thermic dissociation of base molecules. For both donors, the hexane $\Delta H_{\text{sol},\infty}$ is more endothermic than the CCl_4 $\Delta H_{\text{sol},\infty}$. Therefore, the heat of transfer from hexane to CCl_4 should reflect the strength of the CCl_4–base interactions. These heats are −1.71 kcal/mol for pyridine and −1.27 kcal/mol for γ-collidine. The smaller γ-collidine transfer enthalpy probably represents steric interaction (>0.44 kcal/mol) between a CCl_4 molecule and the 2,6-methyl groups of γ-collidine.

Relative adduct solvation energies can be obtained from Haber cycles using the data in the tables. The data in Table II show that for every reaction the enthalpy is larger in hexane than in CCl_4.[8] The difference in hydrogen-bond enthalpies in these two solvents ($\Delta H_{\text{hex}} - \Delta H_{\text{CCl}_4}$) increases in the following order: TFE–pyridine (−1.15 ± 0.06) < TFE–collidine (−1.28 ± 0.03) < HFIP–pyridine (−1.35 ± 0.04) < HFIP–collidine (−1.45 ± 0.06). From the data in Tables I and II and from[1,5] $\Delta H^{\text{TFE}}(\text{hex} \rightarrow CCl_4) = -0.92$ kcal mol^{-1} and $\Delta H^{\text{HFIP}}(\text{hex} \rightarrow CCl_4) = -0.39$ kcal mol^{-1}, it can be shown easily that this increasing difference results mainly from greater solvation by CCl_4 of the TFE adducts then the corresponding HFIP adducts and greater solvation by CCl_4 of the pyridine adducts than the γ-collidine adducts. The adduct transfer solvation energies (kcal mol^{-1}, hexane → CCl_4) are HF·coll = −0.21, HF·py = −0.75, TF·coll = −0.91, TF·py = −1.48. The order of these values is exactly reversed from what one would expect from adduct polarities and is interpreted in terms of solvations which depend on the "congestion" at or the shielding of the polar O–H–B groupings. HFIP is the more sterically hindered acid,[9] while γ-collidine is the more sterically hindered donor. The relative order of HF·py and TF·coll leads us to conclude that collidine affords more shielding of O–H–B than HFIP.

Table II. Hydrogen-Bond Enthalpies for the Acids TFE and HFIP and the Bases Pyridine and γ-Collidine in the Two Solvents CCl_4 and Hexane

Acid	Base	Solvent	$-\Delta H_f$,[b] kcal/mol
TFE	Pyridine	CCl_4	6.67 ± 0.02
TFE	Pyridine	Hexane	7.82 ± 0.04
HFIP	Pyridine	CCl_4	8.40[a] ± 0.02
HFIP	Pyridine	Hexane	9.75[a] ± 0.02
TFE	γ-Collidine	CCl_4	7.52 ± 0.01
TFE	γ-Collidine	Hexane	8.80 ± 0.02
HFIP	γ-Collidine	CCl_4	9.67 ± 0.03
HFIP	γ-Collidine	Hexane	11.12 ± 0.03

[a] Reference 1. [b] The limits on ΔH are precision estimates as determined from sharpness of fit; see ref 5.

Arnett, *et al.*,[4] have recently indicated that pyridine–CCl_4 interactions are small since the same enthalpy of hydrogen-bond formation for the phenol–pyridine reaction is found when CCl_4 is solvent as when pure base is solvent. When adding an acid to pure pyridine, the associated pyridine molecules must be dissociated before a hydrogen bond can form. The energy (~2 kcal) necessary to dissociate these molecules is comparable to the energy (~1.7 kcal) required to disrupt the pyridine–CCl_4 interactions. Thus, it is not surprising that the same enthalpy is obtained by both methods, and the equality demonstrates the importance of CCl_4–pyridine interactions. Whenever base–solvent interactions are suspected, the best approach seems to be method I, using various inert solvents for comparison.

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[8] The possibility that the hexane heats are larger than the CCl_4 heats because of adduct solvation by excess base aggregates in hexane was checked. That this complication is not present is demonstrated by excellent fits of the data to plots of A_0B_0V/Q *vs.* B_0: *cf.* K. F. Purcell, *et al.*, *J. Amer. Chem. Soc.*, **91**, 4019 (1969).

