

anions which are at once so bulky and so retentive of a shape-determining chelation pattern (specifically, that found in $\text{La}(\text{OH}_2)_3\text{A}^-$ and illustrated in Figure 1) as to fix the basic character of the very general crystalline framework. Our observations further suggest that the f-electrons of Ln^{3+} have no voice in determining gross configuration or the pattern of primary bonding.⁷

The chelation pattern in $\text{La}(\text{OH}_2)_3\text{A}^-$ is basically the same as that described⁴ for $\text{La}(\text{OH}_2)_4\text{AH}$, but loss of H^+ from the ten-coordinate molecule is accompanied by a significant tightening of all chelating linkages and rejection of one water molecule. Thus the displacement of La^{3+} from the mean plane of the trapezoidal array of four complexed O_c atoms (Figure 1) becomes 0.60 Å. in $\text{La}(\text{OH}_2)_3\text{A}^-$, a decrease of 0.17 Å., and the averaged $\text{La}-\text{N}$ distance becomes 2.755 Å., a decrease of 0.110 Å. (Standard deviations are 0.005–0.006 Å. for individual $\text{La}-\text{N}$, $\text{La}-\text{O}_c$, and $\text{La}-\text{OH}_2$ bond lengths in $\text{La}(\text{OH}_2)_3\text{A}^-$, approximately twice those in $\text{La}(\text{OH}_2)_4\text{AH}$.) The averaged length of four $\text{La}-\text{O}_c$ bonds is 2.507 Å. in $\text{La}(\text{OH}_2)_3\text{A}^-$, significantly less than the 2.537- and the 2.555-Å. averages for, respectively, three and four $\text{La}-\text{O}_c$ links in $\text{La}(\text{OH}_2)_4\text{AH}$. The average of three $\text{La}-\text{OH}_2$ distances, 2.580 Å., in the anion, by contrast, is only slightly less than the 2.592 Å. for four distances in the neutral molecule. We observe that the pattern of bond distances for the two EDTA chelates of La^{3+} correlates very well with a simple electrostatic model for the bonding interactions.

Replacement of La^{3+} in the $\text{La}(\text{OH}_2)_3\text{A}^-$ configuration by successively smaller Ln^{3+} ions should produce a general shrinkage of the anion with, in particular, a closer approach of Ln^{3+} to the mean plane of the 4O_c atoms. Consideration of relative ionic sizes then suggests that about half-way along in the sequence $\text{La}^{3+} \dots \text{Lu}^{3+}$, transition from nine-coordinate $\text{Ln}(\text{OH}_2)_3\text{A}^-$ to eight-coordinate $\text{Ln}(\text{OH}_2)_2\text{A}^-$ (of evidently dodecahedral type) should occur. Recalling that maintenance of the chelation framework in the anion permits the accommodation of $\text{M}^+ = \text{Na}^+$, K^+ , or NH_4^+ within the general $\text{MLnA} \cdot 8\text{H}_2\text{O}$ crystalline arrangement, we surmise that it allows also the shifts in positions of water molecules required for the transition in coordination type. Change from a nine- to an eight-coordinate $\text{Ln}(\text{OH}_2)_q\text{A}^-$ in reaction 1 increases $h - q$ by unity, which we associate with a sharp increase in the standard entropy, and decreases q by unity to give a less favorable standard enthalpy. Examination of existing thermodynamic data³ suggests that such effects occur—not all at once nor free of perturbations from (differential) crystal field interactions⁷—within the sequence $\text{Sm}^{3+} \dots \text{Tb}^{3+}$; we judge that the chelates of Eu^{3+} and Gd^{3+} are transitional in coordination type between a nine-coordinate $\text{Sm}(\text{OH}_2)_3\text{A}^-$ and an eight-coordinate $\text{Tb}(\text{OH}_2)_2\text{A}^-$. As a first test of this conclusion we are presently collecting three-dimensional X-ray intensity data from a single crystal of $\text{NaTbA} \cdot 8\text{H}_2\text{O}$ preliminary to determination of structure.

