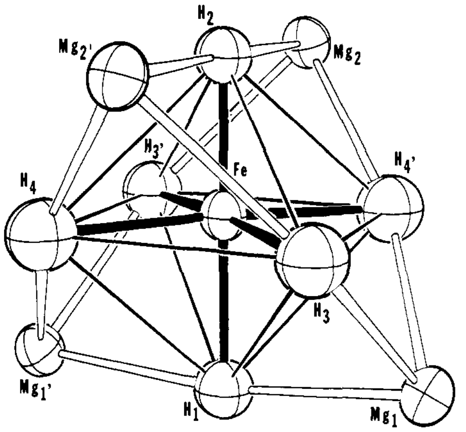

Figure 2. View of the FeH_6^{4-} anion surrounded by a tetrahedral array of magnesium ions.

with a Syntex $P2_1$ automated diffractometer by using Mo Kα radiation. The intensities were corrected for Lorentz, polarization, and absorption effects, yielding 1476 unique reflections with $I > 3\sigma(I)$. An E map generated by a direct-method analysis (using the program MULTAN[7]) revealed the positions of the iron, magnesium, and bromine atoms. All other nonhydrogen atoms were located in subsequent difference-Fourier maps. Least-squares refinement with anisotropic thermal parameters for all atoms in this model resulted in agreement factors of $R = 5.1\%$ and $R_w = 5.3\%$.[8] At this stage, a difference-Fourier synthesis based on low-angle reflections [max $(\sin\theta)/\lambda = 0.36$ Å^{-1}] clearly revealed the hydride positions. The positional and isotropic thermal parameters of these H atoms were included in subsequent refinement cycles and converged to reasonable values.[9] The refined halide populations were consistent with results obtained from elemental analysis.[10] The final agreement factors were $R = 4.9\%$ and $R_w = 5.1\%$.

The molecular geometry of $FeH_6Mg_4Br_{3.5}Cl_{0.5}(THF)_8$ is shown in Figures 1–3. Selected distances and angles are presented in Table I. The molecular structure consists of an FeH_6^{4-} octahedral core (Figure 1), situated on a crystallographic C_2 axis, with face-capping magnesium ions disposed about it in a tetrahedral fashion (Figure 2). A bound bromine atom and the oxygen atoms of two THF molecules complete the coordination sphere around each magnesium ion (Figure 3).

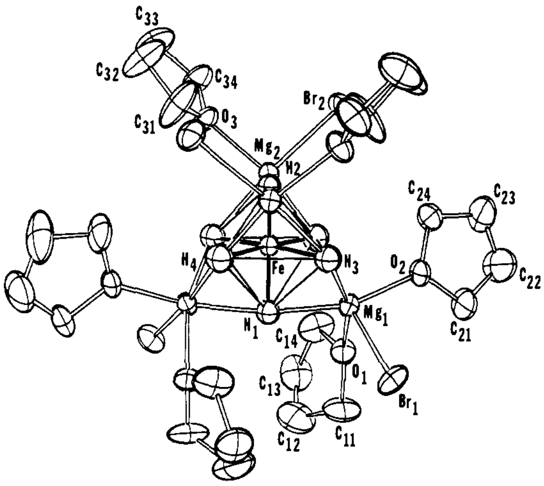

Figure 3. Entire $FeH_6Mg_4Br_{3.5}Cl_{0.5}(THF)_8$ aggregate. Two of the THF molecules have been removed for clarity.

