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 $\pm$ 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.
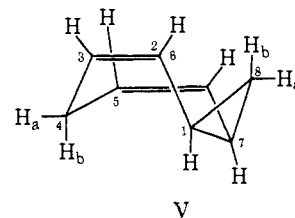
If one assumes that the barrier for interconversion of cisoid and transoid conformations of IV is smaller than the overall energy barrier for the Cope reaction,[20]

V

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.

heptatriene 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]

$$RX + 2M \longrightarrow RM + MX \text{ (M = an alkali metal)} \quad (1)$$
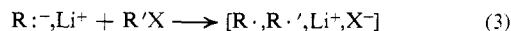
$$RM + RX \longrightarrow R_2 + MX \quad (2)$$
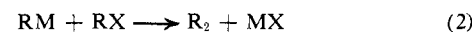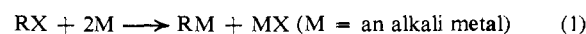
When lithium is involved, the second stage is readily isolated from the first.[2] Recent studies of reactions of alkyllithiums with alkyl halides in homogeneous solutions (in hydrocarbons and ethers) support mechanisms involving alkyl radical intermediates.[3] The initial steps of such mechanisms can be represented as electron transfers from carbanions to alkyl halides.

(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).

(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 cyclo-

$$R:^-,Li^+ + R'X \longrightarrow [R\cdot,R\cdot',Li^+,X^-] \qquad (3)$$

For alkylsodiums, problems of solubility and reactivity toward solvents have precluded analogous studies. Further, the reported studies of heterogeneous systems leave the theory of the Wurtz reaction confused, since some works support SN2 alkyl coupling stages while others seem inconsistent with this view.[1,3d]

We have recently approached the general problem by generating alkylsodiums homogeneously in 1,2-dimethoxyethane (DME) under such conditions that their subsequent reactions with unreduced alkyl halides compete with reactions with the solvent.[4] This amounts to having replaced the sodium metal in classical Wurtz reactions with a homogeneous reducing agent, sodium naphthalene. We concluded that the reactions of simple alkylsodiums with simple alkyl iodides under such circumstances are not adequately described by conventional SN2 theory. Instead, mechanisms involving reactions like (3) appear more reasonable.

As interesting as such data may be, the conditions under which the reactions are carried out are far removed from the heterogeneous situations of classical Wurtz reactions. We now report evidence, in the form of chemically induced nuclear spin polarization phenomena,[5] for the involvement of free alkyl radicals in reactions which ensue when alkyl iodides react with sodium mirrors in DME.

Samples were prepared in the previously described "onion-dome" nmr tubes.[6] A typical experiment was performed as follows. Using a vacuum manifold, alkyl iodide was admitted to the nmr tube, thoroughly degassed, and frozen in liquid nitrogen. Sodium was distilled into the bulb, coating it with a clean mirror. Solvent was then distilled into the bottom of the nmr tube, after which the tube (with its bulb) was sealed off and the contents thawed with the tube upright (bulb at the top). The reaction was carried out by tipping the solution into the bulb (onto the sodium mirror), agitating it for a few seconds (<10), tipping it off the sodium mirror into the lower end of the tube, and then placing the tube in the spectrometer (Hitachi R-20) for scanning.

When the reaction of methyl iodide was carried out in a position near the spectrometer magnet at which the field was of the order of 20 G, the ethane formed was negatively polarized (nmr emitting). Since all theories of chemically induced nuclear spin polarization invoke transitions in the spin systems of paramagnetic species,[5] these results constitute strong evidence for the intermediacy of methyl radicals at some point or points in the mechanism of the reaction of methyl iodide with a sodium mirror.
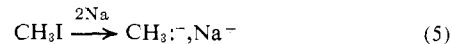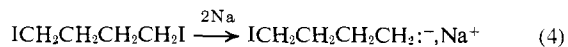
In contrast to these results, the reactions of 1,4-diiodobutane with sodium mirrors under identical conditions gave cyclobutane for which no polarization was detected. This is in further contrast with the results of similar experiments involving reactions of sodium naphthalene with 1,4-diiodobutane, in which case the cyclobutane formed was negatively polarized.[7]