Orthorhombic piezoelectrically active crystals, space group $\text{Fdd}2$, of $\text{KLa}(\text{OH}_2)_3\text{A} \cdot 5\text{H}_2\text{O}$ have $a = 19.82 \pm 0.02$, $b = 36.18 \pm 0.03$, and $c = 12.24 \pm 0.01$ Å.;

(7) Crystal field stabilization by f-electrons probably is substantial, but, for reaction 1, it is just the difference of such stabilizations in $\text{Ln}(\text{OH}_2)_q\text{A}^-$ and $\text{Ln}(\text{OH}_2)_h\text{A}^{3+}$ which contributes to the enthalpy of formation.

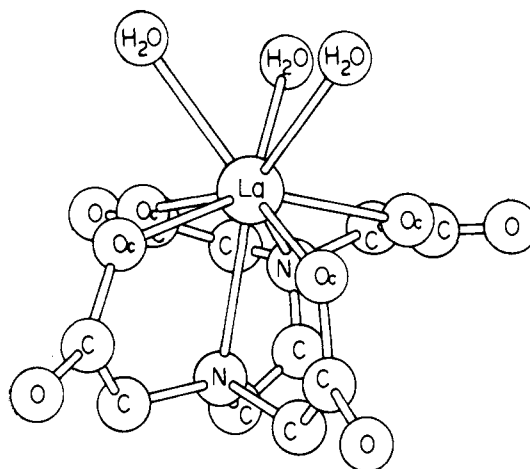


Figure 1. Scaled model of the $\text{La}(\text{OH}_2)_3\text{A}^-$ ion seen in perspective. The plane of the lanthanum and two nitrogen atoms serves as a quasi-mirror for the coordination group. H_2O (in the quasi-mirror), 2N , and 4O_c positions are at seven of the eight vertices of a dodecahedron of $\text{Mo}(\text{CN})_8^{4-}$ type within which La^{3+} is off-center, *i.e.*, out-of-plane from the 4O_c trapezoid, by 0.60 Å. The fourth water molecule present in $\text{La}(\text{OH}_2)_4\text{AH}$ has moved out of the primary coordination sphere of $\text{La}(\text{OH}_2)_3\text{A}^-$, but it remains nearby in the $\text{KLa}(\text{OH}_2)_3\text{A} \cdot 5\text{H}_2\text{O}$ crystalline arrangement.

the cell contains $16\text{KLnA} \cdot 8\text{H}_2\text{O}$ to give a calculated density of 1.847 g./cc. (that measured is 1.840 g./cc.). The technique of intensity measurement and the methods of structure analysis were as specified in the concurrent report⁴ for $\text{La}(\text{OH}_2)_4\text{AH} \cdot 3\text{H}_2\text{O}$ —excepting that only the 1977 independent $\{hkl\}$ recordable for $(\sin \theta)/\lambda < 0.60$ have thus far been used for structural refinement; $R = 0.065$.

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Tricyclic Norbornyl Analogs¹

Sir:

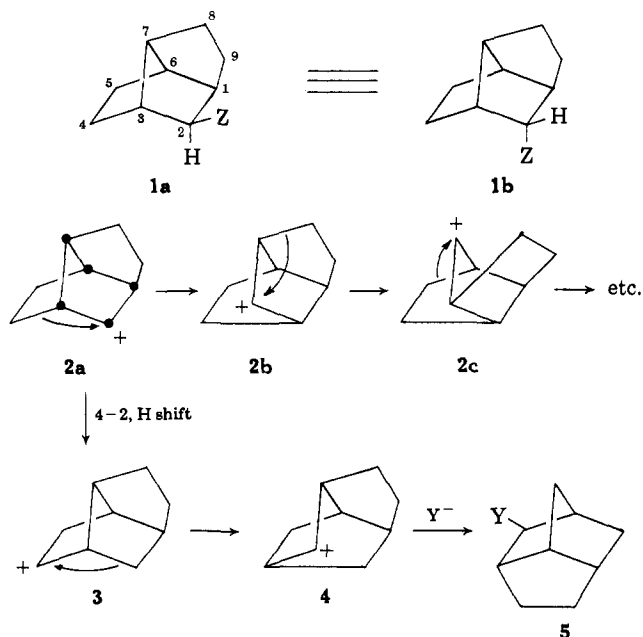
We wish to draw attention to some of the novel geometric features in compound **1**, which may be regarded as two superposed norbornyl frameworks and in which substituent Z is at the same time *exo* to one norbornyl unit and *endo* to the other. Interchange of the two groups (H and Z) at C-2 produces neither a diastereomer nor an enantiomer, but a molecule superposable on the original; *i.e.*, **1a** \equiv **1b**.