Table I. Selected Distances and Angles for $FeH_6Mg_4X_4(THF)_8$

Distances, Å			
Fe-H(1)	1.67 (11)	Mg(2)-H(4')	2.06 (9)
Fe-H(2)	1.47 (11)	Fe···Mg(1)	2.493 (4)
Fe-H(3)	1.90 (8)	Fe···Mg(2)	2.489 (4)
Fe-H(4)	1.74 (10)	Mg(1)-Br(1)	2.526 (4)
Mg(1)-H(1)	2.00 (9)	Mg(2)-Br(2)	2.535 (4)
Mg(1)-H(3)	2.03 (9)	Mg(1)-O(1)	2.090 (9)
Mg(1)-H(4')	2.07 (9)	Mg(1)-O(2)	2.068 (9)
Mg(2)-H(2)	2.02 (9)	Mg(2)-O(3)	2.068 (8)
Mg(2)-H(3')	2.19 (9)	Mg(2)-O(4)	2.083 (9)
Angles, deg			
H(1)-Fe-H(3)	88 (4)	Fe-H(2)-Mg(2)	90 (5)
H(1)-Fe-H(4)	88 (4)	Fe-H(3)-Mg(1)	78 (3)
H(2)-Fe-H(3)	92 (4)	Fe-H(3)-Mg(2')	74 (3)
H(2)-Fe-H(4)	92 (4)	Fe-H(4)-Mg(1')	81 (4)
H(3)-Fe-H(3')	176 (4)	Fe-H(4)-Mg(2')	81 (4)
H(3)-Fe-H(4)	90 (4)	Mg(1')-H(1)-Mg(1)	170 (6)
H(3)-Fe-H(4')	90 (4)	Mg(2')-H(2)-Mg(2)	179 (6)
H(4)-Fe-H(4')	176 (4)	Mg(2')-H(3)-Mg(1)	153 (4)
Fe-H(1)-Mg(1)	85 (4)	Mg(2')-H(4)-Mg(1')	162 (5)

The most remarkable feature of the molecular structure is the FeH_6^{4-} central core. The average Fe–H distance of 1.69 (9) Å agrees reasonably well with known terminal M–H bond lengths[11] and is consistent with a covalent iron–hydride interaction. The scatter in individual Fe–H bond lengths (Table I) is not significant, in our opinion. All H–Fe–H angles conform well with octahedral coordination symmetry.

The observed Mg–Br distances of 2.526 (4) and 2.535 (4) Å are slightly longer than the reported values of 2.44 and 2.48 Å for $C_6H_5MgBr(C_4H_{10}O)_2$[12] and $C_2H_5MgBr(C_4H_{10}O)_2$,[13] respectively, but are comparable to the predicted covalent distance of 2.51 Å.[14] The Mg–O distances range from 2.068 (8) to 2.090 (9) Å. Corresponding Mg–O bonds in the above phenyl and ethyl etherates range from 2.03 to 2.06 Å, while the predicted covalent distance is 2.06 Å. The slight lengthening in magnesium–ligand bonds is consistent with the increase in coordination number (CN 6) and ionic character of the magnesium atoms in $FeH_6Mg_4X_4(THF)_8$ vs. four-coordinate magnesium in the Grignard molecules. The gross geometry of the Mg ions is best de-

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[7] Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368–376.

[8] $R = \sum|F_o - |F_c||/\sum F_o$; $R_w = [\sum w|F_o - |F_c||^2/\sum wF_o^2]^{1/2}$.

[9] The successful refinement of the H positions was carried out in the careful manner described in an earlier publication of ours [Kirtley, S. W.; Olsen, J. P.; Bau, R. *J. Am. Chem. Soc.* **1973**, *95*, 4532–4536].

[10] The populations of the two independent halide sites refined to values of 0.88 (1) Br, 0.12 (1) Cl and 0.89 (1) Br, 0.11 (1) Cl, as opposed to 0.875 Br, 0.125 Cl for the formulation $Br_{3.5}Cl_{0.5}$. Chemical analysis[6] indicated 0.85 Br, 0.15 Cl or $Br_{3.4}Cl_{0.6}$.

[11] (a) Frenz, B. A.; Ibers, J. A. In "Transition Metal Hydrides"; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; pp 33–74. (b) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1–82.

[12] Stucky, G.; Rundle, R. E. *J. Am. Chem. Soc.* **1964**, *86*, 4825–4830.

[13] Guggenberger, L. J.; Rundle, R. E. *J. Am. Chem. Soc.* **1964**, *86*, 5344–5345.

[14] Pauling, L. "The Nature of the Chemical Bond", 3rd Ed.; Cornell University Press: Ithaca, New York, 1960; pp 221–264.

scribed as octahedral, even though the average Br–Mg–O, O–Mg–O, and H–Mg–H angles [97.0 (5), 92 (2), and 73 (1)°, respectively] show significant deviations from ideal values. The assignment of octahedral symmetry for Mg is also supported by the fact that the trans L–Mg–L angles are roughly linear [average 162 (3)°] and the fact that the H_3Mg and MgO_2Br moieties are staggered (Figure 3).