[9] The acid-transfer heats suggest greater solvation of TFE than HFIP, which is in keeping with greater hindrance for the latter.

1,3,5,7-Tetramethylbicyclo[5.1.0]octa-2,5-diene (Tetramethylhomotropilidene) by a 1,4-Homoelimination Reaction. The Stereochemical Analysis of a Cope Rearrangement[1]

Sir:

Degenerate Cope rearrangements, which may easily be studied using established nmr techniques, have become of general interest recently because of the possible bishomobenzene-like transition state or intermediate involved in the rearrangement.[2] In an attempted preparation of a potential bishomobenzene derivative we devised a novel cyclopropane ring opening reaction, a 1,4 homoelimination, as exemplified by the synthesis of 1,3,5,7-tetramethylbicyclo[5.1.0]octa-2,5-diene (tetramethylhomotropilidene). We now wish to report the preparation and nmr behavior of this compound.

Treatment of diol I[3] with dry hydrogen chloride in benzene solution at 0° gave dichloride II,[4] mp 93.5–94°, in 85% yield: nmr (CCl_4) τ 5.60 (2 H, s), 8.72 (12 H, s), 8.84 (2 H, d, $J = 6$ Hz), 9.78 (2 H, d, $J = 6$ Hz). The configuration of II was assigned as follows. The reaction of dichloride II with sodium borohydride in 70% aqueous diglyme[5] at room temperature gave hydrocarbon III[4] in 64% yield: nmr (CCl_4) τ 8.20 (2 H, d, $J = 14.5$ Hz), 8.88 (2 H, d, $J = 14.5$ Hz), 8.91 (12 H, s), 9.79 (2 H, d, $J = 4.5$ Hz), 10.01 (2 H, d, $J = 4.5$ Hz). The presence of an AB quartet for the methylene protons adjacent to the cyclopropane rings in III demonstrates the cis orientation of the latter. Upon irradiation of the methyl signal (τ 8.72) of II, an 11 ± 4% increase in the integral intensity of the methine signal (τ 5.60) was observed. This detection of a nuclear Overhauser effect[6] combined with the observation of a single methine absorption and the cis cyclopropane

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[1] Research supported by the National Science Foundation.

[2] (a) H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, 88, 183 (1966); (b) F. A. L. Anet and G. E. Schenk, submitted for publication.

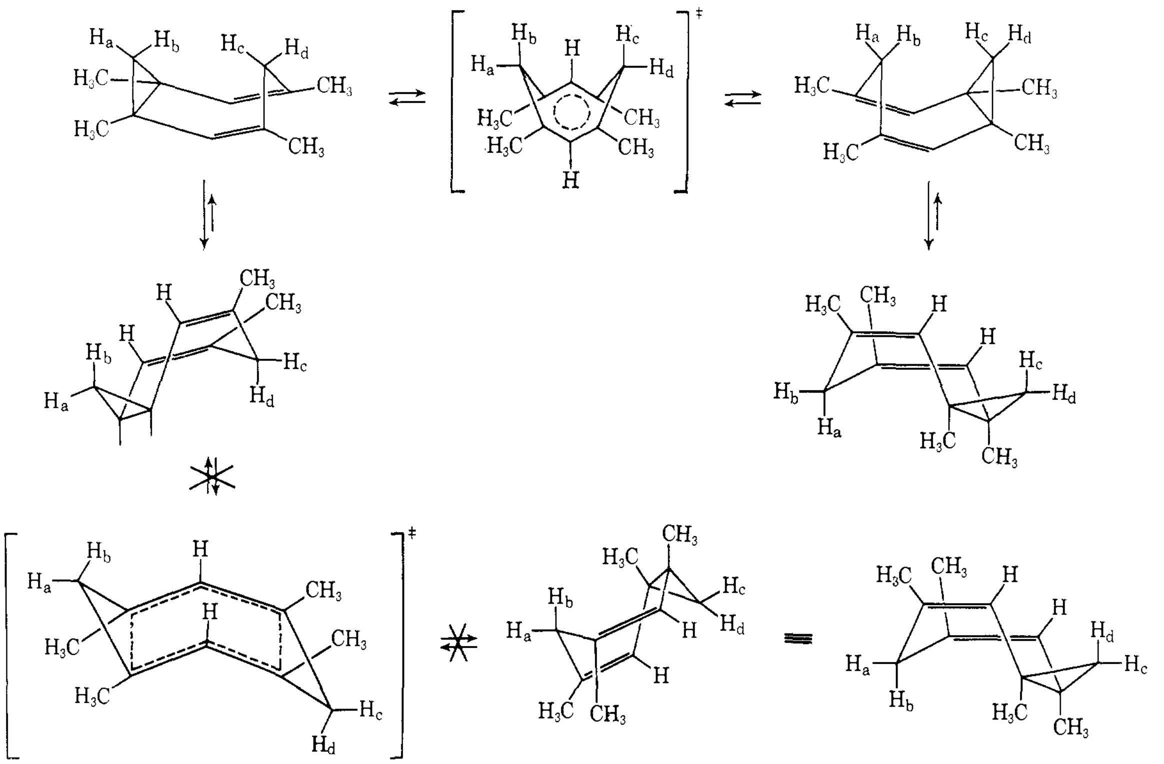
[3] J. M. MacDonald, Ph.D. Dissertation, The University of Western Ontario, London, Canada, 1963.