In norbornyl systems the rates of solvolysis of *exo*-substituted molecules exceed those of the corresponding *endo* analogs,² but disagreement persists whether these differences are attributable to abnormally high *exo* rates (due to anchimeric assistance)³ or to abnormally

(1) We are grateful to the National Science Foundation for financial support (Grant GP 1189). A predoctoral fellowship (to T. S.) from the National Institutes of Health, an Esso Foundation Fellowship (to H. K.), and a Grant-in-Aid from the Hynson, Westcott and Dunning fund are also gratefully acknowledged.

(2) For a perceptive review see J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

(3) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1147, 1154 (1952).



low *endo* rates (due to steric interference by the *endo*-hydrogen directly across the ring).⁴ The ionization behavior of systems such as **1** could provide a unique opportunity to evaluate the relative importance of these two factors because both act on *Z* simultaneously and in opposition to each other.⁵

Like its norbornyl analog, the tricyclic ion **2a**,⁶ derived by loss of *Z*, regenerates its mirror image on Wagner-Meerwein rearrangement (*e.g.*, **2a** and **2b** are enantiomers), but has the added novel feature that repetitive Wagner-Meerwein rearrangements (*e.g.*, **2a** → **2b** → **2c** → *etc.*) involve consecutive movements of essentially antiparallel bonds and transfer the charge successively to every atom of the core ring, which is identified in **2a** by heavy dots. In contrast to norbornyl systems, however, 1,2-hydrogen shifts are not possible without invoking bridgehead carbonium ions, and 1,3-hydrogen shifts (*e.g.*, from C-4 to C-2 in **2a**) are separately detectable because they produce a new ion (**3**) which can terminate with nucleophile and which is formally convertible to a different skeleton (ion **4** or its neutralized counterpart **5**) by a single Wagner-Meerwein shift. In view of the high level of interest^{2-4,7} in ions from bridged systems and the potential usefulness of tricyclic molecules in this area, we describe here the synthesis and characterization of **1** (*Z* = OH)⁸; the accompanying communication reports the other key members in this series.

The sodium salt of keto acid **6a**⁹ was treated with oxalyl chloride, and the derived acid chloride **6b** (ν

(4) For several recent papers by H. C. Brown and co-workers, see: *J. Am. Chem. Soc.*, **86**, 1246, 1247, 1248, 5003, 5004, 5006, 5007, 5008 (1964).

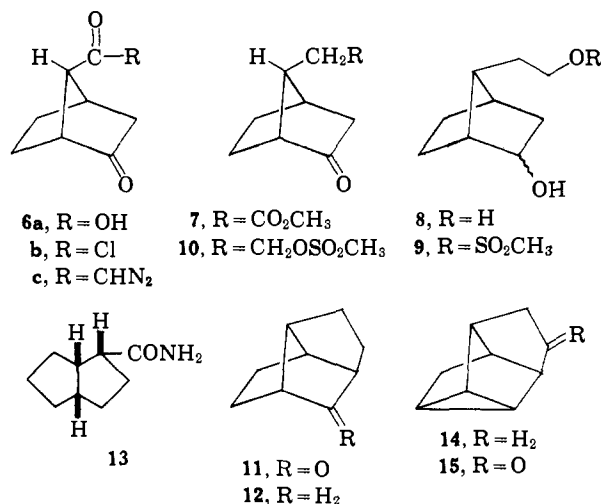
(5) System **1** is also uniquely suited to test recently proposed semi-empirical methods for estimation of solvolysis rates [P. von R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964); C. S. Foote, *ibid.*, **86**, 1853 (1964)].

(6) For simplicity, classical ions with localized charges are used in the formulations. However, various bridged ions can be envisaged, some of which could have unusual capacity for charge delocalization.

