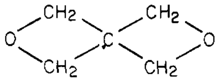
data in Table X show a first-order base dependency for the conversion of MA to DA, as well as a base-equilibrium-controlled rate dependency for cyclization of MA$^-$ to form NE.

Although a similar type study for the conversion of 1,1,1-trimethylolethane mononitrate (DA) to 3-methyl-3-oxetanemethanol (AE) and 1,1,1-tris(hydroxymethyl)ethane (TA) was not accomplished due to the difficulty in reliably analyzing small amounts of TA in the DA hydrolysis runs, the data presented in Tables I and VII lend support to a similar type process. In this regard, it is of interest to compare the ratio of the first-order rate constants for the cyclization of MA to NE and the cyclization of DA to AE, i.e., k_{1NE}/k_{1AE}, at 0.7354 M NaOH in 95% ethanol–water at 55 °C. From the data in Table X, $k_{1NE} = 9.7 \times 10^{-5}\ s^{-1}$ at 0.7354. Since DA was converted to AE in 74 mol % yield, Table VII, $k_{1AE} = 0.74\ k_1(DA)$, where $k_1(DA)$ is the first-order rate constant for base reaction with DA, Table IV. From these data, $k_{1NE}/k_{1AE} = 4.6$. Since these rate constants were calculated at the same base concentration, and since it is assumed that K_{MA} and K_{DA} are not too different, this ratio is suprisingly close to a value of 4.0, which would be expected statistically for a nucleophilic cyclization displacement where MA$^-$ has twice as many nitrate groups as DA$^-$. On the basis of these results, one might very well speculate that the spiral dioxetane would be formed as a major product from the alkaline hydrolysis of the tetranitrate ester, pentaerythrol tetranitrate (PETN).



Acknowledgment. We thank the Naval Sea Systems Command, Washington, DC, for their support under Task SF 65572391 for all phases of this work.

Registry No. MTN, 3032-55-1; MA, 84051-79-6; DA, 84051-80-9; NE, 84051-81-0; TA, 77-85-0; AE, 3143-02-0.

Ionicity in Anionic Photoexcited States. The Effect of the Covalent Character of the Carbon–Metal Bond on the Photochemical Ring Opening of Cyclopropyl Anions

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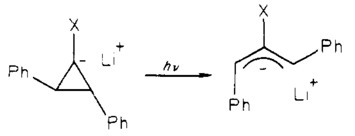
Received May 21, 1982

Although 1-cyano- and 1-carbomethoxy-substituted *trans*-2,3-diphenylcyclopropyllithiums ring open to the corresponding allyllithiums upon photoexcitation, the analogous 1-vinyl- and 1-bromo-substituted cyclopropyllithiums do not. Shifts of the oxidative peak potential in the cyclic voltammetric scans of the photoreactive cyclopropyllithiums imply that they exist as ion pairs at low temperature in THF solution. The importance of the ionic charater of the carbon–metal bond in determining the efficiency of photorearrangement is also implied by MNDO reaction path calculations.

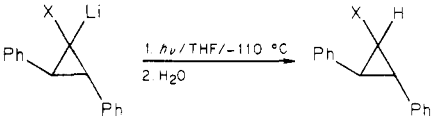
Although several carbanionic photorearrangements are known,[1] the identity of those factors which control anionic photoreactivity are still poorly understood. Previous work has shown, for example, that electron ejection can so dominate the chemistry of anionic excited states that intramolecular rearrangement becomes a pathway of negligible importance.[2] An obvious factor which may significantly influence the reactivity patterns of alkali metal salts of hydrocarbons is the degree of covalency of the carbon–metal bond. We report here studies of substitutent effects on the photoreactivity and the ionicity of the carbon–metal bond in a series of cyclopropyl anions, species which have previously been shown to rearrange with the stereochemistry anticipated from orbital topological considerations.

Previous work in our laboratory has established that several cyclopropyllithiums (**1a** and **1b**) undergo photochemical ring opening at low temperatures by a net disrotatory pathway (eq 1),[3] and the reverse photoreaction, i.e., the photocyclization of cinnamylmagnesium bromide to the corresponding cyclopropylmagnesium bromide, has been described.[4] It was therefore surprising to find in this study that the related organolithiums **1c** and **1d** were completely photostable (eq 2). (The unsubstituted compound **1e** proved to be insufficiently stable to test for photoreactivity.) Since those systems which did photorearrange bore strongly electron-withdrawing substituents, the carbon–lithium bond would be expected to be highly polarized, i.e., to possess substantial ionic character.



