TABLE I

RELATIVE REACTIVITIES OF OLEFINS TOWARD PHENYL(BROMODICHLOROMETHYL)MERCURY AND TOWARD SODIUM TRICHLOROACETATE

Olefin A	k_A/k, for $C_6H_5HgCCl_2Br$ (duplicate)[a,b,e]	k_A/k, for CCl_3CO_2Na[c-e]	Over-all yields of dichlorocyclopropanes for $C_6H_5HgCCl_2Br$ reactions[g,i]	Over-all yields of dichlorocyclopropanes for CCl_3CO_2Na reactions[h]
$\begin{array}{c}CH_3 \quad CH_3 \\ C=C \\ CH_3 \quad C_2H_5\end{array}$	21.5 (23.5)	24.8	93.6 (94.4)	87.7
$\begin{array}{c}C_6H_5 \\ C=CH_2 \\ CH_3\end{array}$	7.16 (7.34)	7.35	93.0 (95.2)	85.7
$(C_2H_5)_2C=CHCH_3$	3.53 (3.55) 3.55[c]	3.52	93.4 (93.2)	80.9
$\begin{array}{c}C_2H_5 \\ C=CH_2 \\ n\text{-}C_3H_7\end{array}$	2.05 (2.09)	2.08	92.0 (92.1)	80.1
$C_6H_5CH=CH_2$	1.23 (1.22)	1.26	92.8 (94.2)	72.7
⬡	1.00	1.00		
$cis\text{-}n\text{-}C_3H_7CH=CHC_2H_5$	0.826 (0.831)	0.800[a]	82.9 (86.4)	49.7
$trans\text{-}n\text{-}C_3H_7CH=CHC_2H_5$	0.523 (0.526) 0.512[c]	0.523	91.2 (93.4)	63.6
$n\text{-}C_5H_{11}CH=CH_2$	0.236 (0.236)	0.219	89.6 (91.5)	60.6
$Cl_2C=CHCl$	0.0146 (0.0158)[f]		85.4 (84.7)	

[a] Reaction time 3 hr. at 80 ± 2°. [b] Solvent, benzene. [c] Solvent, 1,2-dimethoxyethane. [d] Reaction time 8 hr. at 80 ± 2°. [e] Compared with cyclohexene; both in fivefold excess unless otherwise specified. [f] Olefins in sevenfold excess. [g] Per cent based on $C_6H_5HgCCl_2Br$. [h] Per cent based on CCl_3CO_2Na. [i] Yields of C_6H_5HgBr isolated: 95–97%.

involved free dichlorocarbene as an intermediate and $C_6H_5HgCCl_2Br$ reacted as shown in II.

The elimination of the "methylene transfer" mechanism leaves for discussion mechanisms involving attack on the olefin by :CCl₂ or by :CCl₂Br in the case of our mercury reagent. The reaction of cyclohexene with the CHCl₂Br–t-BuOK system has been shown to give (via :CCl₂Br) 7,7-dichlorobicyclo[4.1.0]heptane and 7-bromo-7-chlorobicyclo[4.1.0]heptane in 6:1 molar ratio.[17] In contrast, the reaction of $C_6H_5HgCCl_2Br$ with cyclohexene gave only 7,7-dichlorobicyclo [4.1.0]-heptane and phenylmercuric bromide.[10] This suggests that :CCl₂Br is not involved in mercurial–olefin reactions. For these reasons we favor a mechanism for the $C_6H_5HgCX_3$–olefin reaction which involves a free dihalocarbene intermediate. By implication we also favor a free dichlorocarbene intermediate in the sodium trichloroacetate–olefin reaction. It is to be noted that both of these systems, mercurials[18] and sodium trichloroacetate,[19] insert CX₂ into C–H bonds, a reaction currently thought to be one characteristic of free carbenes.

A kinetic study of the mercurial–olefin reaction is in progress. We present the results above at this time because of the current interest in the mechanism of these reactions and because we wish to point out that not all reactions of olefins leading to cyclopropane formation which involve a metal-containing "divalent carbon carrier" necessarily proceed via transition state II.

