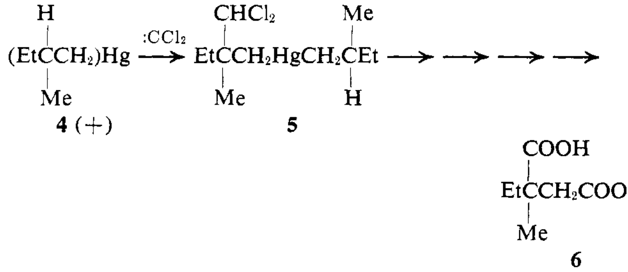
2 and an unusual β-carbon–hydrogen insertion product **3**.[1–3]

$$\underset{\mathbf{1}}{(RR'CHCHR'')_2Hg} \xrightarrow{:CCl_2} \underset{\mathbf{2}}{RR'CHCHR''CCl_2HgCHR''CHRR'} + \underset{\mathbf{3}}{RR'C(CHCl_2)CHR''HgCHR''CHRR'}$$

It was previously reported[2] that the insertion of dichlorocarbene into the β-C–H bond of (+)-bis((*S*)-2-methylbutyl)mercury (**4**) occurred with net inversion of configuration. Subsequent to the appearance of this publication, unpublished data[4] brought to the attention of the authors[5] indicated that the final degradation product of their stereochemical sequence, α-methyl-α-ethylsuccinic acid (**6**), has a concentration-dependent *sign* and magnitude of rotation in chloroform. For example, the rotations of samples of 85% optically pure (*S*)-α-methyl-α-ethylsuccinic acid in chloroform are $[\alpha]^{24}D$ −5.0° (*c* 16.5), −0.6° (*c* 10.6), + 1.7° (*c* 8.5), +9.4° (*c* 4.3), +18.9° (*c* 2.2), and +30° (*c* 1.1).[6]



4 (+) **5** **6**

$$\underset{\mathbf{4}\,(+)}{(Et\overset{H}{\underset{Me}{C}}CH_2)Hg} \xrightarrow{:CCl_2} \underset{\mathbf{5}}{Et\overset{CHCl_2}{\underset{Me}{C}}CH_2HgCH_2\overset{Me}{\underset{H}{C}}Et} \longrightarrow \longrightarrow \longrightarrow \longrightarrow \underset{\mathbf{6}}{Et\overset{COOH}{\underset{Me}{C}}CH_2COOH}$$

Because the rotation of our sample of diacid **6** was $[\alpha]^{25}D$ −6.41° (*c* 1.4, $CHCl_3$), there can be no doubt that it has the *R* configuration, clearly indicating that the dichlorocarbene insertion occurred primarily by retention of configuration. One can estimate from the data of Krow and Hill[6] that at *c* 1.4 the rotation of optically pure (*R*)-α-ethylsuccinic acid should be *ca.* 30°. Using this value we can calculate that the insertion took place with approximately 21% retention and 79% racemization.

More recent work on the extent of carbon–mercury and β-carbon–hydrogen insertion in a series of dialkylmercury compounds (Table I) provides convincing evidence for specificity of the carbon–hydrogen attack by dichlorocarbene at the β position. The data clearly show an increase in the ratio of β-C–H to C–Hg insertion products from 0 to *ca.* 9 as the β-C–H bond progresses from primary to tertiary. No other simple C–H insertion products were detected.[6a]

Table I. Relative Distribution of C–Hg and β-C–H Insertion Products by Dichlorocarbene Attack on R_2Hg[a,b]

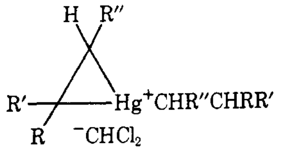
R	β-C–H	% C–Hg insertion	% β-C–H insertion
Ethyl	Primary	100	0
Isopropyl	Primary	100	0
sec-Butyl	Primary, secondary	100	0
n-Propyl	Secondary	53	47
n-Butyl	Secondary	67	33
n-Amyl	Secondary	67	33
Isoamyl	Secondary	65	35
Isobutyl	Tertiary	9	91
2-Methylbutyl	Tertiary	6	94
Cyclohexylmethyl	Tertiary	13	87

[a] Reactions were carried out at ≤5° in alkene-free pentane by treatment of ethyl trichloroacetate with commercial sodium methoxide in the presence of R_2Hg. [b] Product distribution data were obtained by vpc analysis of the brominated reaction mixture.

