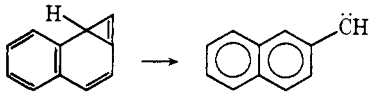
isolated) of the β-naphthylcarbene insertion product **6**. Decomposition in cyclohexene (thermal at 83°) gave a predominance of unidentified products[12] and only a small amount of β-naphthylnorcaranes[11] (**8**) and the corresponding insertion product[11] **9**. The amount of β-naphthylcarbene products relative to the unidentified products was increased by either raising the temperature of the reaction (to 145°) or by dilution of the cyclohexene with diglyme[13] (1:4, respectively). Both of these observations are consistent with a bimolecular reaction of some intermediate with cyclohexene (to give the unidentified products) in competition with a unimolecular rearrangement that gives β-naphthylcarbene. Formation of the various insertion products can, of course, be taken as strong evidence[14] for formation of the rearranged carbene.

To exclude the possibility of the rearrangement of a carbene precursor, β-naphthyldiazomethane and an equivalent amount of benzotropone tosylhydrazone salt were independently heated (108°) in benzene in the presence of an equimolar amount of dimethyl fumarate. As expected, in the β-naphthyldiazomethane reaction, the primary product (50%) was an oil showing all of the properties anticipated for the pyrazoline.[15,16] In contrast, the benzotropone tosylhydrazone sample showed only the familiar benzene addition product of β-naphthylcarbene and no detectable trace of pyrazoline. Thus, the rearrangement must involve a carbene.

The mechanism of the interconversion of aryl and aromatic carbenes has been assumed[1,3,4] to involve a cyclopropene as either an intermediate or a transition state and some evidence has recently been obtained[2] supporting this assumption. It is interesting that, from the results reported here, if a cyclopropene is an intermediate, it must be so unstable as to cleave,



even at temperatures as low as room temperature (and probably considerably lower), to give what is normally considered to be a high energy species, an arylcarbene. A combination of the strain in the fused cyclopropene and the increase in resonance energy upon ring opening might well be sufficient to place the carbene and the cyclopropene at very similar energies.[17]

Finally, a clue to the reason for the rather dramatic effect of annelation on the ease of ring contraction may be found in the effect of annelation on $\mathrm{p}K_{\mathrm{R}^+}$ values of model cations.[18,19] Thus, whereas annelation of the benzyl cation causes the $\mathrm{p}K_{\mathrm{R}^+}$ to become less negative (*i.e.*, a modest stabilizing effect), annelation of the tropyl cation causes a marked decrease in $\mathrm{p}K_{\mathrm{R}^+}$ signaling a substantial destabilization. By analogy, annelation of phenylcarbene and cycloheptatrienylidene should shift an equilibrium toward the arylcarbene and, if the rate of contraction is reflected in the equilibrium, it should be enhanced.

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[12] To date, none of these products has been completely characterized although one appears to be the adduct that would result from the addition of the benzocycloheptatrienylidene to cyclohexene: 60-MHz nmr ($CDCl_3$) τ 2.75 (d, 4 H), 3.25 (d, 1 H), 3.60 (d, 1 H), 4.50 (d, 1 H), 4.66 (d, 1 H), 8.70 (broad m, 10 H); mass spectrum (70 eV) *m/e* 222 (M^+).

[13] In addition to products resulting from reaction of β-naphthylcarbene with cyclohexene, the latter reaction also showed a set of products independently obtained by effecting the decomposition of the sodium salt of benzotropone tosylhydrazone in diglyme. Although the mixture of diglyme products could not be separated and individual components identified, it is identical with the mixture obtained from the decomposition of β-naphthyldiazomethane in diglyme. Furthermore, spectral properties and analysis leave no question but that it is a mixture of naphthylcarbene–diglyme insertion products.

[14] *Cf.* W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964; J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964.

[15] This oil could not be purified and a satisfactory analysis was not obtained.

[16] Decomposition at 160° gave 67% 1,2-dicarbomethoxy-3-naphthylcyclopropane.

[17] From gas-phase rearrangements at 700°, Hedaya[3] has suggested that "relatively small energy barriers separate phenylcarbene, cycloheptatrienylidene, and bicycloheptatriene isomers."