Clearly, no stage of the reaction of 1,4-diiodobutane with a sodium mirror leads to polarization.[8] Since the reduction stage of this reaction should be entirely analogous with that for methyl iodide (eq 4 and 5),[9]

$$ICH_2CH_2CH_2CH_2I \xrightarrow{2Na} ICH_2CH_2CH_2CH_2:^-,Na^+ \qquad (4)$$

$$CH_3I \xrightarrow{2Na} CH_3:^-,Na^- \qquad (5)$$

this implies that the second stage (eq 6) of the reaction

$$CH_3:^-,Na^+ + CH_3I \longrightarrow CH_3CH_3 + NaI \qquad (6)$$

of methyl iodide with a sodium mirror is responsible for the observed polarization.[10] This is inconsistent with the idea that alkyl dimers arise exclusively through SN2 mechanisms in these reactions, but it is consistent with mechanisms for reaction 6 in which radicals are intermediates, being generated, perhaps, in steps analogous with reaction 3.[12]

Parallel reasoning leads to the conclusion that the polarizing stage of the reaction of 1,4-diiodobutane with sodium naphthalene is the first stage, reduction to 4-iodobutylsodium. This was the assumption made in our previous discussion of those results.[6] Reactions of simple monohaloalkanes with sodium naphthalene, however, may involve polarization in both reduction and alkyl coupling stages. It is hoped that the parallel study of polarizations in reactions with sodium mirrors and in reactions of sodium naphthalene will permit correlation of the observed effects with particular reaction stages.

It should be pointed out that the conclusions reached above hinge on the observed data, on assumptions about the chemical mechanisms of the reactions, and on the assumption that paramagnetic intermediates are required to generate nuclear spin polarization, but they do not depend on the nature of the observed polarizations nor on the details of the theory of chemically

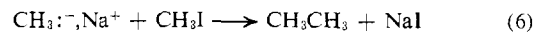(4) J. F. Garst and J. T. Barbas, *Tetrahedron Lett.*, 3125 (1969).

(5) See H. Fischer (*Chem. Phys. Lett.*, 4, 611 (1970)) for a recent list of references to the literature of chemically induced nuclear spin polarization.

(6) R. H. Cox, E. G. Janzen, and J. G. Gerlock, *J. Amer. Chem. Soc.*, 90, 5906 (1968).

(7) (a) J. F. Garst (with R. H. Cox, J. T. Barbas, and R. D. Roberts), *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, 11, 8 (1970); (b) J. F. Garst, R. H. Cox, J. T. Barbas, R. D. Roberts, J. I. Morris, and R. C. Morrison, *J. Amer. Chem. Soc.*, 92, 5761 (1970).

(8) An alternative is that polarization induced in one stage is removed in the other. We assume that this is not the case.

(9) One may imagine an alternative for the reduction stage of 1,4-diiodobutane, one in which both ends of the molecule are simultaneously reduced. In fact, products which could arise in this fashion are found with longer chain α,ω-dihalides (unpublished work of J. T. Barbas). However, no butane is found in the present case, mitigating against this possibility. Further we have shown for the somewhat analogous reaction of 1,4-diiodobutane with sodium naphthalene that simultaneous or successive reduction at the two ends of the molecule does not occur. For these reasons, we assume that it does not occur in the present reactions.

(10) One may question the self-consistency of the conclusion that reaction 6 generates nuclear spin polarized products while the analogous intramolecular reaction of 4-iodobutylsodium does not. In fact, this is consistent with presently available theory and fact. For the reaction of 4-iodobutylsodium, the intermediate analogous with the methyl radical pair in reaction 3 would be 1,4-butadiyl. Closs has enumerated reasons that short-chain biradicals should not be expected to generate nuclear polarization in their reactions, whereas radical pairs should.[11] In keeping with this prediction, no examples of nuclear polarization which could be attributed to the generation and collapse of short-chain biradicals have been reported.

