

in bis(2-ethoxyethyl) ether¹⁵ to the tetracyclic hydrocarbon **14** (C₉H₁₂, b.p. 152–153°, *n*_D²⁰ 1.4928, 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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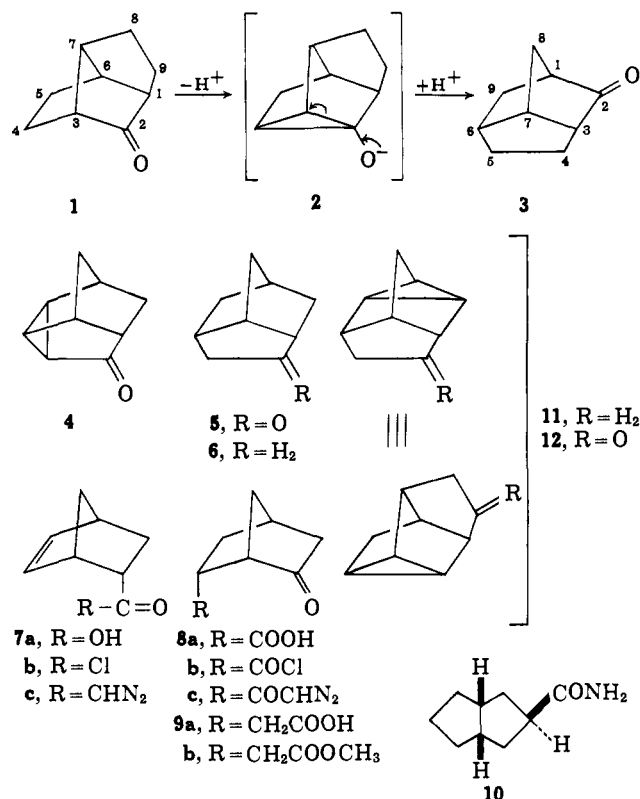
Bridged Ring Systems by Anionic Rearrangement¹

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-dinitrophenylhydrazine, 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.

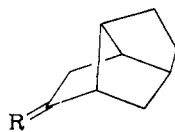
mations corroborated the structure of **3**. Haller-Bauer cleavage with sodium amide led to an amide whose melting point (136.5–138.5°) corresponded to that reported (m.p. 135–136°) for **10**.¹⁶ Conversion of **3** to its *p*-toluenesulfonylhydrazone (C₁₆H₂₀N₂O₂S, m.p. 146.5–147.5°) and treatment with sodium methoxide in bis(2-ethoxyethyl) ether¹⁷ gave the tetracyclic hydrocarbon **11**, prepared earlier.⁵

The rearrangement of **1** → **3** under alkaline conditions most reasonably proceeds through the homoenolate ion **2**, formed by abstraction of a hydrogen from C-4 (or from its equivalent position C-9). The driving force in the isomerization may lie in a greater thermodynamic stability of **3**, a factor that could also be of relevance in the solvolysis behavior of compounds with these skeletons.¹⁸

(16) R. Granger, P. F. G. Nau, and J. Nau, *Bull. soc. chim. France* 1807 (1959); R. Granger, *et al.*, *ibid.*, 1350 (1960).

(17) L. Friedman and H. Schechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959).

(18) We have also developed routes to the brendane skeleton variously functionalized at C-2 and to the brexane skeleton functionalized at C-4 (i) by homoconjugative Diels-Alder addition of norbornadiene and



i, R = O
ii, R = H₂

dienophiles such as α -acetoxyacrylonitrile or methyl vinyl ketone followed by conventional transformations to give the tetracyclic hydrocarbon **11**.^{5,19} Cleavage of **11** with sulfuric acid in acetic or formic acid followed by saponification of the esters and oxidation of the alcohols led to brendan-2-one (**3**) and brexan-4-one (i; C₁₀H₁₂O, *n*²⁵_D 1.4968, ν 1744 and 1407 cm.⁻¹; semicarbazone C₁₀H₁₅N₃O, m.p. 202–204°). Wolff-Kishner reduction of i gave brexane (ii),⁵ and Bamford-Stevens reaction¹⁷ on the *p*-toluenesulfonylhydrazone of i (C₁₅H₂₀N₂O₂S, m.p. 192–192.5° dec.) regenerated hydrocarbon **11**. Solvolytic and other mechanistic studies with appropriate derivatives of brexane, brendane, and the other ring systems shown are in progress.

(19) H. K. Hall, Jr., *J. Org. Chem.*, **25**, 42 (1960).

