anions which are at once so bulky and so retentive of a shape-determining chelation pattern (specifically, that found in $La(OH_2)_3A^-$ 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 $La(OH_2)_3A^-$ is basically the same as that described⁴ for La(OH₂)₄AH, 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 La³⁺ from the mean plane of the trapezoidal array of four complexed O_c atoms (Figure 1) becomes 0.60 Å. in La(OH₂)₃A⁻, a decrease of 0.17 Å., and the averaged La-N distance becomes 2.755 Å., a decrease of 0.110 Å. (Standard deviations are 0.005-0.006 Å. for individual La-N, La-O_c, and La-OH₂ bond lengths in La(OH₂)₃A⁻, approximately twice those in La(OH₂)₄-AH.) The averaged length of four La-O_c bonds is 2.507 Å. in La(OH₂)₃A⁻, significantly less than the 2.537and the 2.555-Å. averages for, respectively, three and four La-Oc links in La(OH2)4AH. The average of three La-OH₂ 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 La³⁺ correlates very well with a simple electrostatic model for the bonding interactions.

Replacement of La³⁺ in the La(OH₂)₃A⁻ configuration by successively smaller Ln³⁺ ions should produce a general shrinkage of the anion with, in particular, a closer approach of Ln³⁺ to the mean plane of the 40_c atoms. Consideration of relative ionic sizes then suggests that about half-way along in the sequence La³⁺...Lu³⁺, transition from nine-coordinate Ln- $(OH_2)_3A^-$ to eight-coordinate $Ln(OH_2)_2A^-$ (of evidently dodecahedral type) should occur. Recalling that maintenance of the chelation framework in the anion permits the accommodation of $M^+ = Na^+$, K⁺, or NH₄⁺ within the general MLnA \cdot 8H₂O 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 nineto an eight-coordinate $Ln(OH_2)_qA^-$ 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 Sm^{3+} ... Tb^{3+} ; we judge that the chelates of Eu³⁺ and Gd³⁺ are transitional in coordination type between a nine-coordinate Sm(OH₂)₃Aand an eight-coordinate $Tb(OH_2)_2A^-$. As a first test of this conclusion we are presently collecting threedimensional X-ray intensity data from a single crystal of NaTbA · 8H₂O preliminary to determination of structure.

Orthorhombic piezoelectrically active crystals, space group Fdd2, of KLa(OH₂)₃A \cdot 5H₂O have $a = 19.82 \pm 0.02$, $b = 36.18 \pm 0.03$, and $c = 12.24 \pm 0.01$ A.;



Figure 1. Scaled model of the La(OH₂)₃A⁻ ion seen in perspective. The plane of the lanthanum and two nitrogen atoms serves as a quasi-mirror for the coordination group. H₂O (in the quasi-mirror), 2N, and 4O_c positions are at seven of the eight vertices of a dodecahedron of Mo(CN)₈⁴⁻ type within which La³⁺ is off-center, *i.e.*, out-of-plane from the 4O_c trapezoid, by 0.60 Å. The fourth water molecule present in La(OH₂)₄AH has moved out of the primary coordination sphere of La(OH₂)₈A⁻, but it remains nearby in the KLa(OH₂)₄A·5H₂O crystalline arrangement.

the cell contains $16KLnA \cdot 8H_2O$ 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 La(OH₂)₄AH \cdot 3H₂O—excepting that only the 1977 independent {*hkl*} recordable for (sin θ)/ λ < 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

⁽⁷⁾ Crystal field stabilization by f-electrons probably is substantial, but, for reaction 1, it is just the difference of such stabilizations in $Ln(OH_2)_qA^-$ and $Ln(OH_2)_h^{3+}$ which contributes to the enthalpy of formation.

⁽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 endohydrogen 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., $2a \rightarrow 2b \rightarrow 2c \rightarrow etc.$) 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 1,3hydrogen 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



1801 and 1749 cm.-1) was converted without purification to the diazoketone 6c ($C_9H_{10}N_2O_2$, m.p. 106.5-107.5°, v (CCl₄) 3116, 2108, 1754, and 1648 cm.⁻¹)¹⁰ with ethereal diazomethane. Rearrangement of 6c in methanol¹¹ gave the liquid keto ester 7 ($C_{10}H_{14}O_3$, n^{23} 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 $C_9H_{16}O_2$ 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 (C₉H₁₂O, n^{26} D 1.4951, v 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 $(C_{10}H_{15}N_3O, \text{ m.p. } 188-189.5^\circ)$ gave the parent hydrocarbon 12 (C₉H₁₄, n^{25} D 1.4845, ν (CCl₄) 1462 and 1307 cm.⁻¹). Treatment of ketone 11 with lithium aluminum hydride gave alcohol 1 (Z = OH; $C_9H_{14}O$, m.p. 84.5-86.5°, v CCl₄ 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 (C16H20N2O2S, m.p. 148-149.5°) which was transformed with sodium methoxide

⁽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 semiempirical 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, (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[4.3.0.03,7]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).

⁽¹⁰⁾ Satisfactory analytical data were obtained for all compounds whose empirical formulas are given. N.m.r. spectra (in CCl4 or CDCl3) 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°, $n^{25}D1.492$ 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.

> A. Nickon, H. Kwasnik, T. Swartz R. O. Williams, J. B. DiGiorgio Department of Chemistry, The Johns Hopkins University Baltimore, Maryland 21218 Received December 23, 1964

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°, v 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-norborneneendo-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. $204-205^{\circ}$; 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-

(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.

(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.

120.5°, v 1744, 1703 (carbonyl doublet), and 1407 cm.⁻¹; semicarbazone, $C_{10}H_{15}N_{3}O$, 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 $(\nu 1739 \text{ cm}.^{-1})$ 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 $9b(C_{10}H_{14}O_3,$ n^{23} D 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 8a¹³ 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 (C_9H_{14} , 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°, v 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.