It is difficult to tell from the structural results if the Mg···H interaction is ionic or covalent. Our feeling is that it is largely ionic, partly because the average Mg–H distance in our compound [2.06 (3) Å] is significantly longer than that in MgH_2 (1.95 Å).[15] However, the possibility that there is a substantial covalent contribution to the Mg···H interaction cannot be entirely dismissed.

Perhaps the best known example of a single-crystal study of a binary transition-metal hydrido anion is that of ReH_9^{2-}.[16,17] Here also, a variety of earlier formulations (Re^-, ReH_4^-, and ReH_8^{2-}) were suggested for the "rhenide" species before a single-crystal neutron diffraction analysis finally established the complex as the tricapped trigonal prismatic ReH_9^{2-} anion.[17] To our knowledge, the only other single-crystal investigation reported is that of the related ternary complexes Li_4RhH_4 and Li_4RhH_5.[18] Although the analysis of the former compound revealed the presence of square-planar RhH_4 units (Rh–H = 1.90 Å), the proposed structures were interpreted in terms of ionic bonding between hydrogen and both the lithium and rhodium atoms. In contrast, the solid-state structure of $FeH_6Mg_4X_4(THF)_8$ consists of well-defined molecular units built on discrete covalently bound FeH_6^{4-} species more analogous with ReH_9^{2-}.

The second and third row analogues of the title compound are as yet unknown. However, the particularly intriguing ternary hydrides M_2RuH_6 (M = Ca, Sr, Eu, Yb) have been reported.[19–21] These compounds are typically prepared by reaction of an alkaline-earth or lanthanide hydride with ruthenium metal at elevated temperatures and under a hydrogen atmosphere. They are insoluble in all common solvents, and attempts to synthesize single crystals of these materials have, as far as we know, been unsuccessful. Nevertheless, powder X-ray and neutron studies of the deuterium analogues of these materials have indicated a remarkably similar lattice structure consisting of octahedral RuD_6 units (Ru–D = 1.69 Å), with each face of the octahedron of deuterium atoms capped by alkaline-earth or lanthanide ions.[19] Also described in that paper is the powder neutron diffraction analysis of Sr_2IrD_5, whose structure could be interpreted to contain square-pyramidal IrD_5 units (Ir–D = 1.70 Å).[22]

In summary, an X-ray structural investigation of $FeH_6Mg_4Br_{3.5}Cl_{0.5}(THF)_8$ has fully established the existence of the binary metal hydrido anion FeH_6^{4-}, which is isoelectronic with the well-known ReH_9^{2-} anion. A neutron diffraction analysis of the title compound is in progress. Finally, it should be noted that, in the original study of Weichselfelder,[1] analogous reactions of PhMgBr with $NiCl_2$, $CoCl_2$, $CrCl_3$, and WCl_6 were also reported, leading to similarly intriguing products. It would be interesting to see if other binary metal hydride anions (e.g., NiH_4^{4-}) could be isolated from such reactions.

Acknowledgment. Financial support from Grant CHE-79-26479 from the National Science Foundation and Grant PRF-12442-AC3 from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Supplementary Material Available: Listings of final positional and thermal parameters (Tables A and B, 2 pages). Ordering information is given on any current masthead page.

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(15) Zachariasen, W. H.; Holley, C. E., Jr.; Stamper, J. F., Jr. *Acta Crystallogr.* **1963**, *16*, 352–353.

(16) Knox, K.; Ginsberg, A. P. *Inorg. Chem.* **1964**, *3*, 555–558.

(17) Abrahams, S. C.; Ginsberg, A. P.; Knox, K. *Inorg. Chem.* **1964**, *3*, 558–567.

(18) Lundberg, L. B.; Cromer, D. T.; Magee, C. B. *Inorg. Chem.* **1972**, *11*, 400–404.

(19) Moyer, R. O., Jr.; Stanitski, C.; Tanaka, J.; Kay, M. I.; Kleinberg, R. *J. Solid State Chem.* **1971**, *3*, 541–549.