(1)

1a, X = CN
b, X = CO$_2$Me



(2)

1c, X = vinyl
d, X = Br
e, X = H

Results

The cyano- and carbomethoxy-substituted cyclopropyllithiums **1a** and **1b** were prepared by treatment of the corresponding cyclopropanes with lithium diisopropyl amide (LDA) as described previously.[5] After a D$_2$O quench at –78 °C in THF in the absence of light, C-deu-

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(1) Fox, M. A. *Chem. Rev.* **1979**, *79*, 253.

(2) Fox, M. A.; Singletary, N. J. *J. Org. Chem.* **1982**, *47*, 3412. Tolbert, L. M. *J. Am. Chem. Soc.* **1980**, *102*, 3531.

(3) Fox, M. A. *J. Am. Chem. Soc.* **1979**, *101*, 4008.

(4) Yogev, A.; Cohen, S. *J. Am. Chem. Soc.* **1976**, *98*, 2013.

(5) Newcomb, M.; Ford, W. T. *J. Am. Chem. Soc.* **1974**, *96*, 2968.

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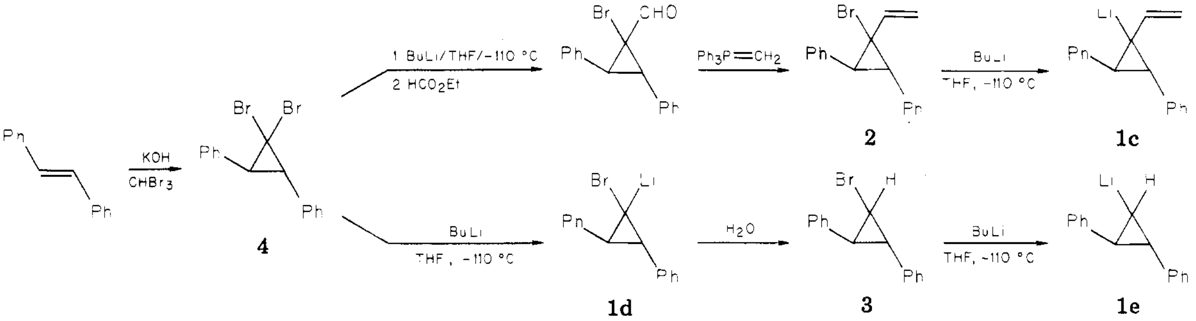
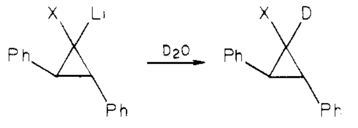
Scheme I



terated cyclopropane was recovered in virtually quantitative yield (eq 3).

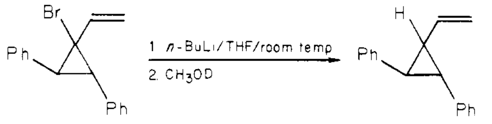


(3)

1a, X = CN
b, X = CO_2Me

The vinyl-substituted cyclopropyllithium **1c** was prepared by metalation of the corresponding bromide **2**, a species accessible through the sequence shown as Scheme I, in a route parallel to that used by Schmidt and Köbrich[6] in the preparation of 1-bromo-1-vinylcyclopropane. The di- (**4**) and monobromocyclopropanes (**3**) obtained along this route were metalated in similar fashion to obtain cyclopropyllithiums **1d** and **1e**, respectively.

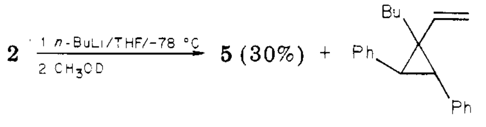
Conditions for these metalations proved to be critical for the success of the generation of the cyclopropyllithiums. For example, treatment of **2** with *n*-butyllithium in tetrahydrofuran (THF) at room temperature, followed by a methanol-*d* quench, gave nearly quantitatively reduction product **5**, with the original cyclopropane ring intact but without deuterium incorporation (eq 4). The same reaction conducted at 0 or at −78 °C gave alkylation as well as reduction, but again no deuterium was incorporated (eq 5).



(4)

2 5

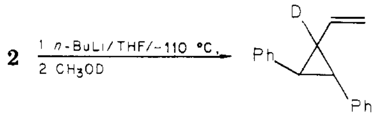
Not until the reaction was conducted at −110 °C could effective demonstration of the formation of a stable organolithium be achieved.



(5)

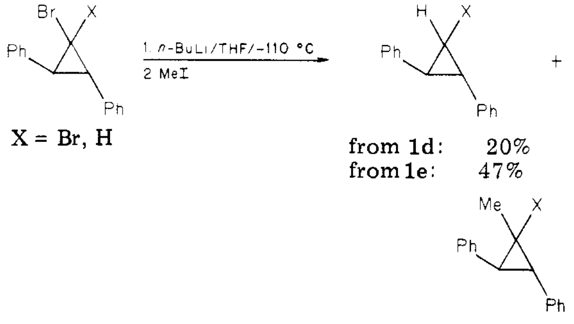
70%

At that temperature, quantitative incorporation of deuterium was observed upon quenching, either after 5 min or after 2 h (eq 6).