[18] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

[19] Carbonium ions should be fair models for these carbenes since, in both aryl[20] and aromatic[21] carbenes, the vacant orbital is probably conjugated with the "π" system with the nonbonded pair in the plane of the σ framework.

[20] R. Hoffmann, G. D. Zeiss, and G. W. VanDine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968).

[21] R. Gleiter and R. Hoffmann, *ibid.*, **90**, 5457 (1968).

[22] On temporary leave from Tokyo University.

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Reaction of Dialkylchloroboranes with Ethyl Diazoacetate at Low Temperatures. A Facile Two-Carbon Homologation under Exceptionally Mild Conditions

Sir:

Ethyl diazoacetate reacts rapidly with dialkylchloroboranes at −78° and protonolysis then produces nearly quantitative yields of the corresponding ethyl alkylacetates. The reaction readily accommodates even bulky alkyl groups which give very poor results in the corresponding reaction involving trialkylboranes. Consequently, this modified Hooz reaction provides a general and convenient two-carbon homologation under remarkably mild experimental conditions.

Trialkylboranes react with a variety of functionally substituted alkyl diazo compounds to provide a facile synthesis of ketones,[1a,b] nitriles,[1c] aldehydes,[1d] esters,[1c] and their α-deuterio derivatives.[1e] In general, organoboranes derived from terminal olefins react smoothly with the diazo compound to give good yields of the homologated products. However, the Hooz reaction is relatively sluggish and the yields are poor in the case of organoboranes containing relatively bulky alkyl groups. For example, 2-methyl-1-pentene produces only a 40% yield of the corresponding homologated

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[1] (a) J. Hooz and S. Linke, *J. Amer. Chem. Soc.*, **90**, 5936 (1968); (b) J. Hooz and D. M. Gunn, *Chem. Commun.*, 139 (1969); (c) J. Hooz and S. Linke, *J. Amer. Chem. Soc.*, **90**, 6891 (1968); (d) H. Hooz and G. F. Morrison, *Can. J. Chem.*, 48, 868 (1970); (e) J. Hooz and D. M. Gunn, *J. Amer. Chem. Soc.*, **91**, 6195 (1969).

Table I. Reaction of Dialkylchloroboranes with Ethyl Diazoacetate for the Formation of the Corresponding Ethyl Alkylacetates[a]

Dialkylchloroborane	Product	Yield, %[b]
Di-*n*-butyl	Ethyl hexanoate	89
Diisobutyl	Ethyl 4-methylpentanoate	98
Di-*sec*-butyl	Ethyl 3-methylpentanoate	89
Dicyclopentyl	Ethyl cyclopentylacetate	94
Dicyclohexyl	Ethyl cyclohexylacetate	93
Di-*exo*-norbornyl	Ethyl norbornylacetate	92

[a] In each experiment 5 mmol of ethyl diazoacetate in 4 ml of ether was added to 5 mmol of dialkylchloroborane in 5 ml of ether at −78°, followed by addition of methanol and water. [b] Analysis by glpc.

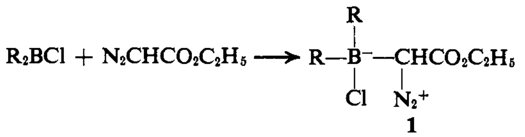
ester.[1a] Attempts to overcome this difficulty by using the corresponding *B*-alkyl-9-borabicyclo[3.3.1]nonanes failed, the reaction involving exclusive migration of the *B*-cyclooctyl bond.[2]

Our recent discovery of the increased reactivity toward organic azides of dialkylchloroboranes[3] as compared to trialkylboranes led us to investigate the related reaction between dialkylchloroboranes and ethyl diazoacetate. Addition of 5 mmol of ethyl diazoacetate to 5 mmol of dicyclopentylchloroborane in 5 ml of diethyl ether at 0° results in an extremely rapid evolution of a gas, presumably nitrogen. However, hydrolysis with water gives only a 7% yield of the desired ethyl cyclopentylacetate. Fortunately, a 94% yield of the desired product is realized when the reaction is carried out at −78°. There are major possibilities in being able to carry out such a two-carbon homologation under such mild conditions. Consequently, we explored the generality of this modified Hooz reaction.