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(17) W. E. Parham and R. R. Twelves, J. Org. Chem., 22, 730 (1957).
(18) D. Seyferth and J. M. Burlitch, J. Am. Chem. Soc., 85, 2667 (1963).
(19) E. K. Fields, ibid., 84, 1744 (1962).

Structural Requirements for Second-Row-Element Functional Groups to Preserve Asymmetry of Carbanions

Sir:

In previous work three functional groups centered about second-row elements have been examined with regard to their effect on the stereochemical capabilities of carbanions. The benzenesulfonyl group has been demonstrated to preserve the asymmetry of attached carbanions[1] whereas the benzenesulfinyl and diphenylphosphinoxy groups have not exhibited this property.[2] Thus, k_e/k_α (ratio of rate constants of base-catalyzed hydrogen isotopic exchange to that of racemization) for I was ≥ 10 in a variety of solvents,[1b] whereas the

$$\begin{array}{ccc}
O \quad CH_3 & CH_3 & CH_3 \\
C_6H_5S-*C-D & C_6H_5S-*C-D & (C_6H_5)_2P-*C-D \\
O \quad C_6H_{13}\text{-}n & O \quad C_6H_{13}\text{-}n & O \quad C_6H_{13}\text{-}n \\
I & II & III
\end{array}$$
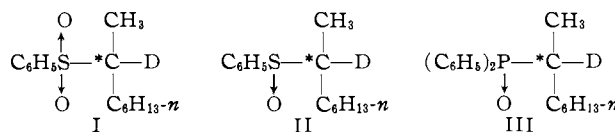
(1) (a) D. J. Cram, W. D. Nielsen, and B. Rickborn, J. Am. Chem. Soc., 82, 6415 (1960); (b) D. J. Cram, D. A. Scott, and W. D. Nielsen, ibid., 83, 3696 (1961); (c) D. J. Cram and A. S. Wingrove, ibid., 85, 1100 (1963); (d) E. J. Corey and E. T. Kaiser, ibid., 83, 490 (1961); (e) E. J. Corey, H. Konig, and T. H. Lowry, Tetrahedron Letters, 12, 515 (1962); (f) H. L. Goering, D. L. Towns, and B. Dittmar, J. Org. Chem., 27, 736 (1962).
(2) D. J. Cram, R. D. Partos, S. H. Pine, and H. Jäger, J. Am. Chem. Soc., 84, 1742 (1962).

TABLE I

RATIO OF RATE CONSTANTS FOR BASE-CATALYZED HYDROGEN ISOTOPE EXCHANGE
WITH MEDIUM AND FOR RACEMIZATION OF FIVE-CARBON ACIDS

Run no.	Substrate Nature	Concn., M	Solvent	Base Nature	Concn., M	T, °C.	Time, hr.	Rac.,[a] %	Exch.,[b] %	k_e/k_α[c]
1	IVh	0.148	t-BuOD[d]	t-BuOK	0.020	25	0.4	0–2	41	>28
2	Vh	0.087	t-BuOD[d]	t-BuOK	0.060	25	3.5	6.4	72	19
3	Vd[e]	0.086	t-BuOH	t-BuOK	0.089	25	1.9	3.1	69	37
4	Vd[e]	0.086	$(CH_3)_2SO$[f]	CH_3OK	0.189	25	4.0	5.3	85	34
5	Vd[e]	0.085	$(CH_2OH)_2$	$HOCH_2CH_2OK$	0.551	100	14	4.3	53	17
6	VIh	0.174	t-BuOD[d]	t-BuOK	0.245	231	61	6.5	73[h]	17
7	VIIh	0.252	t-BuOD[d]	t-BuOK	1.19	146	45	47	62	1.56
8	VIId[g]	0.256	t-BuOH	t-BuOK	1.11	146	69	57	75	1.65
9	VIIIh	1.03	t-BuOD[d]	t-BuOK	0.28	100	20	16.5	18.2	1.11
10	VIIIh	0.95	t-BuOD[d]	t-BuOK	0.28	100	20	17.3	20.2	1.18