(6)

The monobromocyclopropyllithium **1d** and the unsubstituted cyclopropyllithium **1e** proved to be even less stable. Only partial incorporation of electrophile could be achieved 2 min after generation of the cyclopropyllithium at −110° (eq 7).



(7)

X = Br, H

from 1d: 20% 70%
from 1e: 47% 53%

The most stable of these, **1c**, was treated with HMPA, 15-crown-5 ether, or 18-crown-6 ether. The thermal stability of **1c** decreased when such complexants were present, and only partial incorporation of electrophiles at carbon could still be observed after 5 min at −110 °C. The products obtained after workup of **1c**–**e** generated at low temperature retained the cyclopropane ring. Apparently, these cyclopropyllithiums are protonated in THF more rapidly than they can ring open.

Table I. Redox Potentials for Oxidation[a] of Some Substituted Cyclopropyllithiums

compd	E_{pa}, −V vs. SCE	E_{pa}, −V vs. SCE (in presence of HMPA)
1a	−0.85	−1.8
1b	−1.25	−1.3
1c[b]	−2.0	−2.2
1d[b]	−2.0	−2.1
1e[b]	−2.0	−2.5

[a] From cyclic voltammetric scans of 0.001 M degassed solutions in THF containing 0.1 M TBAP at −60 °C; scan rate, 500 V/s. [b] Estimated from the observed reduction of the potentials of the corresponding bromide at room temperature.

Attempts to prepare the cyclopropyllithiums **1c** and **1d** by deprotonation of **5** and **3**, respectively, instead gave deprotonation at the benzyllic carbon. Attempted metalation of **2**–**4** with 1 equiv of alkali metal (Li, Na, or K) led to ring-opened fully reduced product as well as to the desired cyclopropyllithium which ultimately leads to cyclopropane.

Photolysis of these cyclopropyllithiums at −110 °C for periods varying between 5 min and 3 h gave only products with the cyclopropyl ring completely intact after an electrophilic quench, e.g., eq 2.

The electrochemistry of **1a**–**e** was studied by cyclic voltammetry. The irreversible electrooxidative peak potentials so obtained for dilute THF solutions of **1a** and **1b**, with and without the presence of metal ion complexing additive, are listed in Table I. The limited solubility of

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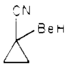
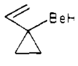
[6] Schmidt, A.; Köbrich, G. *Tetrahedron Lett.* **1974**, *2561*.

Table II. MNDO Calculated Geometries and Energies for Ring Openings of Cyclopropyl Anions and Metalated Cyclopropanes

compd	ground state optimized C_2-C_3 bond length, Å	calcd heats of formation, kcal/mol $H_f(S_0)$	$H_f(S_1)$	$H_f^{\ddagger}(S_0)$	min S_0-S_1 surface separation at funnel
 **6e**	1.55	56	122	19	24
 **7e**	1.54	0	157	61	74
 **6a**	1.54	43	105	32	32
 **7a**	1.51	32	178	69	71
 **6c**	1.54	38	129	34	23
 **7c**	1.51	20	142	74	62

acceptable electrolytes at −110 °C, a temperature low enough to ensure the stability of the cyclopropyllithiums, made direct measurement of the oxidation peak potentials for **1c–e** impossible, but estimates for these values could be obtained by measuring the reduction potentials of their brominated precursors. These are also listed in Table I.

Discussion

Those systems which photorearrange are those in which substituents at carbon tend to effectively stabilize negative charge. It is reasonable to suppose that such compounds will have significant charge separation in the carbon–metal bond and will behave as ground-state ion pairs rather than as organolithiums. Since the requirement for contact-ion pairing is less severe in excited states than in ground states,[7] even looser association should be encountered upon photoexcitation.

That association differences exist in this series is supported by the electrooxidative behavior observed in compounds **1**. Although the waves observed here are irreversible, as is typical in the electrochemical oxidation of anions,[8] Kochi and Arnold have shown that such peak potentials can be profitably utilized to predict relative oxidative reactivity.[9] A typical example of a cyclic voltammetric scan observed for one such anion, **1a**, is shown in Figure 1. The significant shift in peak potentials observed in the absence (top scan) and in the presence (bottom scan) of hexamethylphosphoramide (HMPA) is characteristic of carbanion–alkali metal ion pairs. In contrast, with highly covalent organolithiums, oxidative waves are usually observed at high negative potentials, e.g., methyllithium.[8] Thus, those compounds which rearrange upon photoexcitation also show well-defined anodic waves which shift to more negative potentials upon addition of metal ion complexant. Those organolithiums which resist photorearrangement exhibit electrochemical behavior very much like that observed for organolithiums known to possess carbon–metal bonds of high covalent character.

