

to the nonsymmetric stretch. The fact that this was the case for the addition of methylene to ethylene is somewhat surprising since here one might expect a large interaction constant due to the two bonds being attached to a common atom. These results, together with the discussion of the previous paragraph, indicate that, in general, transition states for cycloaddition reactions will very likely be nonsymmetric.

Finally, it is worth remarking that although transition states for cycloadditions may be nonsymmetric, this does not necessarily mean that these reactions will proceed *via* a nonconcerted (stepwise) mechanism. This can only be determined by locating the true transition states and examining the force constants.

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Synthesis of *trans*-Bicyclo[4.1.0]heptanes¹

Sir:

Since the first synthesis of a *trans*-bicyclo[*n*.1.0]alkane (1)² a considerable number of reports have appeared on the syntheses³⁻¹⁰ and reactions¹¹⁻¹⁴ of *trans*-bicyclo[6.1.0]nonanes and *trans*-bicyclo[5.1.0]octanes and their derivatives. The *trans*-bicyclo[*n*.1.0]alkanes in addition to the angle strain that is common to all cyclopropanes have a torque or twist on the zero bridge if the size of the *n* bridge is sufficiently small.¹⁵ From the reports that have appeared¹¹⁻¹⁴ the enhanced reactivity can be detected when *n* = 5 but should be much more obvious if *n* were reduced to 4.

We wish to report that we have synthesized *trans*-bicyclo[4.1.0]heptan-2-one (2) and *trans*-bicyclo[4.1.0]

(1) Financial support from National Science Foundation Grant No. GP 15334 and an instrument grant to the Department of Chemistry for the purchase of an XL-100-15 nmr spectrometer is gratefully acknowledged. For the first paper in this series see J. V. Paukstelis and Jar-lin Kao, *Tetrahedron Lett.*, 3691 (1970).

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(3) E. J. Corey and J. I. Schulman, *Tetrahedron Lett.*, 3655 (1968).

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(7) W. Kirmse and Ch. Hase, *Angew. Chem., Int. Ed. Engl.*, **7**, 891 (1968).

(8) A. J. Ashe, III, *Tetrahedron Lett.*, 523 (1969).

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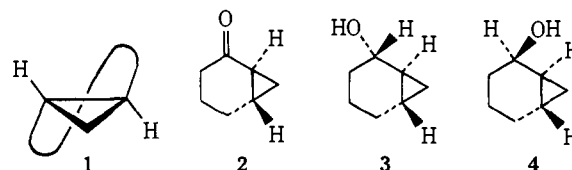
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(12) P. G. Gassman and F. J. Williams, *ibid.*, **93**, 2704 (1971).

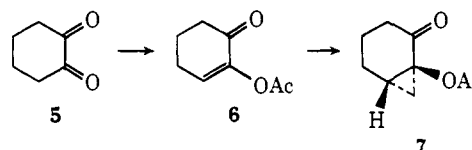
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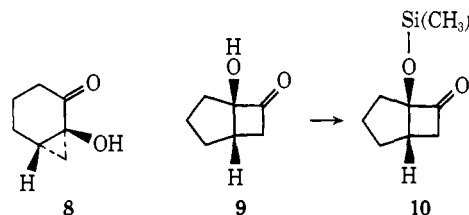
(15) P. G. Gassman, *Chem. Commun.*, 793 (1967).



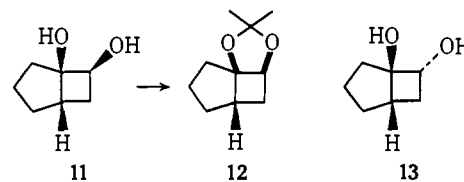
heptan-*trans*- and -*cis*-2-ols (3 and 4), the first examples of a *trans*-bicyclo[4.1.0]heptane. The synthesis was carried out starting with cyclohexane-1,2-dione (5) which on treatment with acetic anhydride gave the enol acetate 6 in 90% yield.¹⁶ Treatment of 6 under Simmons-Smith conditions gave the acetoxy ketone 7, mp 69–70°, in 20% yield.^{17,18} Reaction of 7 with



sodium methoxide at room temperature for 3 min resulted in the alcoholysis of the acetate and partial rearrangement (89%) to give a mixture of ketols 8 and 9 which had $\nu_{\max}^{\text{CCl}_4}$ at 1785 and 1695 cm^{-1} .¹⁹ The mixture on reaction with trimethylchlorosilane gave in 89% yield an ether (90% purity) which was further purified by spinning band distillation (bp 93° (16 mm)) and was identified from its carbonyl stretching (CCl_4) at 1780 cm^{-1} as 10.²⁰



Reduction of 10 with lithium tri-*tert*-butoxyaluminum hydride gives two diols in 88% yield. After separation of the two diols by column chromatography on alumina the major product 11 could be converted in 79% yield to the acetonide 12 on treatment with 2,2-dimethoxypropane²¹ establishing that 11 was a *cis* diol and that the minor product, an isomer of 11, must be the *trans* diol 13.²⁰



(16) K. W. Rosenmund and G. Kositzke, *Chem. Ber.*, **92**, 486 (1959).