[a] Analyzed by isolation and determination of rotation. [b] All analyses by combustion and falling drop method. [c] Single-point rate constants. [d] 0.97–0.99 atom of deuterium per molecule. [e] 0.95 atom of deuterium per molecule. [f] 2.6 M in methanol. [g] 0.98 atom of deuterium per molecule. [h] Total exchange 4 atoms of deuterium per molecule; 3.27 atoms of deuterium in phenyl as determined by n.m.r. with methylene iodide as internal standard.

value of the ratio for II and III was not far from unity in the same solvents.[3] We now report values for k_e/k_α obtained for base-catalyzed hydrogen isotope exchange of compounds IV–VIII with solvents containing the appropriate protium or deuterium reservoirs.[4]

Compounds VIIh and VIId were prepared by a refinement of a published procedure,[5] $[\alpha]_{546}^{31.5}$ +12.04° for
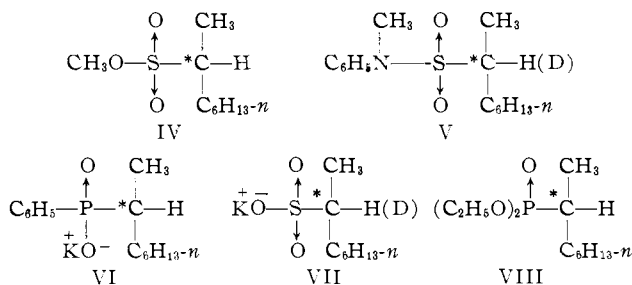
VIIh and $[\alpha]_{546}^{27.5}$ −12.13° for VIId (c 5%, water). Conversion of (+)-VIIh to its corresponding acid and treatment with diazomethane gave IV, $[\alpha]^{25}$obsd. +2.81°, λ 5460 Å., neat, l = 0.5 dm. The corresponding acids derived from (−)-VIIh and (−)-VIId were converted to their corresponding acid chlorides, which when treated with N-methylaniline in pyridine gave amide products Vh, $[\alpha]_{546}^{27}$ −18.27°, and Vd $[\alpha]_{546}^{27}$ −18.31° (c 5%, absolute ethanol). No loss in deuterium was noted in passing from the acid chloride to the amide, and thus a sulfene must not be an intermediate.[6] Optically active ester VIII was prepared from optically pure (−)-2-octyl tosylate by a recorded procedure[7] to give material, $[\alpha]_{546}^{27}$ +6.83° (c 23%, chloroform). The phosphinic acid derived from salt VI was prepared from optically pure (−)-2-octyl tosylate via its n-butyl ester by refinements of recorded procedures,[8] $[\alpha]_{546}^{26}$ +20.15° (c 3%, chloroform).

(3) D. J. Cram and S. H. Pine, J. Am. Chem. Soc., 85, 1096 (1963); (b) D. J. Cram and R. D. Partos, ibid., 85, 1093 (1963).

(4) Elemental analysis of all new compounds gave values within 0.3% of theory, whereas the physical properties of known compounds corresponded to literature values.

(5) P. A. Levene and L. A. Mikeska, J. Biol. Chem., 59, 473 (1924).

(6) Attempts to prepare the N,N-dimethylamide gave about 46% loss of deuterium, and attempts to prepare ester IV from the acid chloride resulted in complete deuterium loss. Sulfene intermediates probably intervened to some extent in these reactions (see J. F. King and T. Durst, J. Am. Chem. Soc., 86, 287 (1964), and W. E. Truce, R. W. Campbell, and J. R. Norell, ibid., 86, 288 (1964)).

(7) A. Michaelis and Th. Becker, Chem. Ber., 30, 1003 (1897).