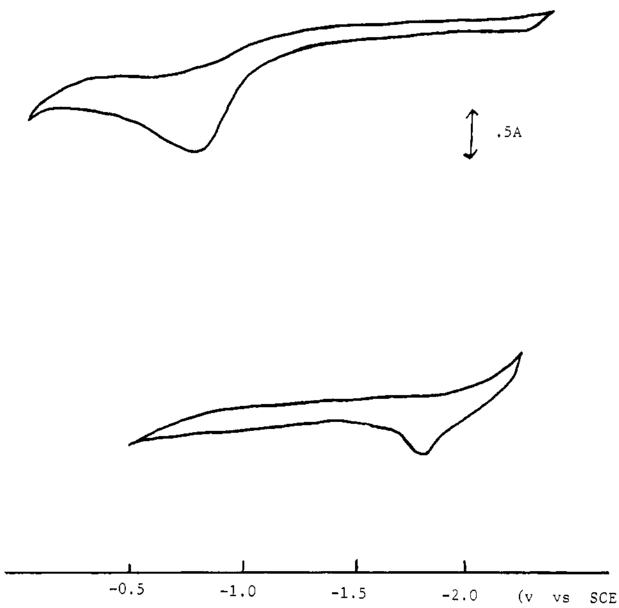
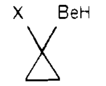


Figure 1. Cyclic voltammogram of **1a** in anhydrous THF containing 0.1M tetrabutylammonium ammonium perchlorate at −60 °C and a scan rate 500 mV/s: (top) without hexamethylphosphoramide present, (bottom) with hexamethylphosphoramide present.

Parallel conclusions can be reached by studying these reactions with semiempirical calculational techniques. MNDO[10] studies were undertaken for free ions **6a,c,e**[11] and

6a, X = CN
b, X = vinyl
c, X = H



7a, X = CN
b, X = vinyl
c, X = H

for metalated[12] cyclopropanes **7a,c,e**, the nonphenylated

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(7) Fox, M. A.; Voynick, T. A. *Tetrahedron Lett.* **1980**, 3943.

(8) Jaun, B.; Schwarz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741.

(9) Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4790. Arnold, D. R.; Wong, P. C. *Can. J. Chem.* **1979**, *57*, 2098.

(10) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907.

(11) Dewar, M. J. S.; Nelson, D. J. *J. Org. Chem.* **1982**, *47*, 2614.

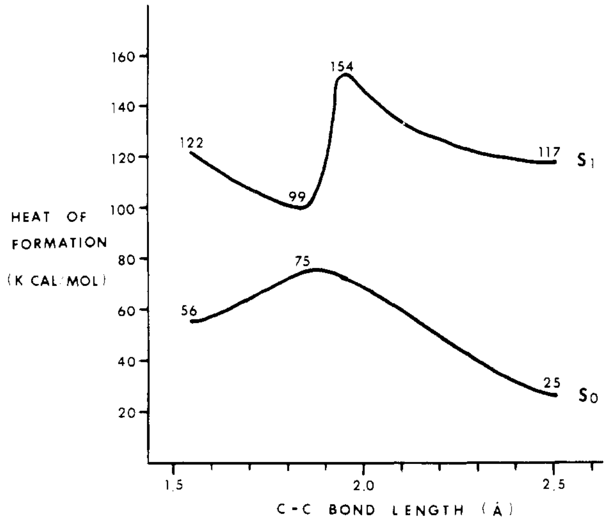

Figure 2. Calculated (MNDO) reaction pathways for the ground- and excited-state ring openings of cyclopropyl anion (**6e**).

analogues of **1a,c,e**, respectively. In this series, we find that the carbon–carbon bond to be cleaved in this rearrangement is shorter, consistently, in the organometallic cyclopropane than in the free anion (Table II). This observation implies a stronger C–C bond and is consistent with our observation of increased difficulty in thermal rearrangement of cyclopropyllithiums compared with ion pairs.

These results are highly reminiscent of the dramatic rate accelerations of (3,3),[13] (1,3),[14] and (1,5)[15] thermal rearrangements observed upon increasing the ionic character of the oxygen–metal bond of appropriately unsaturated allylic alcohols. Rationalization of these effects has been made from both calculations and from experimental thermochemical considerations. Ab initio calculations have shown, for example, that substantial molecular reorganization takes place upon deprotonating methanol, the C–H bond being weakened by 10–12 kcal/mol.[16] Similarly, the gas-phase bond-dissociation energies of the carbon–carbon bond adjacent to the functional group in ethanol and 3-buten-1-ol were found to be about 14 kcal/mol lower in the free alkoxide than in the alcohol. If analogous effects pertain to cyclopropyl anions, the strength of the carbon–carbon bond broken during ring opening might be greatly weakened (and both the thermal and photochemical rearrangements made accordingly more facile) upon making the carbon–alkali metal bond more ionic.