(20) Thompson, J. S.; Moyer, R. O., Jr.; Lindsay, R. *Inorg. Chem.* **1975**, *14*, 1866–1869.

(21) Lindsay, R.; Moyer, R. O., Jr.; Thompson, J. S.; Kuhn, D. *Inorg. Chem.* **1976**, *15*, 3050–3053.

(22) A recent reinvestigation of the structure of Sr_2IrD_5 at low temperature has confirmed the square-pyramidal geometry of the IrD_5^{4-} units (Zhuang, J.; Hastings, J. M.; Corliss, L. M.; Bau, R.; Wei, C. Y.; Moyer, R. O., Jr. submitted for publication).

Carbenoid Insertion Reactions: Formation of [4.1.1]Propellane[1]

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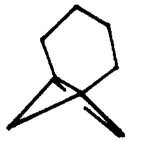
Received April 2, 1981

In 1978 we observed[1] the probable formation of [4.1.1]propellane (**1**). The recent acquisition of a microprobe for ^{13}C NMR determinations has enabled us to obtain further evidence supporting this claim. In view of the current interest in [*n*.1.1]propellanes,[2–4] we offer our observations at this time. In particular, we find chemical shift values in the ^{13}C NMR spectrum which are remarkably different from those reported earlier[4] for the closely related homologue [3.1.1]propellane (**2**) or its derivative.[3]



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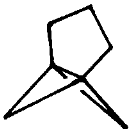

2

Following an earlier observation[5] that 2,2,4,4-tetramethylbicyclo[1.1.0]butane is formed in the pyrolysis of the salt of the tosylhydrazone of 2,2,4-trimethylpent-3-enal, we sought to extend this methodology[3] as a means of preparing 1,3-bridged bicyclobutanes, i.e., [*n*.1.1]propellanes. From a consideration of the geometry of bicyclobutane derivatives[6] it seemed likely that the introduction of a four-carbon bridge to such a molecule would add the least additional strain, and therefore this system was chosen to test the methodology.

An outline of the route by which 3-methylenecycloheptanone (**3**) was synthesized is given in Scheme I. Pyrolysis, at 180–200 °C, of the dry sodium salt of the tosylhydrazone derivative **4** gives an evolution of nitrogen, and a volatile component distills from the reaction vessel (ca. 20% yield). This component is mainly a mixture of 3-methylenecycloheptene (**5**), 4-methylenecycloheptene (**6**), and [4.1.1]propellane (**1**). The evidence which supports this contention is as follows. The mixture can be separated into two major components by preparative GC (15% SE30, base-washed Chrom. A, 140 °C). The first component to elute is 4-methylenecycloheptene (**6**),[7] as established by the synthesis of an authentic sample by the route outlined in Scheme II. The second component is a mixture of 3-methylenecycloheptene (**5**) and another very reactive compound. For a long time this component

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(1) V. C. Trenerry, Ph.D. Thesis, Adelaide, 1978. An alternative name for this compound is tricyclo[$4.1.1.0^{1,6}$]octane.

(2) U. Szeimies-Seebach, J. Harnish, G. Szeimies, M. V. Meerssche, G. Germain, and J.P. Declerq, *Angew. Chem. Int. Ed. Engl.*, **17**, 848 (1978); U. Szeimies-Seebach and G. Szeimies, *J. Am. Chem. Soc.*, **100**, 3966 (1978).

(3) K. Mlinarić-Majerski and Z. Majerski, *J. Am. Chem. Soc.*, **102**, 1418 (1980).

(4) P. G. Gassman and G. S. Proehl, *J. Am. Chem. Soc.*, **102**, 6862 (1980).

(5) D. P. G. Hamon and H. P. Hopton, *Tetrahedron Lett.*, **1675** (1973).

(6) P. L. Johnson and J. P. Schaefer, *J. Org. Chem.*, **37**, 2762 (1972).

(7) P. G. Gassman and E. A. Amour, *Tetrahedron Lett.*, **1431** (1971).

(8) E. A. Zeuch, D. C. Crain, and R. F. Kleinschmidt, *J. Org. Chem.*, **33**, 771 (1968).

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