[4] Satisfactory analytical data were obtained for all new compounds; TMS was used as an internal standard for all nmr spectra.

[5] (a) H. C. Brown and H. M. Bell, *J. Org. Chem.*, **27**, 1928 (1962); (b) S. Winstein, A. Lewin, and K. Pande, *J. Amer. Chem. Soc.*, **85**, 2324 (1963); (c) H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963).

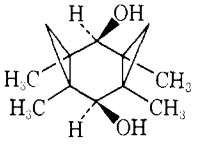
[6] F. A. L. Anet and A. J. R. Bourn, *ibid.*, **87**, 5250 (1965).

Scheme I

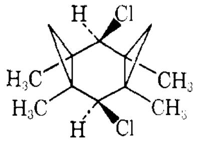


orientation demonstrates the all-cis configuration of II. Since the diol I also has been shown to have an all-cis configuration,[7] formation of II from I must occur with retention of configuration, as has been observed in a similar system.[8]

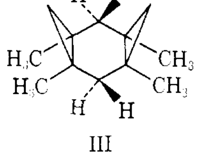
Upon treatment with lithium amalgam in ether at room temperature[9] or sodium in liquid ammonia at −78°, dichloride II is converted essentially quantitatively to tetramethylhomotropilidene (IV), bp 55–56° (4 mm).[4,10] The spectrum of IV is temperature dependent, denoting the existence of a Cope rearrangement. At −47° (60 MHz) the nmr spectrum is that of the static tetramethylhomotropilidene structure: (CS$_2$) τ 4.81 (2 H, m), 6.68 (1 H, broad d, J = 14 Hz), 8.38 (1 H, d of t, J = 14, 1 Hz), 8.39 (6 H, d, J = 1 Hz), 8.87 (6 H, s), 9.69 (1 H, d, J = 3 Hz), 9.86 (1 H, d, J = 3 Hz).



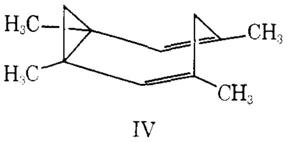
I



II



III



IV

The averaged spectrum of IV was obtained at +138°: (neat) τ 4.81 (2 H, m), 8.25 (2 H, broad d, J = 8.5 Hz), 8.60 (12 H, s), 9.03 (2 H, broad d, J = 8.5 Hz). $\Delta G^{\ddagger}$ for the exchange process at the coalescence temperature for the methyl signals (0°) is calculated to be 13.6 kcal/mol.

One interesting feature of the Cope rearrangement of IV is its high $\Delta G^{\ddagger}$ compared to dihydrobullvalene (9.5 kcal/mol),[11] barbaralane (7.8 kcal/mol),[12] and octamethylsemibullvalene (6.4 kcal/mol).[2a] The diene IV may exist in either cisoid or transoid conformations and the transition state for the Cope could be either cis-like or trans-like.[13] We analyzed the nmr spectra of IV and were able to prove that the more stable conformation of IV is the transoid and that the Cope rearrangement procedes through a cis-like (bishomobenzene type) transition state as predicted by Doering[14] in 1963.