Reaction path calculations can also be used to explain the contrasting photoreactivity of those substituted cyclopropanes which exist as ion pairs and those which exist as organolithiums. Reaction profiles for geometry-optimized C–C stretching leading to the ring opening of **6e** and **7e** are shown in Figures 2 and 3, respectively. It is clear that an implied crossing from the excited-state surface to the ground state of product is much easier with ion pairs than with organometallics where movement of the metal must accompany the carbon–carbon bond fission. Parallel behavior is similarly observed for the substituted analogues. Thus, calculations suggest that funnels exist on the anionic excited-state surface near the transition state for the ground-state ring opening, whereas wide separations between the excited singlet and ground-state surfaces prevail along the entire reaction coordinate for the organometalated cyclopropanes. Furthermore, much more modest activations are required to move an anion along the reaction coordinate than are needed for the corresponding organometallic. Typical enthalpies of activation for the ring openings calculated for the ground states and heats of formation for the ground and excited states, as well as energy differences for the appropriate surface crossings, are listed in Table II for **6a,c,e** and **7a,c,e**.

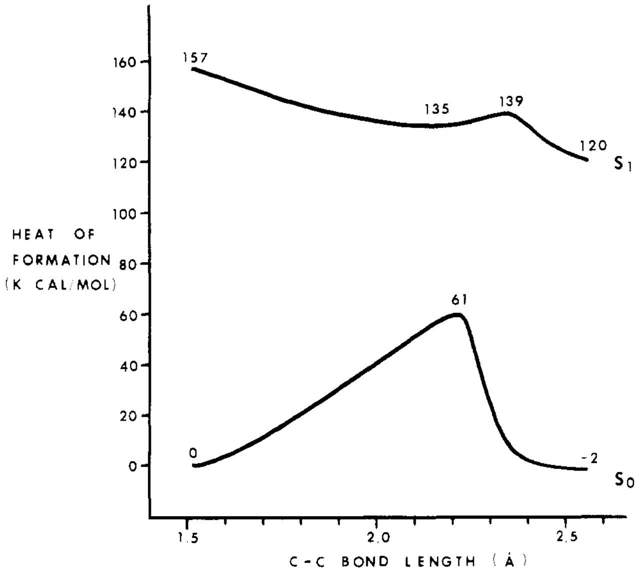

Figure 3. Calculated (MNDO) reaction pathways for the ground- and excited-state ring openings of metalated cyclopropane (cyclopropylberyllium hydride, **7e**).

Our results imply that enhanced photoreactivity might reasonably be anticipated upon increasing the ionicity of the carbon–lithium bond in compounds **1**. The success in observing the photorearrangement in **1a** and **1b** probably follows, therefore, from the effect of the strongly electron-withdrawing substituent on the C–Li ionicity, much greater charge separation having been observed in the calculated geometrically optimized structure of cyano-sustituted cyclopropyl anion than in the unsubstituted or vinyl-substituted analogues. Attempts to disrupt the strong C–Li association in **1c–e** by adding a metal complexant, and hence to produce a species more amenable to photorearrangement, were complicated by the enhanced thermal reactivity (proton abstraction from solvent or in an E_2 transition state from butyl bromide generated in situ or enhanced S_N2 reactivity with the latter species) in the sterically less congested, highly basic, nonaggregated, free cyclopropyl anions. It is probable that the enhanced basicity of **1c–e**, compared with their nonphenylated counterparts, can be attributed, at least in part, to the disruption of aggregation by the relatively bulky phenyl substituents at the 2- and 3-positions of **1c–e**.

Experimental Section

General Methods. Tetrahydrofuran (THF) was freshly distilled from potassium or benzophenone ketyl. Electrolytes were dried in vacuo overnight. Other reagents were used as supplied from commercial sources.

Spectral data for new compounds were obtained on a Varian 390 nuclear magnetic resonance (NMR) spectrometer, with chemical shifts being reported in parts per million downfield from tetramethylsilane as an internal standard, or on a Beckman Acculab 7 infrared (IR) spectrophotometer. High-resolution mass

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(12) MNDO is not parametrized at present for lithium. Beryllium hydride was therefore employed in these studies as an analogous metal expected to form highly covalent carbon–metal bonds.

(13) Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765.

(14) For example, see: Franzus, B.; Scheinbaum, M. L.; Waters, D. L.; Bowlin, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 1241.

(15) Steigerwald, M. L.; Goddard, W. A., III; Evans, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 1994.