This reaction was applied to a series of dialkylchloroboranes at −78°. All of the reactions evolved the theoretical amount of nitrogen within 15 min. Excellent results were obtained even for alkyl groups which give poor results in the case of trialkylboranes. The results are summarized in Table I.

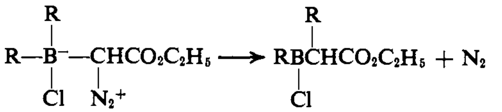
The following procedure for the preparation of ethyl cyclopentylacetate is illustrative. A dry 250-ml flask equipped with a magnetic stirrer and septum inlet was flushed with nitrogen. The flask was cooled to 0° and charged with 55 ml of a 0.91 *M* solution of chloroborane etherate.[4] Hydroboration was achieved by the dropwise addition of 6.8 g of cyclopentene (100 mmol) followed by an additional 1 hr of stirring at 0°. The solution was cooled to −78° (Dry Ice–acetone bath) and 5.7 g of ethyl diazoacetate (50 mmol) in 10 ml of ether was added dropwise over 20 min. The mixture was stirred for an additional 15 min at −78°, and then treated at this temperature with 5 ml of methanol, followed by 5 ml of water. The reaction mixture was then allowed to come to room temperature. The aqueous layer was saturated with potassium carbonate. The organic phase was separated, dried with magnesium sulfate, and distilled. There was obtained 6.1 g (78%) of ethyl cyclopentylacetate, bp 98–100° (28 mm), ir and nmr spectra identical with the literature spectra.[5]

While a detailed study of the mechanism has not been completed, it appears likely that the reaction involves the following steps: the diazo compound coordinates with the borane (eq 1) to produce the quaternary boron intermediate **1**. This is followed by loss of nitrogen from **1** with either subsequent or concurrent migration of an alkyl (eq 2) or chlorine (eq 3) moiety. Since



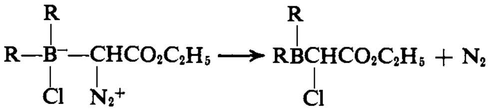
$$R_2BCl + N_2CHCO_2C_2H_5 \longrightarrow R-\overset{R}{\underset{Cl}{B^-}}-\underset{N_2^+}{CHCO_2C_2H_5} \qquad (1)$$

1



$$R-\overset{R}{\underset{Cl}{B^-}}-\underset{N_2^+}{CHCO_2C_2H_5} \longrightarrow R\overset{R}{\underset{Cl}{B}}CHCO_2C_2H_5 + N_2 \qquad (2)$$

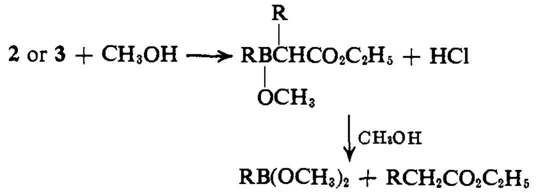
2



$$R-\overset{R}{\underset{Cl}{B^-}}-\underset{N_2^+}{CHCO_2C_2H_5} \longrightarrow R\overset{R}{\underset{Cl}{B}}CHCO_2C_2H_5 + N_2 \qquad (3)$$

3

α-haloboranes rearrange upon addition of a nucleophile, methanolysis of either intermediate (eq 4) gives



$$\textbf{2}\text{ or }\textbf{3} + CH_3OH \longrightarrow R\overset{R}{\underset{OCH_3}{B}}CHCO_2C_2H_5 + HCl \qquad (4)$$
$$\big\downarrow CH_3OH$$
$$RB(OCH_3)_2 + RCH_2CO_2C_2H_5$$

the desired product.[6] Alternatively, it has been proposed that intermediates such as **2** can exist in the isomeric enol borinate form.[7] Such an intermediate should be rapidly hydrolyzed to product.

