suction. A yellow crystalline solid, dibenzoylmethane was obtained (1.05 g). This represents 92% recovery of the diketone from the hydrolytic decomposition of the starting material.

A sample of bis(1,3-diphenyl-1,3-propanediono)diacetatosilicon(IV) prepared from the reaction of bis(2,4-pentanediono)diacetatosilicon(IV) and dibenzoylmethane was treated in a similar manner as described above. The chelate (1.2 g, 0.002 mole) gave 0.85 g (93%) of dibenzoylmethane.

Attempted Reaction of Bis(2,4-pentandiono)diacetatosilicon(IV) with Ferric Chloride. In a 125-ml flask was placed 2.5 g (0.007 mole) of bis(2,4-pentanediono)diacetatosilicon(IV) dissolved in 20 ml of dried chloroform. To this was added 1.86 g (0.008 mole) of ferric chloride. A maroon solution formed. The solution was filtered under suction, and the filtrate was poured into 50 ml of dry ether. After cooling in a refrigerator overnight no solid precipitate of iron salt was observed.

Acknowledgment. We wish to thank the Silicones Division, Union Carbide Corp., Tonawanda, N. Y., for partial support of this work through a research fellowship, 1962–1963.

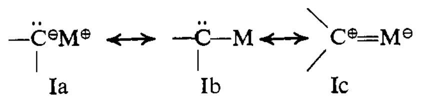
The Synthesis of Aluminoles *via* the Addition and Cyclization Reactions of Arylaluminum Compounds[1]

John J. Eisch[2] and William C. Kaska

Contribution from the Department of Chemistry, The Catholic University of America, Washington, D. C. 20017, and the Department of Chemistry, University of Michigan, Ann Arbor, Michigan. Received February 21, 1966

Abstract: In order to study the possible importance of p_π–p_π effects in organoaluminum chemistry, a study of the synthesis and properties of vinylaluminum compounds has been undertaken. Aryl-substituted vinylaluminum systems have been prepared by the addition of triphenylaluminum, in turn, to diphenylacetylene, methylphenylacetylene, and 1,3,3,3-tetraphenylpropyne. Examination of the hydrolysis products has permitted considerable insight into the electronic and steric factors involved in such additions. Parallel efforts to add the Al–H bond of diphenylaluminum hydride to alkynes were frustrated by the inability to prepare pure diphenylaluminum hydride from lithium hydride and diphenylaluminum chloride. The foregoing *cis*-β-phenylvinylaluminum compounds were found to undergo a novel metalative cyclization with the formation of the aluminole ring system. The preparation, isolation, and chemical structure proof were carried through in considerable detail for 1,2,3-triphenylbenzaluminole and 5-phenyldibenzaluminole. The mechanistic kinship between the addition of aluminum aryls to alkynes and the metalative formation of aluminoles is assessed in terms of reaction conditions and electronic factors. The import of these results to further synthetic and theoretical studies is emphasized.

The importance of carbon–metal bond polarity in correlating the properties of organometallic compounds is abundantly recognized.[3] Electron release by a metal center can cause σ bonding to range from almost homopolar linkages (Ib, M = B, Si, Al, etc.) to that of ion pairing (Ia, M = Li, Na, K, etc.). On the other hand, a substantial body of evidence suggests that metals, by virtue of their *n*p or *n*d available orbitals, may withdraw electrons from adjacent unsaturated centers by π bonding (Ic). This latter type of bonding might be especially favored in covalent organometallic compounds where the metal differs little from carbon in polarity and size. Indeed, physical and chemical evidence has been adduced in support of p_π–p_π bonding in vinylboranes[4] and of d_π–p_π bonding in vinylsilanes.[5] Consequently, the possible significance of such π bonding to an understanding of organoaluminum chemistry has aroused our curiosity and has prompted the study of vinylaluminum compounds. The present report deals with the synthesis and structure proof of certain novel vinylaluminum systems.[6] Subsequent papers will pursue the nature of the carbon–aluminum bonding as revealed by spectroscopic data.



$$-\ddot{C}^{\ominus}M^{\oplus} \longleftrightarrow -\ddot{C}-M \longleftrightarrow \;\rangle C^{\oplus}{=}M^{\ominus}$$

Ia Ib Ic

Of particular interest in this research were aryl-substituted vinylalanes, since the carbon chain conjugation might be expected to enhance the possible importance of carbon–aluminum π bonding (IIa–IIc).

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[1] Part VI of the series, Organometallic Compounds of Group III. Previous paper: J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.*, **88**, 2213 (1966).

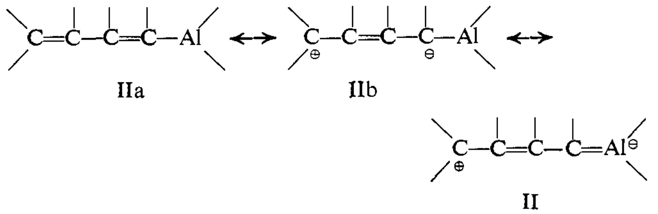
[2] To whom inquiries should be addressed at the Maloney Chemical Laboratory, The Catholic University of America, Washington, D. C. 20017.

[3] *Cf.* the lucid treatment of bond polarity by E. G. Rochow, D. T. Hurd, and R. N. Lewis in "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New, York, N. Y., 1957, pp 16–25.