(16) Evans, D. A.; Baillargeon, D. J. *Tetrahedron Lett.* **1978**, 3319.

spectra (HRMS) were obtained with a CEC 21-110 instrument. Chromatographic purifications and analyses were performed with a Waters LC 500A liquid chromatograph or with a Varian 920 gas chromatograph equipped with a 5 ft × 0.25 in. 10% Carbowax on Chromosorb P or a 5 ft × 0.25 in. 5% QF-1 on Firebrick column. Melting points were obtained on a Fisher-Johns melting point block and are uncorrected.

General Procedure for Cyclopropyllithium Generation. Two routes were followed for the generation of cyclopropyllithiums: deprotonation of the parent hydrocarbon or transmetalation of the brominated precursor. In a typical deprotonation sequence, the hydrocarbon was dissolved in THF and the solution was cooled to the appropriate reaction temperature. A solution of lithium diisopropylamide (LDA)[5] in THF was cooled to the reaction temperature and was added dropwise to the hydrocarbon solution. After an appropriate reaction period, the mixture was quenched by the addition of electrophile, and the resulting solution was allowed to equilbrate to room temperature. The layers were separated, and the aqueous layer was extracted with ether. The combined organic extracts were stripped of solvent before standard analysis was undertaken.

In the metalation route, a cooled solution of the bromide in THF was treated with a cooled solution of freshly titrated *n*-BuLi (1 equiv) in hexane. After an appropriate reaction period, the reaction was quenched by the addition of electrophile. The workup was identical with that described for the deprotonation route.

1a and 1b. The hydrocarbon precursors to **1a** and **1b** were prepared by previously described routes.[5] Deprotonation with LDA in THF at −78 °C, followed by a D_2O quench, gave 1-deuterio-*trans*-2,3-diphenylcyclopropane in quantitative yield. At room temperature, rapid ring opening ensued, giving an equimolar mixture of *cis*- and *trans*-benzocinnamonitriles from **1a**, after quench.

1c. To a cooled (−110 °C) solution of 1,1-dibromo-*trans*-2,3-diphenylcyclopropane[17] (12.7 g, 0.034 mol) in 130 mL of 10:3 THF/diethyl ether was added dropwise over a 15-min period 21 mL of 1.6 M *n*-BuLi (0.033 mol). The mixture was stirred for 5 min. As ethyl formate (27 g, 0.36 mol) was added, the brown color of the solution was discharged. The resulting mixture was stirred for 4 h at low temperature before being warmed slowly to room temperature. The mixture was quenched with water, and the aqueous layer was extracted with ether. The combined organic layers were washed successively with 5% HCl, 5% K_2CO_3, H_2O, and saturated NaCl(aq). After the mixture was dried over anhydrous $MgSO_4$, the solvent was removed, yielding 10.3 g (100%) of 1-bromo-*trans*-2,3-diphenylcyclopropanecarboxyaldehyde (**8**): NMR (CCl_4) δ 9.12 (s, 1 H), 7.27 (m, 10 H), 3.55 (s, 2 H); IR ($CHCl_3$) 1728 cm^{-1}; MS, *m*/*e* 302, base 221.

To a cooled (0 °C) solution of triphenylmethylphosphonium bromide (12.8 g, 0.035 mole) in 50 mL of THF was added 20 mL of 1.6 M *n*-BuLi (0.032 mol) over a 10-min period. The solution was stirred for 4 h before **8** (10.3 g, 0.034 mol) was added. The resulting solution was stirred for 2 h at room temperature before being heated under reflux overnight. The reaction mixture was allowed to cool to room temperature before being quenched with water, washed with saturated NaCl(aq), and extracted with ether. The combined organic layers were dried over anhydrous $MgSO_4$. After solvent removal, the product was purified by HPLC on Porasil A, giving **2** as a colorless oil: 5.4 g (57%); NMR (CCl_4) δ 7.0–7.3 (m, 10 H), 4.8–5.4 (m, 3 H), 3.2 (d, J = 7.5 Hz, 1 H), 2.7 (d, J = 7.5 Hz, 1 H); IR ($CHCl_3$) 3310, 3010, 1630, 1600, 1500, 1450, 700 (br) cm^{-1}; HRMS, calcd *m*/*e* 298.0358, found *m*/*e* 298.0362.

Metalation of **2** by the general procedure at room temperature, followed by a CH_3OD quench, gave only 1-vinyl-*trans*-2,3-diphenylcyclopropane: NMR (CCl_4) δ 7.25 (m, 10 H), 4.8–5.3 (m, 3 H), 2.0–2.8 (m' 3 H); IR ($CHCl_3$) 3000, 1605, 1498, 1210 cm^{-1}; HRMS, calcd *m*/*e* 220.1252, found *m*/*e* 220.1248. The absence (less than 2%) of the cis-diphenyl- and the ring-opened isomers was established by GLC.