One interesting characteristic of this modified Hooz reaction, not accounted for by this mechanism, should be pointed out. If the reaction mixture is allowed to warm up to room temperature before the methanol and water are added, the yield of the desired product becomes negligible, approximately 7%. It was shown that the intermediate, whatever it may be, is stable at −78° for at least 6 hr, but begins to be lost relatively rapidly at −30 to −40°.

Irrespective of the precise mechanism involved, this reaction proceeds under exceedingly mild conditions. Moreover, it accommodates bulky alkyl groups which are unsatisfactory in the original Hooz synthesis. Consequently, it promises to provide a general method of broad applicability to achieve carbon bond formation under remarkably mild conditions not previously considered possible. Perhaps even more important is the implication that the dialkylchloroboranes appear to be very reactive species capable of facilitating many reactions which proceed exceedingly sluggishly with

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(2) J. Hooz and D. M. Gunn, *Tetrahedron Lett.*, 3455 (1969); H. C. Brown and M. M. Rogić, *J. Amer. Chem. Soc.*, 91, 2146 (1969).

(3) H. C. Brown, M. M. Midland, and A. B. Levy, *ibid.*, **94**, 2114 (1972).

(4) H. C. Brown and N. Ravindran, *ibid.*, **94**, 2112 (1972).

(5) Sadtler Standard Infrared Spectra, Sadtler Research Laboratories, Philadelphia, Pa., 1962, spectrum 19679; Sadtler Standard NMR Spectra, Sadtler Research Laboratories, Philadelphia, Pa., 1969, spectrum 6056.

(6) H. C. Brown and Y. Yamamoto, *J. Amer. Chem. Soc.*, **93**, 2796 (1971).

(7) D. J. Pasto and P. W. Wojtkowski, *Tetrahedron Lett.*, 215 (1970).

trialkylboranes. We are continuing to explore these possibilities.

[8] National Science Foundation Predoctoral Fellow, 1970–1972.

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Application of Chemically Induced Dynamic Nuclear Polarization to a Study of the Decomposition of Unsymmetric Azo Compounds[1]

Sir:

The mechanism of the thermal and photochemical decomposition of azo compounds has been the focus of several recent investigations.[2–5] The development of the radical pair theory of CIDNP opened the way for a new and potentially powerful approach to the problem.[6]

Two fundamentally different dissociation mechanisms can be visualized in which the loss of nitrogen may occur either by concerted cleavage of both C–N bonds or by a stepwise process giving rise to an intermediate diazenyl radical (eq 1). Because of the expected differences in the magnetic properties of the initial radical pairs associated with the two mechanisms, CIDNP should be capable of distinguishing between them. In this communication we wish to demonstrate the application of this method to the thermal and photochemical decompositions of azo compounds **1** and **2**.

$$\begin{tikzcd} \mathrm{RN{=}NR'} \arrow[rr] \arrow[dr] & & \mathrm{R\cdot \ \cdot R' + N_2} \\ & \mathrm{RN_2\cdot \ \cdot R'} \arrow[ur] & \end{tikzcd} \qquad (1)$$

$$\underset{\mathbf{1}}{\mathrm{PhN{=}NC(CH_3)_2Ph}} \qquad \underset{\mathbf{2}}{\mathrm{(Ph)_2CHN{=}NCH_2Ph}}$$

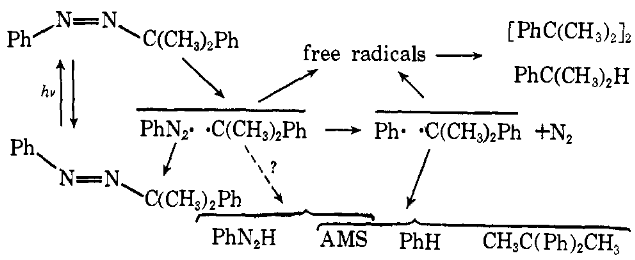
A 0.2 *M* solution of the trans isomer of **1** in benzene was irradiated with ultraviolet light inside an nmr spectrometer probe.[7] The resulting CIDNP spectrum showed enhanced absorption (A) and emission (E) lines identified to arise from dicumyl (weak A), cumene (AE multiplet), 2,2-diphenylpropane (E), α-methylstyrene (E), and benzene (E).[8] In addition, the intensity of the methyl signal of *trans*-**1** is greatly reduced during photolysis (only to increase again after irradiation has been stopped), indicating CIDNP emission during photolysis counterbalanced by normal absorption of the starting material. Product analysis showed dicumyl and biphenyl to be the main products (48 and 20%, respectively), while α-methylstyrene (AMS), cumene, and diphenylpropane were produced in minor amounts. Several high-boiling unidentified products were also present and are presumably formed from radical attack on the solvent.