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The Conformational Free Energy (ΔG) of the Nitro Group¹

Sir:

In a recent paper on the proton magnetic resonance spectra of nitroalkanes² it was suggested that, under the experimental conditions used, nitrocyclohexane exists solely in the chair conformation with the nitro group equatorial (I, Figure 1). We wish to report that on

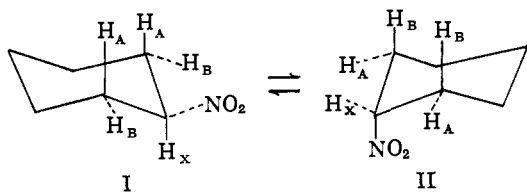


Figure 1. I, mole fraction = m ; II, mole fraction = $(1 - m)$.

(1) Conformational Analysis by Nuclear Magnetic Resonance, Part V. For Part IV, see H. Feltkamp, N. C. Franklin, M. Hanack, and K.-W. Heinz, *Tetrahedron Letters*, 3535 (1964).

(2) W. Hofman, L. Stefaniak, T. Urbanski, and M. Witanowski, *J. Am. Chem. Soc.*, **86**, 554 (1964).

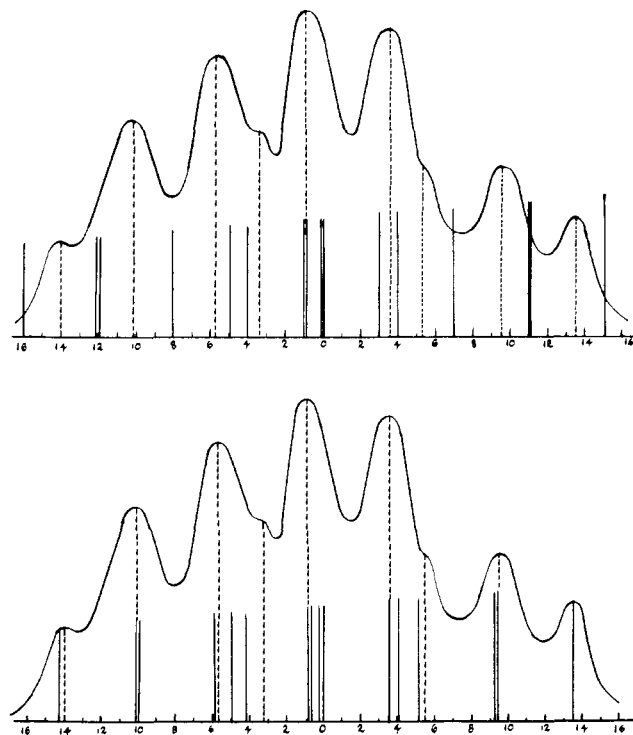


Figure 2. Spectrum 1 (upper) of Urbanski, *et al.*; spectrum 2 (lower) by Feltkamp and Franklin, ----- experimental; ——— theoretical.

further calculation we have found that the nitro group has a conformational free energy (ΔG) of approximately 1 kcal./mole and at room temperature exists as only 85% in conformer I. Using a method recently developed³ for measuring the equilibrium constant K from the band width of the methine multiplet of the tertiary (X) proton, it has been found that the equilibrium constant may be expressed as

$$K = \frac{w_a - w}{w - w_e} \quad (1)$$

The values of w_e (the band width of the X proton in conformer I) and w_a (the band width of the X proton in conformer II) were obtained from the n.m.r. spectra of *trans*- and *cis*-4-*t*-butyl-1-nitrocyclohexane,⁴ respectively. It was found that w_a was 14 ± 0.5 c.p.s.⁵ and w_e was 30 ± 0.5 c.p.s., while w (the band width of the X proton of nitrocyclohexane at 26°) was reported as 27.5 ± 0.5 c.p.s.² Hence K was calculated to be 5.7 ± 1.5 , which indicated a mole fraction of $84.5 \pm 3\%$ of conformer I present at 26°. This value of K was used to calculate a ΔG value of the nitro group of 1.02 ± 0.15 kcal./mole. As a check of the above results, the method developed by Eliel⁶ to calculate the equilibrium constant from the chemical shift of the X proton was used. From eq. 2 and the published

$$K = \frac{\tau_a - \tau}{\tau - \tau_e} \quad (2)$$

(3) H. Feltkamp and N. C. Franklin, *Ann. Chem.*, **683**, 55 (1965).

(4) A. C. Huitric and W. F. Trager, *J. Org. Chem.*, **27**, 1926 (1962).

(5) This value has been calculated from available data on the values of J_{ae} (4.2 c.p.s.) and J_{ee} (2.7 c.p.s.).

(6) E. L. Eliel, E. W. Della, and T. H. Williams, *Tetrahedron Letters*, 831 (1963).