(11) G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, 91, 4554 (1969).

(12) A referee inquired whether methyl iodide itself becomes polarized in our experiments. In the reaction of methyl iodide with sodium naphthalene the excess methyl iodide is negatively polarized, but the polarization vanishes rapidly after the reactions are run, implying a very short relaxation time for protons in methyl iodide. As yet, we have not observed corresponding methyl iodide polarization in its reactions with sodium mirrors. We suspect that we simply have not yet been fast enough in getting the reactions done and transferred to the spectrometer.

induced nuclear spin polarization. One may inquire how the results compare with predictions of theory. If one assumes, for the reaction of methyl iodide with a sodium mirror, that ethane is formed in geminate combinations of methyl radicals generated in steps analogous to (3), and if one applies the CKO model, extended to include t_1-s interactions, one reaches the prediction that the ethane formed should exhibit enhanced absorption, not the observed emission.[7b] This conclusion is predicated on the assumption of an electronic *singlet* initial state for the critical radical pairs. In order to obtain a prediction of emission from the extended CKO model, one would have to assume initially *triplet* radical pairs, the formation of a substantial portion of the ethane in nongeminate encounters, or an effective J value for the critical pairs corresponding to a lower lying triplet than singlet. Alternatively, the extended CKO model used may be at fault for its neglect of dipolar nuclear-electron coupling terms in the Hamiltonian employed.[7b,13]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(13) S. H. Glarum has treated the anisotropic nuclear-electron coupling with the finding that for polarization arising from t_1-s interactions the contribution from this term is in the opposite direction from the contribution due to isotropic coupling: personal communication from S. H. Glarum.
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Stereoselective Synthesis and Stereochemistry of Optically Active Isopropyl Methylphosphinothionate

Sir:

We wish to report the first example of an optically active hydrogen phosphinothionate (2), and offer a preliminary account of our studies of the stereochemistry of this synthetically versatile compound, in comparison to its phosphinate analog (1).[1]

Treatment of 4.1 mmol of (R)-(−)-isopropyl methylphosphinate[1] (1), [α]D −29.9° (EtOH), with 0.47 mmol of P_4S_{10} in benzene, essentially according to Schrader's procedure[2] for the synthesis of ethyl ethylphosphinothionate, gave after vacuum distillation at room temperature 1.4 mmol of (S)-(−)-isopropyl methylphosphinothionate (2), readily distinguishable from 1 by its ir spectrum (no $\nu_{P=O}$; $\nu_{PH}^{CCl_4}$ 2312 cm^{-1}) and longer glpc retention time on a 10-ft, 10% SE-30 column. This product had [α]D −16.2° (benzene), −17.4° (CCl$_4$), and −20.4° (ethanol). It is believed to be 68% optically pure, and was formed (see below) with predominant retention of configuration. The reaction thus represents a new addition to a small but growing number of displacements in acyclic systems that are known to proceed with retention of configuration at the phosphorus atom.[3] In this case, ap-

(1) L. P. Reiff and H. S. Aaron, *J. Amer. Chem. Soc.*, **92**, 5275 (1970).
(2) K. Sasse in "Methoden der Organischen Chemie," Vol. 12, Part 1, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1963, p 332.
(3) (a) J. Michalski, *Colloq. Nat. Cent. Nat. Rech. Sci.*, 203 (1965) [*Chem. Abstr.*, **67**, 90169x (1967)]; (b) J. Michalski and R. Ratajczak,

parently, a four-membered ring is formed as the reaction intermediate.[4]