(7) For some leading references see C. C. Lee and E. W. C. Wong, *J. Am. Chem. Soc.*, **86**, 2752 (1964); R. Hoffmann, *ibid.*, **86**, 1259 (1964); P. R. Story and S. R. Fahrenholtz, *ibid.*, **86**, 527 (1964); N. A. LeBel and L. A. Spurlock, *Tetrahedron*, **20**, 215 (1964).

(8) The parent hydrocarbon (**12**), numbered as shown in **1a** (*Z* = H), is tricyclo[4.3.0.0^{3,7}]nonane. A convenient name for this skeleton (in which there exists a bridge involving an *exo*-norbornyl bond) is *brexane*.

(9) S. Beckman and H. Geiger, *Chem. Ber.*, **94**, 48 (1961).



1801 and 1749 cm^{-1}) was converted without purification to the diazoketone **6c** ($\text{C}_9\text{H}_{10}\text{N}_2\text{O}_2$, m.p. 106.5–107.5°, ν (CCl_4) 3116, 2108, 1754, and 1648 cm^{-1})¹⁰ with ethereal diazomethane. Rearrangement of **6c** in methanol¹¹ gave the liquid keto ester **7** ($\text{C}_{10}\text{H}_{14}\text{O}_3$, $n^{23\text{D}}$ 1.4803, ν 1736 and 1748 (shoulder) cm^{-1}). Reduction with lithium aluminum hydride converted **7** to a viscous oily diol **8** (ν 3324, 1095, 1038, and 1008 cm^{-1}) the analysis of which corresponded to $\text{C}_9\text{H}_{16}\text{O}_2$ but which might consist of a mixture of epimers. The next three steps were carried through without purification of intermediates and involved conversion to the monomesylate **9** (ν 3542, 3391, 3020, and 1353 cm^{-1}) by treatment with methanesulfonyl chloride in pyridine, then oxidation¹² to the keto mesylate **10** (ν 3022, 1744, and 1352 cm^{-1}). Finally, ring closure¹³ with sodium hydride in dimethylformamide at 60° gave **11** ($\text{C}_9\text{H}_{12}\text{O}$, $n^{26\text{D}}$ 1.4951, ν 1841 (weak) and 1746 cm^{-1}) which did not incorporate any deuterium when refluxed 7 days in deuterium oxide containing potassium carbonate. Wolff-Kishner reduction of the derived semicarbazone ($\text{C}_{10}\text{H}_{15}\text{N}_3\text{O}$, m.p. 188–189.5°) gave the parent hydrocarbon **12** (C_9H_{14} , $n^{23\text{D}}$ 1.4845, ν (CCl_4) 1462 and 1307 cm^{-1}). Treatment of ketone **11** with lithium aluminum hydride gave alcohol **1** (*Z* = OH; $\text{C}_9\text{H}_{14}\text{O}$, m.p. 84.5–86.5°, ν CCl_4 3626, 3352, 1080, 1058, and 1008 cm^{-1}) which was oxidized to ketone **11** with Brown's reagent¹² or with manganese dioxide in hexane. The structure of **11** follows from its method of synthesis, but independent evidence was obtained in two ways. Cleavage of **11** with sodamide in diisopropyl ether gave amide **13**, identical in all respects (melting point, mixture melting point, infrared spectrum) with an authentic sample.¹⁴ Finally, **11** was converted to a *p*-toluenesulfonylhydrazone ($\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$, m.p. 148–149.5°) which was transformed with sodium methoxide

(10) Satisfactory analytical data were obtained for all compounds whose empirical formulas are given. N.m.r. spectra (in CCl_4 or CDCl_3) and mass spectra were recorded where relevant and were consistent with proposed structures. Infrared spectra of liquids were obtained on neat films, unless noted otherwise.

(11) M. Newman and P. Beal, *J. Am. Chem. Soc.*, **72**, 5163 (1950).

(12) H. C. Brown and C. Carg, *ibid.*, **83**, 2951, 2952 (1961).

(13) Compare a similar sequence used by H. Whitlock, Jr., *ibid.*, **84**, 3412 (1962). We wish to thank Dr. Whitlock, who kindly provided us with experimental details of his method.