At −78 °C, the same procedure led to a 70:30 mixture of two compounds. The minor component was identical with that observed at room temperature. Spectral analysis of the major component led to a tentative identification as 1-*n*-butyl-1-vinyl-*trans*-2,3-diphenylcyclopropane: NMR (CCl_4) δ 7.25 (m, 10 H), 4.8–5.5 (m, 3 H), 2.5–2.8 (m, 2 H), 0.75–1.6 (m, 9 H); IR ($CHCl_3$) 2960, 1610, 1505, 1460, 710 cm^{-1}; HRMS calcd *m*/*e* 276.1878, found *m*/*e* 276.1883.

Metalation at −110 °C followed by a CH_3OD quench gave quantitative 1-deuteration: NMR (CCl_4) δ 7.3 (m, 10 H), 5.2 (m, 2 H), 4.95 (m, 1 H), 2.7 (d, J = 6 Hz, 1 H), 2.45 (d, J = 6 Hz, 1 H); IR ($CHCl_3$) 3000, 2396, 1215 cm^{-1}; HRMS, calcd *m*/*e* 221.1315, found *m*/*e* 221.1321. GLC was used to show the absence of the isomeric *cis*-diphenylcyclopropane and of the ring opened product.

If the metalation mixture formed at −110 °C was treated with 1 equiv of 18-crown-6 ether, 15-crown-5 ether, or hexamethylphosphoramide (HMPA) before the CH_3OD quench, nearly no deuteration could be observed.

1d. Metalation of **4**[17] at −110 °C, followed by a water quench, gave rise to **3**.[18] An analogous quench of this reaction mixture with methyl iodide gave 1-bromo-1-methyl-*trans*-2,3-diphenylcyclopropane: NMR ($CHCl_3$) δ 7.35 (m, 10 H), 3.13 (d, J = 8 Hz, 1 H), 2.45 (d, J = 8 Hz, 1 H), 1.66 (s, 3 H); IR ($CHCl_3$) 3060–2930, 1605, 1500, 1450, 1138, 690 cm^{-1}.

1e. Metalation of **3**[18] by the general procedure at −110 °C, followed by a methyl iodide quench after 2 min, gave a 47:53 mixture of products after the standard workup. The minor product was shown to be 1,2-*trans*-diphenylcyclopropane by comparison of its properties with a standard sample. The major product was assigned as 1-methyl-*trans*-2,3-diphenylcyclopropane from its spectral properties: NMR (CCl_4) δ 7.15 (m, 10 H), 2.40 (dd, J = 5, 9 Hz, 1 H), 2.00 (t, J = 5 Hz, 1 H), 1.0–1.5 (m, 1 H), 0.98 (d, J = 6 Hz, 3 H); IR ($CHCl_3$) 3015, 1620, 1510, 710 cm^{-1}; HRMS, calcd *m*/*e* 208.1252, found *m*/*e* 208.1257.

Analogous reaction of **3** at room temperature, followed by a D_2O quench, gave only 1,2-diphenylcyclopropane. Treatment with lithium or potassium metal either at room temperature or at −110 °C gave 1,3-diphenylpropane and 1,2-*trans*-diphenylcyclopropane.

Photolysis of Cyclopropyllithiums. The THF solutions of metalated cyclopropanes described above were cooled to −110 °C and were irradiated for 2 h through an unsilvered Pyrex Dewar flask with a 250-W high-pressure mercury arc (wavelengths greater than 300 nm) while the cooling was continued. A Pyrex flat ensured direct excitation of the solutions without the filtering effect of the coolant mixture. An electrophilic quench and the usual workup (vide supra) gave products previously described for **1a** and **1b**[4] and products identical with those described above for the thermal reactions of **1c**–**e**.

Oxidation Potentials. Electrochemistry was performed on a Princeton Applied Research Model 173 potentiostat equipped with a universal programmer. The current-voltage curves were recorded on a Houston Instruments x–y recorder. The electrochemical cell was a standard three-electrode cell with an adaptor for adding reagents attached to the side. The cell was equipped with a glassy carbon working electrode (0.05 cm^2), a platinum coil counterelectrode, and a silver wire quasi-reference electrode. Degassed solvent was added to the cell containing electrolyte, and the mixture was scanned to ensure the absence of electroactive impurities before the reagent of interest was added and a cyclic voltammogram was obtained. The temperature of the mixture was maintained by immersing the cell in a bath cooled by a Flexicool cold finger. After each experiment, ferrocene (5 mM), a compound whose redox chemistry is known,[19] was added as an internal reference for reporting observed peak potentials.

Calculations. Calculations were conducted by using the standard MNDO format.[10] All geometries were optimized by the standard Davidson–Fletcher–Powell procedure, with no assumptions of any kind being made. All stationary points were characterized by using force constant calculations, i.e., by diagonalizing the Hessian matrix.