The stereochemical stability of (−)-2 is similar to that of (−)-1. Thus, (−)-2 has been stored for 6 weeks under nitrogen in the refrigerator, or refluxed for 15 min in benzene solution, with no racemization. It showed no racemization after 8 days in benzene solution containing either isopropyl methylphosphonothioic acid (racemic 4, 0.5 equiv) or triethylamine (0.7 equiv), or for 17 hr in 95% methanolic 0.05 M HCl. However, it was instantaneously racemized by 0.15 equiv of 0.06 M sodium methoxide in methanol solution, presumably *via* the phosphinothioyl anion [Me(*i*-PrO)P(S)]$^-$. In MeOD, it exchanged the P–H for a P–D bond (followed by pmr spectra), with little or no change in specific rotation, hence with total retention of configuration.

Stereochemical studies of the reactions of (−)-2 are summarized in Chart I. In this work, the (−)-2

Chart I
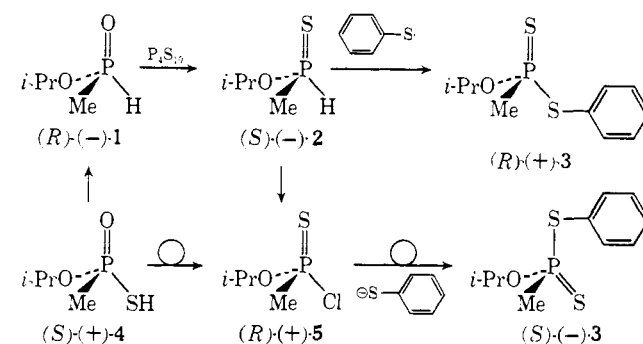
was first diluted with racemic 2 (prepared as above from racemic 1), and the optical purities of the isolated products were adjusted accordingly. Thus, (S)-(−)-2, [α]D −0.26° (CCl$_4$), αD −0.284° (neat, 1 dm), reacted smoothly and rapidly with ice-cold CCl$_4$ containing tributylamine[5] to give (R)-(+)-O-isopropyl methylphosphonochloridothionate (5), bp 43° (4 mm), as the sole product. This product is deduced below to have been formed with predominant if not complete retention of configuration, as in the corresponding phosphinate (1) reaction.[1] It was 1% optically pure, in comparison to (+)-5, [α]D +69.9° (CCl$_4$), obtained (undoubtedly with inversion of configuration)[6] on treatment of optically pure (S)-(+)-isopropyl methylphosphonothioic acid (4), αD +14.00° (neat, 1 dm), with PCl$_5$ in ether solution. Assuming a stereospecific conversion of (+)-4 to (+)-5 (by analogy to the reaction of ethyl ethylphosphonothioic acid)[6] and of (−)-2 to (+)-5, the specific rotation of optically pure 2 is tentatively assigned as [α]D −24° (benzene), −26° (CCl$_4$), and −30° (ethanol).

(S)-(−)-2 reacts with N-chlorosuccinimide[7] (NCS) in ice-cold CCl$_4$ to give a mixture, from which (R)-(+)-5 was isolated, only 30% optically pure, however, in

Rocz. Chem., **37**, 1185 (1963); (c) L. Horner and H. Winkler, *Tetrahedron Lett.*, 175 (1964); (d) W. E. McEwen, W. F. Kumli, A. Bladé-Font, M. Zanger, and C. A. VanderWerf, *J. Amer. Chem. Soc.*, **86**, 2378 (1964).
(4) K. E. DeBruin, K. Naumann, G. Zon, and K. Mislow, *ibid.*, **91**, 7031 (1969).
(5) F. R. Atherton, H. T. Openshaw, and A. R. Todd, *J. Chem. Soc.*, 660 (1945).
(6) J. Michalski and M. Mikalajczyk, *Tetrahedron*, **22**, 3055 (1966).
(7) G. W. Kenner, A. R. Todd, and F. J. Weymouth, *J. Chem. Soc.*, 3675 (1952).