(14) We are grateful to Professor A. C. Cope for a sample of amide **13** prepared in his laboratories [A. C. Cope and M. Brown, *ibid.*, **80**, 2859 (1958)].

in bis(2-ethoxyethyl) ether¹⁵ to the tetracyclic hydrocarbon **14** (C₉H₁₂, b.p. 152–153°, *n*_D²⁰ 1.492 8, ν 3067–3055 cm.⁻¹) identical with the product obtained by Wolff–Kishner reduction of the known ketone **15**.¹⁶

(15) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); **83**, 3159 (1961).

(16) H. K. Hall, Jr., *J. Org. Chem.*, **25**, 42 (1960). We are grateful to Dr. Hall, who kindly furnished a sample of **15** to facilitate identification with material we prepared by independent routes.

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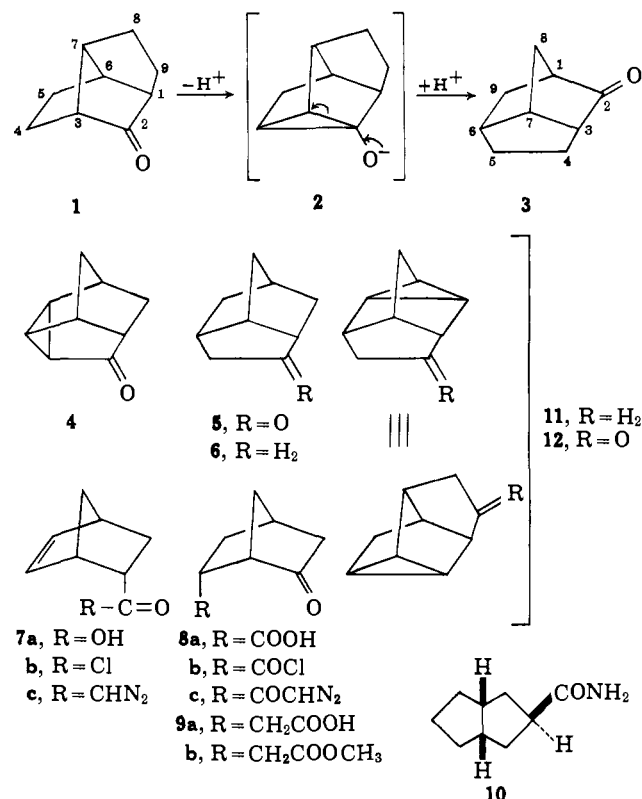
Bridged Ring Systems by Anionic Rearrangement¹

Sir:

The propensity of bridged-ring molecules to undergo carbonium ion rearrangements is well appreciated.² Recent evidence for the existence of homoenolate ions³ led us to explore the possibility that skeletal rearrangements *via* such anions might afford direct routes to systems otherwise difficultly obtainable. We now demonstrate the potential usefulness of this approach by applying it to the synthesis of tricyclo[4.2.1.0^{3,7}]nonan-2-one (**3**).⁴ This skeleton along with other bridged systems presented here is of inherent interest in studies of carbonium ions and carbanions.⁵

Treatment of brexan-2-one (**1**)⁵ with potassium *t*-butoxide in *t*-butyl alcohol at 185° for 150 hr. transformed it (*ca.* 60% yield) into an isomeric ketone, C₉H₁₂O (m.p. 118.5–119.5°, ν 1747, 1169, and 1022 cm.⁻¹; semicarbazone, C₁₀H₁₅N₃O, m.p. 159.5–162°).⁶ The following interconversions established the structure of this isomer as **3**. The sodium salt of 5-norbornene-endo-2-carboxylic acid (**7a**)⁷ was converted to its acid chloride (**7b**) (ν 1801 cm.⁻¹) with oxalyl chloride and then directly to the liquid diazoketone **7c** (ν 3062, 2005, and 1633 cm.⁻¹) by treatment with diazomethane. Without purification, the diazoketone was heated with copper powder in tetrahydrofuran⁸ and afforded the tetracyclic ketone **4** (C₉H₁₀O, m.p. 90.5–92°, ν 3045 and 1731 cm.⁻¹, λ (95% ethanol) 271 m μ (ϵ 50),⁹ no olefinic protons by n.m.r.; semicarbazone, C₁₀H₁₃N₃O, m.p. 204–205°; 2,4-dinitrophenylhydrazone, C₁₅H₁₄N₄O₄, m.p. 210–211°). Hydrogenation of **4** with palladium in ethyl acetate cleaved a cyclopropyl bond¹⁰ and gave a tricyclic ketone shown to be **5** (C₉H₁₂O, m.p. 120–

120.5°, ν 1744, 1703 (carbonyl doublet), and 1407 cm.⁻¹; semicarbazone, C₁₀H₁₅N₃O, m.p. 195–196°) as follows.