A particularly interesting example is that of diisoamylmercury in which the carbon–hydrogen insertion went exclusively into the secondary C–H bond at the β position, although there was a tertiary C–H bond at the γ position. Such an observation would appear to rule out a simple free-radical process in which tertiary C–H bonds at various positions along the alkyl chain other than the β position should be susceptible to attack.

We have previously expressed the belief that the initial attack of dichlorocarbene on a dialkylmercury compound might be at the mercury atom with the resultant formation of a complex or ylide structure which could then undergo further reaction.[1] While it is possible that dichlorocarbene could be transferred from its position in the complex directly into the β-C–H bond, a glance at approximate models would suggest that such a transfer should also be made into the γ-C–H bond and that the transfer process should be highly stereospecific, neither of which is realized experimentally.

Our current hypothesis attempts to account for the facts by postulating formation and collapse of an intermediate mercurinium ion pair,[7a–c] **7**. Experimental support, now being sought, will be published later.



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[1] J. A. Landgrebe and R. D. Mathis, *J. Amer. Chem. Soc.*, **88**, 3545 (1966).

[2] J. A. Landgrebe and D. E. Thurman, *ibid.*, **89**, 4542 (1967).

[3] D. Seyferth and S. S. Washburne, *J. Organometal. Chem.*, **5**, 389 (1966).

[4] G. R. Krow, Ph.D. Dissertation, Princeton University, 1967.

[5] We are indebted to the astute observations of Dr. John Jacobus and the helpful correspondence with Professor K. Mislow and Dr. G. R. Krow.

[6] See footnote 6 in G. Krow and R. K. Hill, *Chem. Commun.*, 430 (1968).

[6a] NOTE ADDED IN PROOF. Dr. John Jacobus has communicated to us that he has independently carried out the β-C–H insertion reaction by dichlorocarbene on **4** with net retention of configuration.

[7] (a) K. Ichikawa, K. Nishimura, and S. Takayama, *J. Org. Chem.*, **30**, 1593 (1965); (b) N. S. Zefirov, *Russ. Chem. Rev.*, **34**, 527 (1965); (c) J. Chatt, *Chem. Rev.*, **48**, 7 (1951).

[8] We wish to thank the National Science Foundation for generous support for our work.

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Received June 19, 1968

The Photochemical Generation of a Subvalent Phenylaluminum Species from Triphenylaluminum(III)

Sir:

Recent interest in lower valent intermediates of groups IIIA and IVA, typified by numerous reports on carbenes,[1] as well as on silenes[2] and subvalent boron[3]

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[1] *Cf.* W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1960, for a critical survey.

[2] (a) P. S. Skell and E. J. Goldstein, *J. Am. Chem. Soc.*, **86**, 1442 (1964); (b) R. West and R. E. Bailey, *ibid.*, **85**, 2871 (1963).

[3] M. A. Kuck and G. Urry, *ibid.*, **88**, 426 (1966).