(17) R. J. Rawson and I. T. Harrison, *J. Org. Chem.*, **35**, 2057 (1970).

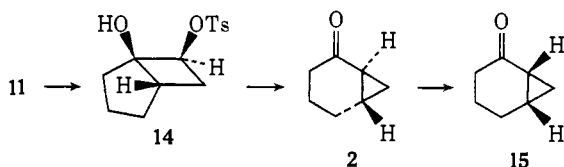
(18) All new compounds had carbon and hydrogen analyses consistent with the proposed structures.

(19) J. V. Paukstelis and D. N. Stephens, *Tetrahedron Lett.*, 3549 (1971).

(20) The alternate product, 1-trimethylsilyloxybicyclo[3.1.1]heptan-6-one, which might have a carbonyl adsorption at about the same frequency was eliminated by oxidation of 11 to 2-cyclopentanoneacetic acid and comparison of its methyl ester to an authentic sample prepared according to R. P. Linstead and E. M. Meade, *J. Chem. Soc.*, 935 (1934), and E. J. Corey and R. L. Carney, *J. Amer. Chem. Soc.*, **93**, 7318 (1971).

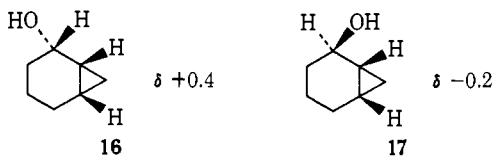
(21) B. R. Brown and J. A. H. MacBride, *J. Chem. Soc.*, 3822 (1964).

With **11** on hand we proposed to take advantage of the stereospecificity of the glycol monotosylate rearrangement to form the desired product **2**. The stereospecificity of such rearrangements has been well established in the synthesis of many bicyclic systems²²⁻²⁴ including *trans*-bicyclo[7.1.0]decan-2-one.¹ The most important feature for our choice was that the rearrangement could be run under very mild conditions.^{1,22} Thus, treatment of **11** with tosyl chloride in pyridine and rearrangement of the monotosylate **14** with 1 equiv of potassium *tert*-butoxide in THF for 10 min gave a product in 83% yield which we assigned as **2**. Molecular distillation gave a pure product which exhibited $\nu_{\max}^{\text{CCl}_4}$ 3010 and 1703 cm^{-1} and δ (CCl_4) +0.4 ppm (1 H, m, cyclopropyl and no resonances below 2.5 ppm).¹³ When the reaction was allowed to proceed for 19 hr and with 2 equiv of potassium *tert*-butoxide, a different product was isolated in 73% yield. This product, **15**, was identical in all respects with *cis*-bicyclo[4.1.0]heptan-2-one prepared by a known route:²⁵ $\nu_{\max}^{\text{CCl}_4}$ 1690 cm^{-1} and δ (CCl_4) 1.0 ppm (highest field multiplet). The isolation of **15** is consistent with the initial formation of **2** followed by isomerization to **15**. When the rearrangement was



run in *tert*-butyl alcohol-*d* the product contained less than 33 mol % deuterium²⁶ indicating that the rearrangement proceeds primarily without enolization of any kind.

If the rearrangement of **14** is done in the presence of a reducing agent, such as potassium tri-*tert*-butoxyaluminum hydride, the ketone **2** can be reduced to a mixture of alcohols **3** and **4** in a ratio of 2:1, respectively. Comparison of the nmr and infrared spectra of **3** and **4** and the known *cis*-bicyclo[4.1.0]heptan-*cis*- and -*trans*-2-ols²⁵ (**16** and **17**) indicated that the com-



pounds were not the same. The presence of the complex multiplets in the nmr spectrum of **3** at δ (CCl_4) -0.5 ppm and for **4** at 0.2 ppm clearly indicated the presence of cyclopropyl in **3** and **4**. On the basis of the chemical shifts of **16** and **17** and the possible conformations for **3** and **4** one can tentatively assign the structure of the two alcohols as *trans*-bicyclo[4.1.0]heptan-*trans*-2-ol for **3** and *trans*-bicyclo[4.1.0]heptan-*cis*-2-ol for **4**.¹⁴ The alcohols are not stable to glpc but can be purified by trap-to-trap distillation (54% yield). Acetates and other derivatives of **3** and **4** can

(22) G. Buchi, W. Hofheiz, and J. V. Paukstelis, *J. Amer. Chem. Soc.*, **91**, 6473 (1969).