In both the cisoid and transoid conformations of IV, one allylic proton is in the plane of the double bond ("outside" proton) while the other is perpendicular to the plane ("inside" proton). It is known that an allylic proton perpendicular to the plane of the adjacent double bond has a negative, long-range, four-bond coupling constant (^4J) with the vinyl proton, while ^4J for an allylic proton in the plane of the double bond is positive.[15] It is also known that geminal coupling constants of the type in question are negative.[16] Therefore, by selec-

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(7) W. C. Howell, private communication. We are grateful to Professor Howell for informing us of his results prior to publication.

(8) L. Birladeanu, T. Hanafusa, B. Johnson, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 2316 (1966).

(9) R. Criegee and G. Louis, *Chem. Ber.*, **90**, 417 (1957).

(10) This reaction is similar to the known conjuate 1,4 elimination: E. E. van Tamelen and T. L. Burkoth, *J. Amer. Chem. Soc.*, **89**, 151 (1967).

(11) G. Schröder, J. F. M. Oth, and R. Merenyi, *Angew. Chem., Int. Ed. Engl.*, **4**, 752 (1965).

(12) W. v. E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967).

(13) We point out that, although it might appear that trans double bonds would be formed if the Cope were to occur through a trans-like transition state, the dihedral angle between C$_1$–CH$_3$ and C$_2$–H is about 80° in the transoid conformation of IV, which would allow cis double bond formation in the rearrangement product.

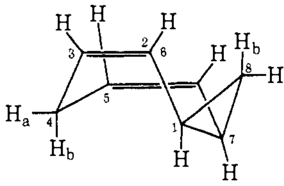
(14) W. v. E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(15) E. W. Garbish, Jr., *J. Amer. Chem. Soc.*, **86**, 5561 (1964).

(16) M. Barfield and D. M. Grant, *Advan. Magn. Resonance*, **1**, 149 (1965).

tively decoupling[17] the allylic methylene proton signals in the nmr spectrum of IV while monitoring the vinyl resonance (−40°, 100 MHz), it was possible to determine that the τ 6.68 absorption is due to the "inside" proton. This proton is deshielded compared to τ 7.85 for the average chemical shift of the bisallylic methylene protons in cycloheptatriene. Models show that in the cisoid conformation both cyclopropane and allylic "inside" methylene protons should be deshielded due to the double bond anisotropy. On the other hand, in the transoid conformation, the "inside" cyclopropane proton should be shielded by the double bonds while the "inside" allylic methylene proton should be deshielded not only by the double bonds, but also by the cyclopropane ring. Since both cyclopropane protons are at quite high field and clearly are not deshielded, the transoid conformation must be attributed to the static structure of IV. Upon double irradiation of the cyclopropane methyl signal (τ 8.87) at −75°, a 12 ± 3% increase in the integrated area of the τ 9.86 signal was observed. This signal must then be attributed to the "outside" cyclopropane methylene proton.

As may be seen in Scheme I, if the degenerate Cope rearrangement were to occur through a trans-like transition state, H_a would exchange with H_c and H_b with H_d; however, if the rearrangement would take place through a cis-like transition state, H_a would exchange with H_d and H_b with H_c. The protons which undergo exchange may be identified from the average chemical shifts in the high-temperature "fast exchange" nmr spectrum, but a more convenient[18] method, involving double resonance techniques, is to introduce a "label" in the system by saturating one of the methylene proton signals at a temperature at which the rate of exchange is greater than the inverse of the spin–lattice relaxation time.[19] Thus, exchange was observed between H_d (τ 6.68) and H_a (τ 9.86) as well as between H_c (τ 8.38) and H_b (τ 9.69) at −40°. Therefore, the degenerate Cope rearrangement must occur in IV through a cis-like transition state. We were also able to show that the same is true in 3,4-homotropilidine[13] (V). Here, the corresponding protons were easily assigned from the coupling constant data and it was found that H_{8b} (τ 9.81, $J_{1,8b} = 5$ Hz, $J_{8a,8b} = 3$ Hz) exchanges with H_{4a} (τ 7.35, $J_{3,4a} = 7$ Hz, $J_{4a,4b} = 20$ Hz) and H_{8a} (τ 8.81, $J_{1,8a} = 8$ Hz, $J_{8a,8b} = 3$ Hz) exchanges with H_{4b} (τ 6.92, $J_{3,4b} = 2$ Hz, $J_{4a,4b} = 20$ Hz). Since no exchange was detected between the two sets of averaged methylene protons of IV at +138°, a lower limit of $\Delta G^{\ddagger}$ for the degenerate Cope rearrangement through a trans-like transition state is calculated to be 22.8 kcal/mol, which is reasonable considering the poor orbital overlap seen in models.