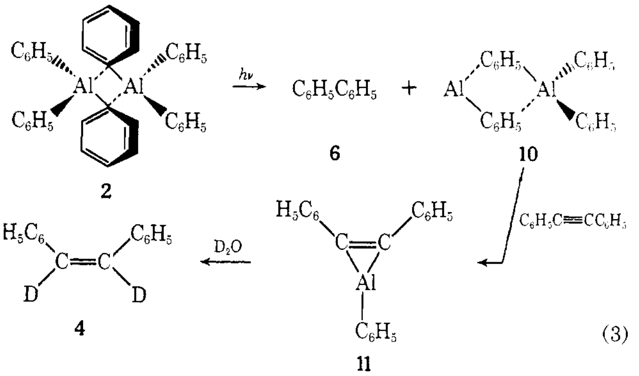
species, has induced us to search for the existence of subvalent organoaluminum intermediates in certain reactions of trisorganoaluminum(III) compounds.[4] Precedent for the formation of such species is provided by the thermal behavior of triphenylthallium(III), which decomposes at 140° into biphenyl and presumably phenylthallium(I) (**1**). The intermediate **1** disproportionates into triphenylthallium and thallium metal, but it can be captured with carbon dioxide to yield thallium(I) benzoate.[5] Since the thermal decomposition of triphenylaluminum(III) (**2**) at 200–250° involves autometalation leading chiefly to benzene evolution,[6,7] rather than biphenyl formation, the photolysis of **2** seemed appealing as an alternative route to subvalent organoaluminum compounds. At this time we wish to report chemical evidence pointing to the generation and capture of an aluminum(I) or aluminum(II) species as a significant reaction occurring in the photolysis of triphenylaluminum(III) (**2**).

When 0.0078 mol of **2** in 450 ml of either benzene or toluene was irradiated for 24 hr,[8] biphenyl, aluminum metal, and an organoaluminum hydride[8b] were the only significant reaction products (eq 1). In order to intercept any subvalent organoaluminum intermediate, the photolysis was repeated in the presence of a fourfold excess (0.0337 mol) of diphenylacetylene (**3**).[9] The expectation was that any organoaluminum(I) fragment might add, like a carbene,[1] to the triple bond of **3** in a *cis* fashion; on the other hand, organoaluminum(II) radicals, R_2Al, might add both in a *cis* and a *trans* fashion to the triplet bond of **3**. The already described addition of **2** to **3**, leading to triphenylethylene upon hydrolysis,[10] was not expected to interfere with the trapping of subvalent organoaluminum intermediates. Thus, the photolysis of 0.0078 mol of **2** in a solution containing 0.0337 mol of **3** in 450 ml of toluene for 24 hr led to the formation of a clear, dark red solution *without any deposition of aluminum metal.* Solvent removal under reduced pressure, hydrolysis, and glpc analysis of the organic extract revealed the presence of biphenyl, *cis*-stilbene, and triphenylethylene in a molar ratio of 2.7 : 1.0 : 2.5.[11] To label the positions of carbon–aluminum bonds in the photolysis products, the reaction was repeated as described above, but the concentrated reaction residue was then treated with deuterium oxide (99.8%). The reaction products were separated from the excess **3** and each other by a combination of column chromatography (activated alumina and hexane) and preparative glpc (30% silicone oil on Firebrick). *cis*-Stilbene was shown by mass spectrometry (10 eV) and nmr spectroscopy to consist of at least 60% $C_6H_5CD{=}CDC_6H_5$ (**4**) and about 40% $C_6H_5CD{=}CHC_6H_5$ (**5**). The infrared spectrum of the biphenyl isolated (**6**) was compared with that of an authentic sample of 2-deuteriobiphenyl (**7**); the intense doublet at 780 cm^{-1} in **7** was clearly evident in biphenyl (**6**). Mass spectral analysis of **6** confirmed the presence of at least 36% $C_6H_5C_6H_4D$.

$$\underset{\mathbf{2}}{[(C_6H_5)_3Al]_2} \xrightarrow[C_6H_5R]{h\nu} \underset{\mathbf{6}}{C_6H_5C_6H_5} + Al + Ar_nAlH_{3-n} \qquad (1)$$