Acknowledgment. Financial support for this research by the National Science Foundation and by the Robert A. Welch Foundation is gratefully acknowledged. M.A.F. is

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also grateful for support as an Alfred P. Sloan Research Fellow and as a Camille and Henry Dreyfus Teacher-Scholar.

Registry No. *trans*-**1a**, 50930-15-9; *trans*-**1b**, 84064-83-5; *trans*-**1c**, 84064-84-6; *trans*-**1d**, 84064-85-7; *trans*-**1e**, 84064-86-8; *trans*-**2**, 84064-87-9; *trans*-**3**, 61608-79-5; *trans*-**4**, 33044-88-1; *trans*-**5**, 84064-93-7; **6a**, 76510-29-7; **6b**, 84064-88-0; **6c**, 1724-45-4; **7a**, 84064-89-1; **7b**, 84064-90-4; **7c**, 84064-91-5; *trans*-**8**, 84064-92-6; *n*-BuLi, 109-72-8; 1-buty-1-vinyl-*trans*-2,3-diphenylcyclopropane, 84064-94-8; 1-bromo-1-methyl-*trans*-2,3-diphenylcyclopropane, 84064-95-9; 1-methyl-*trans*-2,3-diphenylcyclopropane, 84064-96-0.

Wittig Reagents Bound to Cross-Linked Polystyrenes

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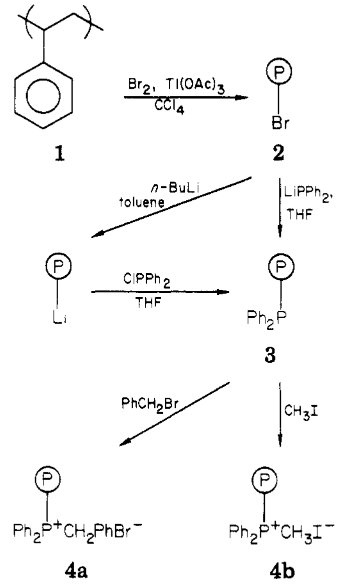
Received May 7, 1982

Insoluble benzyltriarylphosphonium and methyltriarylphosphonium salts have been prepared on 2% and 8% divinylbenzene cross-linked polystyrene and on 20% divinylbenzene cross-linked macroporous polystyrene. Phosphoranes were generated with sodium methoxide or sodium ethoxide in THF and with the dimethylsulfinyl carbanion in Me_2SO from the benzyl- and methylphosphonium salts, respectively. Reactions of the phosphoranes with a variety of aldehydes and ketones provided alkenes in 73–96% yields (by GLC analysis) with the 2% cross-linked polymer, 52–77% yields with the 8% cross-linked polymer, and 72–87% yields with the 20% cross-linked macroporous polymer. The rates of phosphorane generation and alkene formation depend on the polymer, decreasing in the order 2% > 20% macroporous > 8% cross-linked. The fraction of *E* double bond product from the benzylphosphonium salt and either benzaldehyde or cinnamaldehyde is greater with the 20% cross-linked macroporous polymer than with the 2% cross-linked polymer. The byproduct polymer-bound phosphine oxides were reduced to phosphines with trichlorosilane, and the phosphines were reused for Wittig syntheses. A quantitative ^{31}P NMR analysis of phosphine and phosphine oxide residues in polystyrene gels is reported.

Polymer-supported reagents in organic synthesis allow separation of the insoluble polymeric byproduct from the reaction mixture by simple filtration.[1] In some cases the polymeric reagent can be regenerated. The byproduct triphenylphosphine oxide from Wittig reactions in solution is often hard to separate from the product olefin. After use of a polymer-supported Wittig reagent the triarylphosphine oxide can be separated by filtration and can be recycled after reduction to the phosphine. The Wittig reaction is one of the most valuable in synthetic chemistry, for it gives regiospecific introduction of a carbon–carbon double bond.[2]

Earlier papers on polymer-supported Wittig reagents[3-8] reported syntheses of olefins in widely variable yields, depending on the particular reaction conditions and the polymer used. Heitz and Michels[5] found higher yields with a 0.5% cross-linked polystyrene support than with the standard 2% cross-linked polystyrene, which implies that more highly cross-linked polystyrenes would give poor yields of Wittig products. A phase-transfer-catalyzed method of phosphorane generation from the polymer-bound phosphonium salts offers the highest reported yields of olefins from activated benzyl and allyl phosphonium salts.[8] Use of soluble Wittig reagents with polymer-bound aldehydes also has been reported.[9] (Polystyrylmethyl)triphenylphosphonium ions have been used to prepare alkenes bound to the polystyrene.[8b,c,10]

Scheme I



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