V

If one assumes that the barrier for interconversion of cisoid and transoid conformations of IV is smaller than the overall energy barrier for the Cope reaction,[20] then the observed free energy of activation is the sum of the free energy difference between the cisoid and transoid conformations and the free energy of activation of the Cope reaction from the cisoid conformation. The latter may be estimated to be similar to that observed in dihydrobullvalene, and therefore it is estimated that the transoid conformation of IV is *ca.* 4 kcal/mol more stable than the cisoid.

Acknowledgment. We are very grateful to Professor F. A. L. Anet for helpful discussions and to Professor M. Brookhart for recording some of the nmr spectra.

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(17) R. A. Hoffman and S. Forsen, *Progr. Nucl. Magn. Resonance Spectrosc.*, 1, 143 (1966).

(18) When two of the chemical shifts involved in a system are similar as in IV, this technique is not only the most convenient, but also the safest, because some chemical shifts have been found to be temperature dependent.

(19) (a) S. Forsen and R. A. Hoffman, *J. Chem. Phys.*, **39**, 2892 (1963); (b) I. C. Calder, P. J. Garratt, and F. Sondheimer, *Chem. Commun.*, **2**, 41 (1967); (c) B. G. Derendyaev, V. I. Mamatyuk, and V. A. Koptyug, *Tetrahedron Lett.*, **33**, 5 (1969).

(20) The barrier for ring inversion in the structurally similar cycloheptatriene is only 6.1 kcal/mol: F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 458 (1964).

(21) Deceased, November 23, 1969.

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On the Wurtz Reaction. Chemically Induced Nuclear Spin Polarization in Reactions of Alkyl Iodides with Sodium Mirrors

Sir:

Wurtz reactions are believed to proceed through two mechanistic stages, reduction and alkyl coupling.[1]

$$RX + 2M \longrightarrow RM + MX \ (M = \text{an alkali metal}) \tag{1}$$

$$RM + RX \longrightarrow R_2 + MX \tag{2}$$

When lithium is involved, the second stage is readily isolated from the first.[2] Recent studies of reactions of alkyllithiums with alkyl halides in homogeneous solutions (in hydrocarbons and ethers) support mechanisms involving alkyl radical intermediates.[3] The initial steps of such mechanisms can be represented as electron transfers from carbanions to alkyl halides.

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(1) Annotated summaries of older mechanistic investigations of Wurtz reactions are available in several texts and monographs: (a) E. R. Alexander, "Ionic Organic Reactions," Wiley, New York, N. Y., 1950, pp 203–206; (b) E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, New York, N. Y., 1954, pp 114–120; (c) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, pp 245–246; (d) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill, New York, N. Y., 1968, pp 354–355.

(2) Reactions of preformed alkyllithiums with alkyl halides are often loosely referred to as "Wurtz reactions."

(3) (a) G. A. Russell and D. W. Lamson, *J. Amer. Chem. Soc.*, **91**, 3967 (1969); (b) H. R. Ward, R. G. Lawler, and R. A. Cooper, *ibid.*, **91**, 746 (1969), and earlier works; (c) A. R. Lepley and R. L. Landau, *ibid.*, **91**, 748 (1969), and earlier works; (d) D. Bryce-Smith, *J. Chem. Soc.*, 1603 (1956); *Bull. Soc. Chim. Fr.*, 1418 (1963); (e) F. S. D'yachkovskii and A. E. Shilov, *Russ. Chem. Rev.*, **35**, 300 (1966), and works cited; (f) P. T. Lansbury, V. A. Pattison, J. D. Sidler, and J. Bieber, *J. Amer. Chem. Soc.*, **88**, 78 (1966); (g) H. Fischer, *J. Phys. Chem.*, 73, 3834 (1969); (h) J. Sauer and W. Braig, *Tetrahedron Lett.*, 4275 (1969). (i) Electron transfer has been proposed as the general mode of reaction of alkyllithiums with other substrates, including alkyl halides: C. G. Screttas and J. F. Eastham, *J. Amer. Chem. Soc.*, **88**, 5668 (1966).