The isolation of stilbene points unequivocally to a phenylaluminum(I) or a diphenylaluminum(II) intermediate in the photolysis of **2**. The absence of significant amounts of bibenzyl or methylbiphenyls rules against the formation of free phenyl radicals as intermediates in the photolysis of **2** in toluene solution.[12] Furthermore, the formation of the stilbene precursor, $C_6H_5C(AlR_2){=}C(AlR_2)C_6H_5$ (**8**), by the addition of diphenylaluminum(II) radicals, $R_2Al\cdot$ (**9**), to **3** might be expected to occur either unselectively or in a *trans* fashion. In this case, the stilbene first formed would be expected to consist of a relatively large proportion of *trans*-stilbene. Therefore, the initial formation of predominantly *cis*-stilbene (*cf.* ref 11) and the absence of solvent attack by phenyl radicals argue against the principal reaction being eq 2. Since biphenyl (**6**) is known to stem from **2**, and as **2** is known to exist largely as a dimer in these solvents,[13] eq 3 may be proposed for the generation of a phenylaluminum(I) intermediate.[14] Whether the phenylaluminum(I) species actually remains bridged, as depicted in **10**, remains unresolved. Likewise, the aluminum precursor of **4** may be the novel triphenylaluminacyclopropene (**11**) or its dimeric

$$\underset{\mathbf{2}}{[(C_6H_5)_3Al]_2} \overset{h\nu}{\underset{C_6H_5CH_3}{-\!\!/\!\!/\!\!\longrightarrow}} (C_6H_5)_3Al + (C_6H_5)_2Al\cdot + C_6H_5\cdot \qquad (2)$$



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[4] (a) *Cf.* H. Hoberg and E. Ziegler, *Angew. Chem.*, **79**, 411 (1967), for the generation of organic radicals by the heating of $(C_6H_5)_2MC(C_6H_5)_3$, where M = B or Al. (b) E. P. Schram, *Inorg. Chem.*, **5**, 1291 (1966), has reported chemical evidence for the existence of Al–Al bonds in $Al_4B(NMe_2)_3(Me)_6$.

[5] H. Gilman and R. G. Jones, *J. Am. Chem. Soc.*, **62**, 2357 (1940).

[6] A. W. Laubengayer and J. Kotz, Cornell University [*cf. Dissertation Abstr.*, **25**, 1551 (1964)].

[7] J. J. Eisch and W. C. Kaska, *J. Organometal. Chem.* (Amsterdam), **2**, 184 (1964).

[8] (a) A Rayonet photochemical reactor, Model 100, equipped with a low-pressure (2537 Å) mercury lamp and operating at an ambient temperature of 45°, was employed. The moles of triphenylaluminum are based upon its actual dimeric form. (b) The reaction mixture was filtered carefully under nitrogen and the resulting organic solution evaporated under reduced pressure. Treatment of the pasty residue with D_2O caused a vigorous evolution of hydrogen gas, which by mass spectrometry was shown to be >95% H–D.

[9] In a control experiment the toluene solution of diphenylacetylene, free of stilbenes, was irradiated for 24 hr; no stilbene or any significant amount of other products was formed.

[10] J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.*, **88**, 2976 (1966).

[11] Small amounts of *trans*-stilbene (15% of the *cis*-stilbene) were formed during the first 12 hr. After 32 hr the *cis*:*trans* ratio was 1.0:0.5.

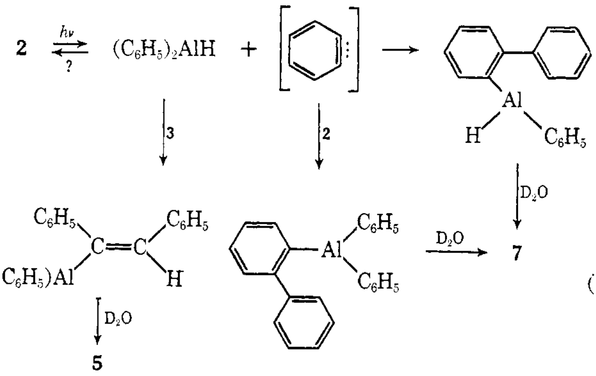
[12] D. H. Hey, B. W. Pengilly, and G. H. Williams, *J. Chem. Soc.*, 1463 (1956).