Table I records the results of the exchange and racemization experiments. The carbon acids whose conjugate bases are stabilized by second-row-element functional groups fall into two distinct classes: those whose exchange reactions exhibit values of k_e/k_α which are well in excess of unity, and those whose values are close to unity. The former systems appear to produce intrinsically asymmetric carbanions which undergo substitution with high retention of configuration. The latter appear to give symmetrical carbanions, and the low stereospecificity exhibited by the substitution reaction is due to asymmetric solvation effects.[9]

Functional groups which induce carbanion asymmetry	Functional groups which provide symmetrical carbanions
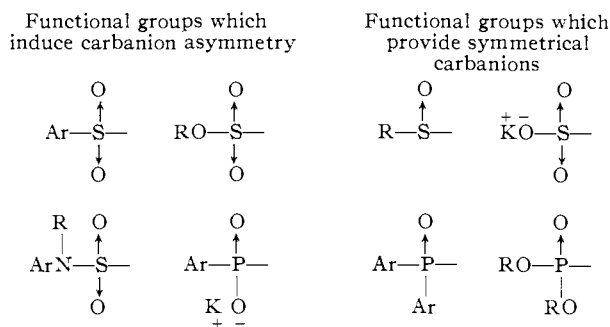
Comparison of the structural features of these two classes of groups indicates that *those which induce asymmetry have two unsubstituted oxygens bound to the second-row element, and those which do not have either one or three unsubstituted oxygens* attached to the second row element. The presence or absence of a formal charge on one of these oxygens seems to make no qualitative difference. Quantitative comparisons in a variety of solvents will be forthcoming.

Two general explanations have been advanced for the asymmetry induced in the carbanion by the sulfone group.[1a–c] (1) The carbanion is tetrahedral, and the partial charge on the oxygens provides electrostatic inhibition of this asymmetric species. (2) The carbanion is planar, is formed and captured in an asymmetric conformation for electrostatic and steric reasons, and electrostatic and steric inhibition of rotation effects

(8) (a) M. Kosolapoff, J. Am. Chem. Soc., 72, 4292 (1950); (b) V. M. Clark and A. R. Todd, J. Chem. Soc., 2030 (1950).

(9) D. J. Cram, Pure Appl. Chem., 7, 155 (1963).

maintain the asymmetric conformation. The present data do not differentiate these possibilities.[10]

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Direct Detection of the Borane Molecule and the Boryl Radical by Mass Spectrometry

Sir:

The BH_3 molecule has been postulated as an intermediate in many of the pyrolysis and exchange reactions of the boron hydrides[1] while the BH_2 radical has been postulated as an intermediate in some radiolysis reactions.[2] However, no direct experimental evidence of the existence of these species has been offered to date. The following is a report on their mass spectrometric detection in the pyrolysis of diborane.

The mass spectrometric method provides an elegant way to detect unstable species.[3-7] Basically, detection of radicals by this method involves the use of low energy electrons so that the observed current of the radical positive ion arises almost entirely from the ionization of the corresponding radical, and the contribution by dissociative ionization of molecules is small. The principles of the method are detailed in the references given.

Experimentally, samples must be removed from the reacting gas in a manner such that the unstable species are not destroyed by reactions or wall collisions. With this in mind, a special mass spectrometer having a 7-cm. radius of curvature and utilizing a quadrupole lens, wide slits, and electron-multiplier detection for maximum sensitivity was constructed. The ionizing region is open on four sides to minimize wall collisions and a small tubular quartz furnace is positioned with its exit about 5 mm. from the electron beam. The reactant diborane flows through the furnace with a contact time of about 2 msec., and the crude molecular beam issuing from the furnace is analyzed about 25 μsec. later. Differential pumping is employed, and during a run with a pressure of about 5×10^{-4} torr in the furnace, the background pressure in the ionizing region is 5×10^{-7} torr, while in the analyzer tube and electron-multiplier sections it is 3×10^{-8} torr.