When refluxed in MeOD–D₂O containing potassium carbonate, ketone **5** incorporated up to two deuterium atoms (mass spectral analysis). Oxidation of **5** with trifluoroperacetic acid gave a semisolid mixture of δ -lactones (ν 1739 cm.⁻¹) which were saponified with aqueous potassium hydroxide. Neutralization with hydrochloric acid preferentially relactonized one of the hydroxy acids and thus preserved it while the other hydroxy acid underwent esterification on treatment with diazomethane followed by oxidation to a keto ester.¹¹ Saponification and neutralization with hydrochloric acid gave keto acid **9a** (C₉H₁₂O₃, m.p. 98.5–99°, ν (KBr) 1703 and 1738 cm.⁻¹), which was readily separated from the surviving lactone¹² and which was converted with diazomethane to the keto ester **9b** (C₁₀H₁₄O₃, *n*_D²³ 1.4757, ν 1750, 1738, and 1409 cm.⁻¹). The same keto ester **9b** (identical infrared and n.m.r. spectra) was independently synthesized from keto acid **8a**¹³ by a conventional Arndt–Eistert homologization (*via* the acid chloride **8b** and the diazoketone **8c** and then rearrangement of **8c** in methanol).¹⁴ That **5** and **3** have identical carbon skeletons was established by Wolff–Kishner reductions, which transformed each ketone to the same tricyclic hydrocarbon **6** (C₉H₁₄, m.p. 98–99°, sealed tube).¹⁵ Two additional transfor-

(11) H. C. Brown and C. Carg, *J. Am. Chem. Soc.*, **83**, 2951, 2952 (1961).

(12) The surviving lactone (C₉H₁₂O₂, m.p. 125–126.5°, ν 1738; n.m.r., 2 H at δ 4.42) is the expected isomer corresponding to methylene group migration in the Baeyer–Villiger step.

(13) S. Beckman and H. Geiger, *Chem. Ber.*, **94**, 48 (1961).

(14) M. Newman and P. Beal, *J. Am. Chem. Soc.*, **72**, 5163 (1950).

(15) Dr. D. Heywood and E. Marcus (Union Carbide Chemicals Company) have informed us that a hydrocarbon assigned structure **6** has been prepared in their laboratory by a different route (unpublished). They kindly sent us infrared and n.m.r. spectra which proved identical in all essential respects with those of our hydrocarbon.

(1) This research was supported by the National Science Foundation (Grant GP 1189) and also by the Petroleum Research Fund administered by the American Chemical Society. A National Institutes of Health predoctoral fellowship (to T. S.), an Esso Foundation Fellowship (to H. K.), and a Grant-in-Aid from the Hynson, Westcott and Dunning Fund are also gratefully acknowledged.

(2) For a review see J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

(3) A. Nickon and J. L. Lambert, *J. Am. Chem. Soc.*, **84**, 4604 (1962).

(4) A convenient name for the parent hydrocarbon **6** (numbered as in **3**) is *brendane*, which emphasizes the existence of a bridge involving an *endo*-norbornyl bond.

(5) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *J. Am. Chem. Soc.*, **87**, 1613 (1965).

(6) Satisfactory analytical data were obtained for all compounds identified by empirical formulas. Spectra were recorded as reported earlier.⁵

(7) J. Berson and D. Ben-Efraim, *J. Am. Chem. Soc.*, **81**, 4083 (1959).

(8) G. Stork and J. Ficini, *ibid.*, **83**, 4678 (1961).

(9) E. M. Kosower and M. Ito, *Proc. Chem. Soc.*, **25** (1962).

(10) Interestingly, reduction with lithium in ammonia–ether also gave **5**, but in lower yield.