The possible importance of *cis*-**1** as a key intermediate in the photochemical decomposition of **1** suggested itself by the observation of an induction period of several minutes for the full development of the CIDNP signals. Also, after irradiation had been stopped the signals persisted for a period much longer than the nuclear relaxation times of the products, suggesting the photochemical formation of an intermediate which underwent thermal decomposition. Subsequently, *cis*-**1** was successfully prepared by low-temperature irradiation (−40°) and chromatography (−5°). The crystalline stable solid (48–50° dec) decomposes in benzene solution with a half-life of 10 min at 25° to give 47% *trans*-**1**, 13% dicumyl, and 11% biphenyl with AMS, cumene, and 2,2-diphenylpropane formed in less than 1% yield.

When the thermal decomposition of *cis*-**1** in benzene is followed by nmr, a CIDNP spectrum is obtained (Figure 1) which is almost identical with that observed on photolysis of *trans*-**1** except that the methyl groups of *trans*-**1** are now clearly seen in emission.

From the application of the rules of the radical pair theory[6] and from product analysis, Scheme I emerges as a plausible reaction sequence. The intermediacy of the phenyldiazenyl radical is clearly established by the re-formation of *trans*-**1** as evidenced by its methyl group emission signal. The singlet multiplicity of the radical pair precursor (thermal reaction from ground state) with the known signs of the hyperfine coupling constants in the cumyl radical led to the conclusion that $g_{\mathrm{PhN_2\cdot}} < g_{\mathrm{PhC(CH_3)_2\cdot}}$. The emission signals obtained from AMS, 2,2-diphenylpropane, and benzene suggest that these products also are derived from reactions of the geminate phenyldiazenyl–cumyl radical pair. For the latter two products, however, it is necessary to invoke a phenyl–cumyl secondary correlated pair (derived from the primary pair by loss of nitrogen). AMS may in principle arise from either pair although the presence of polarized benzene points to the secondary pair as its origin.[9]

Scheme I



Comparison of the signal intensities of AMS and *trans*-**1** (Figure 1) with their relative yields indicates a specific polarization of AMS ~10² times greater than

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[1] Supported by National Science Foundation Grants GP 18719 (G. L. C.) and GP 27650 (N. A. P.).

[2] W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 5403 (1970).

[3] N. A. Porter, M. E. Landis, and L. J. Marnett, *ibid.*, **93**, 795 (1971).

[4] N. A. Porter and P. M. Iloff, *Chem. Commun.*, 1575 (1971).

[5] (a) K. Tagaki and R. J. Crawford, *J. Amer. Chem. Soc.*, **93**, 5910 (1971). (b) For a related study of pentazdienes see J. Hollander and W. P. Neumann, *Angew. Chem.*, **82**, 813 (1970).

[6] For recent reviews see: G. L. Closs, "Special Lectures from XXIIIrd International Congress of Pure and Applied Chemistry," Vol. 4, 1971, p 19, and R. Kaptein, "Chemically Induced Dynamic Nuclear Polarization," Ph.D. Thesis, Leiden, 1971.

[7] *trans*-**1** was synthesized by methods analogous to those previously reported.[3] Elemental analysis and nmr, uv, and ir spectra support the structure.

[8] To detect the benzene signal the reaction was run in dichloromethane.

[9] Disproportionation of the primary pair should give phenyldiazene with the N–H proton in emission. No signal attributable to this compound was found although the fast quadrupole relaxation of the nitrogen would probably erase the CIDNP signal.