With diborane flowing through the reactor, the spectrometer was focused on the $m/e = 14$, BH_3^+, ion peak at a low ionizing voltage. Recording the ion current as a function of the furnace temperature produced a record similar to that shown in Fig. 1a. The presence of BH_3 is clearly indicated.[8] Examination of the $m/e =$

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(2) V. V. Subbanna, L. H. Hall, and W. S. Koski, J. Am. Chem. Soc., 86, 1304 (1964).
(3) G. C. Eltenton, J. Chem. Phys., 10, 403 (1942); 15, 455 (1947).
(4) J. A. Hipple and D. P. Stevenson, Phys. Rev., 63, 121 (1943).
(5) F. P. Lossing, Ann. N. Y. Acad. Sci., 67, 499 (1957).
(6) S. N. Foner and R. L. Hudson, Advances in Chemistry Series, No. 36, R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1962, p. 34.
(7) A. J. B. Robertson, "Mass Spectrometry," John Wiley and Sons, Inc., New York, N. Y., 1954.
(8) For example of similar evidence see: S. N. Foner and R. L. Hudson, J. Chem. Phys., 21, 1608 (1953); 23, 1364 (1955).
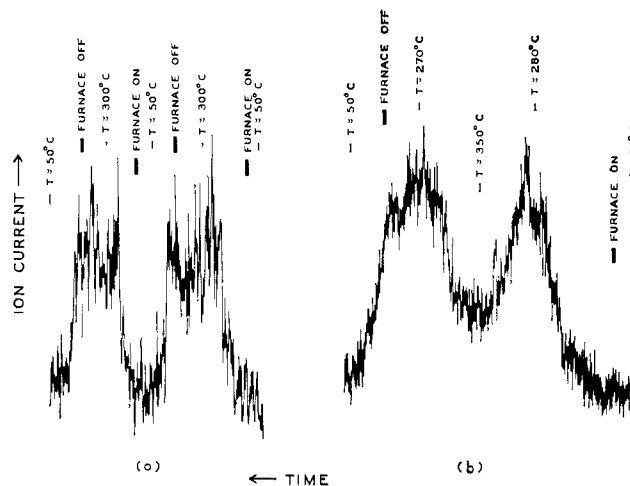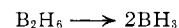

Fig. 1.—(a) Recording of the $m/e = 14$ ion peak as a function of furnace temperature measured by a platinum:platinum-rhodium (90-10) thermocouple centered in the furnace and gas stream. An ionizing voltage of 13.0 v., ion trap current of 1 μa. and an electron-multiplier voltage of 2000 v. were used. (b) Recording of the $m/e = 13$ ion peak as a function of furnace temperature. An ionizing voltage of 12.5 v. was used. Other conditions were the same as (a).

13, BH_2^+, ion peak in the same manner indicates that BH_2 is also present (Fig. 1b).

These experiments were completely reproducible both with pure diborane and mixtures of diborane with argon or hydrogen. Because of the basic experimental arrangement and the use of a bakeable, welded, stainless steel vacuum envelope with copper gasketed flanges, no background was observed at $m/e = 13$ or 14 at the voltages indicated in Fig. 1. Using pure dilutant gas and examining these or other ion peaks as a function of temperature produced no change in the ion intensity even at higher ionizing voltages. Stopping the flow of diborane eliminated BH_3 and BH_2 production. Examination of the $B_2H_5^+$ ion peak above its appearance potential showed an expected decrease in intensity with furnace temperature as diborane was destroyed. The $m/e = 17$ and $m/e = 15$ ion peaks were examined using the deuterated B^{11} compound. BD_3 and BD_2 were observed in the same manner eliminating the possibility that impurities are the cause of this effect.

The remaining alternative is that the temperature variation of BH_3^+ and BH_2^+ is being caused by the fragmentation of some other unstable species. Appearance potential measurements given below rule out the possibility that BH_3 fragmentation is causing the temperature variation of the BH_2^+ ion peak. BH_4 was not observed and would hardly be expected to be stable at these temperatures. Simple activation energy considerations indicate that other conceivable secondary reactions would be improbable.

Our conclusion, then, is that the borane molecule and the boryl radical are definitely present in the pyrolysis of diborane. It is apparent that the initial step in the pyrolysis is a combination of the processes

$$B_2H_6 \longrightarrow 2BH_3$$

$$B_2H_6 \longrightarrow BH_2 + BH_4 \longrightarrow 2BH_2 + H_2$$

A qualitative examination of the recombination of these species has been made. Addition of argon to diborane markedly decreased BH_3 recombination but