[13] (a) P. G. Perkins and M. E. Twentyman, *ibid.*, 1043 (1965); (b) J. Kotz, *Dissertation Abstr.*, **25**, 1551 (1964).

[14] *Cf.* J. F. Malone and W. S. McDonald, *Chem. Commun.*, 444 (1967), for the X-ray crystallographic analysis of structure **2**. Intermediate **10** may rearrange to form transitorily the unknown species, $(C_6H_5)_2AlAl(C_6H_5)_2$ (*cf.* ref 4b), which might then add to **3** in a *cis* manner. Again, deuteriolysis would yield **4**. However, an aluminum(I) species has attractive precedents; *cf.* ref 5 and R. K. McMullan and J. D. Corbett, *J. Am. Chem. Soc.*, **80**, 4761 (1958), for the structure of Ga_2Cl_4 as $Ga^I(Ga^{III}Cl_4)$.

counterpart, hexaphenyl-1,4-dialumina-1,4-cyclohexadiene (**12**).[15]

Finally, the formation of significant amounts of 2-deuteriobiphenyl (**7**) and α-deuterio-*cis*-stilbene (**5**) can be jointly reconciled by a minor, alternative photodecomposition of **2** into benzyne and diphenylaluminum hydride (eq 4) (*cf.* ref 8b).



(4)

This technique of trapping lower valent organometallic intermediates currently is being extended to diverse photolyses and redox reactions. Also, the applicability of these findings to the development of new approaches to arynes and to organometallic heterocycles is being evaluated.

Acknowledgment. We are grateful to the National Science Foundation for support of this research under Grant GP-6679. Dr. Henry Fales of the National Institutes of Health was of great assistance in the measurement and interpretation of the mass spectral data reported herein.

[15] *Cf.* J. J. Eisch and L. J. Gonsior, *J. Organometal. Chem.* (Amsterdam), **8**, 53 (1967), for evidence in support of boron counterparts of **11** or **12**.

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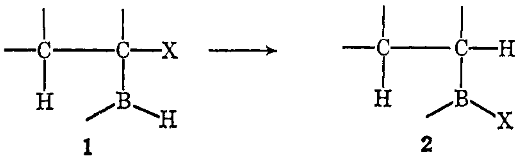
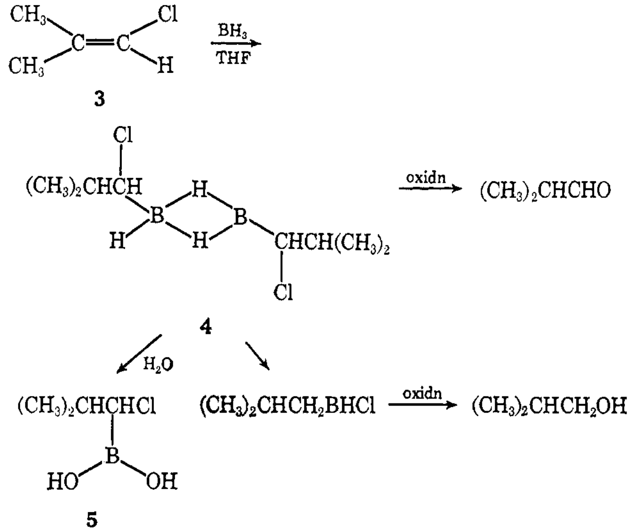
Received April 26, 1968

Transfer Reactions Involving Boron. XVII. On the Kinetics of the α-Transfer Reaction[1]

Sir:

Recent studies in our laboratories have been concerned with the chemistry of α- and β-heterosubstituted organoboranes which are formed in the hydroboration of heterosubstituted olefins.[2–6] These studies have indicated that the α-heterosubstituted organoboranes **1** undergo reaction to give derivatives having structure **2**. Previously we had pictured this rearrangement as proceeding *via* an intramolecular four-centered transition state. Brown[7] has suggested that the replacement of X by hydrogen could occur *via* a nucleophilic displacement, apparently employing a borohydride species in an intermolecular displacement.[7] All of the pertinent facts concerning the conversion of **1** → **2** will be cited later in this communication and incorporated into a consistent mechanistic description of the reaction. Unfortunately, the systems studied previously underwent reaction at a sufficiently fast rate that kinetic measurements were not possible. Recently, however, Brown and Sharp[7] have shown that the adduct formed in the hydroboration of 1-chloro-2-methylpropene (**3**) was reasonably stable to rearrangement. It is reported that immediate oxidation of the hydroboration product of **3** produces isobutyraldehyde.[6] We observed that if the hydroboration reaction mixture were allowed to stand in tetrahydrofuran at room temperature for several hours and then subjected to oxidation, only 2-methyl-1-propanol was isolated. We therefore investigated this system in greater detail.





The hydroboration of 1-chloro-2-methylpropene (**3**), with 0.99 mol of borane in tetrahydrofuran per 1.00 mol of olefin, produced **4**. The ^{1}H nmr spectrum of **4** displayed a double doublet at δ 0.95 (6 H, $(C\mathit{H}_3)_2CH$), the remaining peaks being obscured by the solvent resonance peaks. The ^{11}B nmr spectrum displayed only a double triplet at -29.3 ppm (relative to boron trifluoride etherate internal capillary) with J_{BH} (terminal) = 130 Hz and J_{BH} (bridge) = 47 Hz, corresponding to a symmetrical dialkyldiborane.[8] Addition of water and careful removal of the solvent under reduced pressure gave 1-chloro-2-methylpropylboronic acid (**5**); mp 63–64°.[9]

The ^{1}H nmr spectrum of **5** in deuteriochloroform displayed two doublets at δ 1.00 and 1.06 (6H, $(C\mathit{H}_3)_2CH$, $J = 6.6$ Hz), a multiplet at 2.22 (1 H, $(CH_3)_2C\mathit{H}$) overriding a broad absorption ($B(O\mathit{H})_2$), and a doublet at 3.62 (1 H, $C\mathit{H}ClB(OH)_2$, $J = 3.3$ Hz). The ^{11}B nmr spectrom of **5** displayed a broad singlet at -29.3 ppm characteristic of an alkylboronic acid.[10] During the course of several hours the ^{1}H nmr spectrum of **4** changed quite dramatically, eventually displaying an AB portion of an ABX system at δ 0.55 (2 H, $C\mathit{H}_2$-

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[1] Part XVI: D. J. Pasto and J. Hickman, *J. Amer. Chem. Soc.*, **89**, 4445 (1967). Taken from the Ph.D. Thesis of J. H., University of Notre Dame, 1967.

[2] D. J. Pasto and J. Miesel, *J. Amer. Chem. Soc.*, **85**, 2118 (1963).

[3] D. J. Pasto and C. C. Cumbo, *ibid.*, **86**, 4343 (1964).

[4] D. J. Pasto and R. Snyder, *J. Org. Chem.*, **31**, 2773 (1966).

[5] D. J. Pasto and R. Snyder, *ibid.*, **31**, 2777 (1966).

[6] D. J. Pasto and J. Hickman, *J. Amer. Chem. Soc.*, **89**, 5608 (1967).

[7] H. C. Brown and R. L. Sharp, *ibid.*, **90**, 2915 (1968).

[8] D. J. Pasto and V. Balasubramaniyan, unpublished results.

[9] See footnote 34 of ref 7.

[10] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966, p 972.