(23) M. Nussim and Y. Mazur, *Tetrahedron*, **24**, 5337 (1968), and references therein.

(24) D. Redmore and C. D. Gutsche, *Advan. Alicycl. Chem.*, **3**, 1 (1971), and references therein.

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(26) The mass spectral analysis indicated 67% *O-d*, 17% *1-d*, 14% *2-d*, and 2% *3-d*.

be formed by standard methods without undue difficulty.

We are examining the reaction of the ketone **2**, the alcohols **3** and **4**, and the derivatives of **3** and **4** to determine the reactivity of *trans*-bicyclo[4.1.0]heptanes. We have also synthesized by similar methods *cis*- and *trans*-bicyclo[5.1.0]octanes and *cis*- and *trans*-bicyclo[6.1.0]nonanes and are examining their reactivity toward a variety of reagents.

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New Anionic Rearrangements. XVI. 1,2-Anionic Rearrangement from Sulfur to Carbon in Benzylthiotrimethylsilane¹⁻³

Sir:

Many organic ethers may be converted to isomeric alcohols in the presence of excess organolithium reagent by the classical Wittig rearrangement.⁴ The analogous rearrangement of organic sulfides to mercaptans has not previously been observed.⁵ Generally, metalation of the rather acidic proton α to sulfur in sulfides,⁶ sulfoxides,¹⁰ and sulfones¹¹ produces stable carbanions which do not rearrange.

We now find that benzylthiotrimethylsilane (**1**) rearranges rapidly and in high yield^{12,14} to α -trimethylsilylbenzylmercaptan (**2**) in the presence of excess *tert*-butyllithium.¹⁷ This is apparently the first example

(1) Previous paper in this series: R. West and P. Boudjouk, *J. Amer. Chem. Soc.*, in press.

(2) For a review of silylanionic rearrangements see R. West, *Pure Appl. Chem.*, **19**, 291 (1969).

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(5) A Wittig-like mechanism has been used to explain the formation of stilbene from benzyl sulfide and strong base. See T. J. Wallace, H. Pobiner, J. E. Hofmann, and A. Schriesheim, *J. Chem. Soc.*, 1271 (1965).

(6) For example: $\text{CH}_3\text{SCH}_2\text{Li}$;⁷ PhSCH_2Li ;⁸ lithiated 1,3-dithianes.⁹

(7) D. J. Peterson, *J. Org. Chem.*, **32**, 1717 (1967).

(8) H. Gilman and F. J. Webb, *J. Amer. Chem. Soc.*, **71**, 4062 (1949).

(9) E. J. Corey and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **4**, 1075 (1965).

(10) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1345 (1965).

(11) B. S. Thyagarajan, *Mech. React. Sulfur Compounds*, **4**, 115 (1969).

(12) Recently we reported the almost quantitative Wittig-type rearrangement of triethylbenzylsilyloxilane to phenyltriethylsilylcarbinol in the presence of excess *tert*-butyllithium.¹³

(13) R. West, R. Lowe, H. F. Stewart, and A. Wright, *J. Amer. Chem. Soc.*, **93**, 282 (1971).

(14) The migratory aptitude of silicon in 1,2 anionic rearrangements is remarkable.^{2,13} When carbon migrates, as in the Wittig rearrangement, a simple 1,2 sigmatropic suprafacial shift is disallowed by the Woodward-Hoffmann rules^{15,16} with the result that rearrangements proceed slowly, often in low yield, and apparently by a cleavage-recombination mechanism. Silicon probably migrates *via* a pentacoordinate transition state without the above symmetry restrictions.¹⁶

(15) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(16) A. G. Brook, G. E. LeGrow, and D. M. MacRae, *Can. J. Chem.*, **45**, 239 (1967).

(17) The remote rearrangement $\text{LiC}_6\text{H}_5\text{SiMe}_3 \rightarrow \text{Me}_3\text{SiC}_6\text{H}_5\text{SLi}$ has been reported: see A. R. Bassindale and D. R. M. Walton, *J. Organometal. Chem.*, **25**, 389 (1970).