[4] *Cf.* the appraisal of the properties of vinylboranes by T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *J. Chem. Soc.*, 3103 (1961).

[5] (a) J. J. Eisch and J. T. Trainor, *J. Org. Chem.*, **28**, 487 (1963); (b) R. Summitt, J. J. Eisch, J. T. Trainor, and M. T. Rogers, *J. Phys. Chem.*, **67**, 2362 (1963); (c) L. Goodman, A. H. Konstam, and L. H. Sommer, *J. Am. Chem. Soc.*, **87**, 1012 (1965); (d) *Cf.* C. Eaborn, "Organosilicon Compounds," Academic Press Inc., New York, N. Y., 1960, pp 91–113.

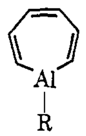
[6] A preliminary account of the first synthesis of the aluminole system has appeared: J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.*, **84**, 1501 (1962).


IIa IIb

II

A correlary of this assumption is that cyclic arrays of such atoms might be especially favorable for such conjugation, either because of coplanarity (III) or by virtue of Hückel aromaticity (IV).[7] The participation of the unoccupied aluminum 3p orbital presumably would permit the cyclic delocalization of the six π electrons in the latter case.[8] A further consideration


III

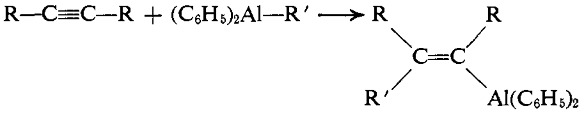

IV

in the study of substituted vinylalanes is the association tendency of aluminum alkyls.[9] Since simple vinyl systems, such as trivinylaluminum[10] and diethyl-*cis*-1-butenylaluminum,[11] are at least dimeric in solution, these would offer little opportunity of studying electronic effects operative in the monomeric vinylalane. Aryl substituents on the vinylalane, on the other hand, could be expected to favor the existence of the monomer by a primary steric inhibition of dimerization.[12]

Apart from the preparation of several alkyl-substituted vinylalanes from alkynes and aluminum alkyls or dialkylaluminum hydrides,[11] or the synthesis of several arylaluminum compounds from mercury aryls and aluminum metal,[13] little systematic attention has been given to substituted vinylalanes.[14] Therefore, this research set out to investigate the synthesis of arylated vinylalanes by the addition of phenylaluminum derivatives to alkynes. In the course of this study, a novel cyclization reaction was uncovered, which has led to the first synthesis of the aluminole ring system.[6]

Results

The addition of triphenylaluminum and of diphenylaluminum hydride to the triple bond of internal alkynes appeared to be a most promising approach to arylated vinylalanes (eq 1). The synthesis of the requisite diphenylaluminum hydride, unknown at the time of this


(1)

$R' = C_6H_5, H$

work,[15] was undertaken in analogy with the successful preparation of diethylaluminum hydride by Ziegler and co-workers[16] (eq 2 and 3). The novel diphenylaluminum chloride could be obtained readily according to

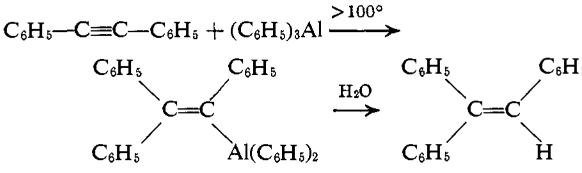
$$2(C_6H_5)_3Al + AlCl_3 \longrightarrow 3(C_6H_5)_2AlCl \qquad (2)$$

$$(C_6H_5)_2AlCl + LiH \longrightarrow (C_6H_5)_2AlH + LiCl \qquad (3)$$

the redistribution reaction indicated in eq 2. However, the chloride reacted only very slowly with lithium hydride suspended in benzene. Addition of ethyl ether to the reagents caused a fairly prompt deposition of lithium chloride, but attempted isolation of the diphenylaluminum hydride yielded only needles of triphenylaluminum etherate and an insoluble aluminum hydride fraction. Therefore, although there is little doubt that diphenylaluminum hydride was formed, disproportionation according to eq 4 seems to be facile.[17]

$$3(C_6H_5)_2AlH \xrightarrow{(C_2H_5)_2O} 2(C_6H_5)_3Al\cdot O(C_2H_5)_2 + (AlH_3)_x\downarrow \qquad (4)$$

The interaction of the stable triphenylaluminum with internal[18] alkynes proved more propitious. Diphenylacetylene was found to react readily with triphenylaluminum at temperatures over 100° to yield triphenylethylene upon hydrolysis (eq 5). The response of the


V

(5)

unsymmetrical alkyne, 1-phenylpropyne, was even more instructive; not only did it react spontaneously with

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(7) *Cf.* A Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, New York, N. Y., 1961, pp 256–304, for the basis and implications of E. Hückel's $4n + 2$ rule for aromaticity.

(8) *Cf.* E. E. van Tamelen, G. Brieger, and K. G. Untch, *Tetrahedron Letters*, No. **8**, 14 (1960), for the synthesis of the dibenzoborepin system.

(9) E. G. Hoffmann, *Ann.*, **629**, 104 (1960).

(10) B. Bartocha, A. J. Bilbo, D. E. Bublitz, and M. Y. Gray, *Z. Naturforsch.*, **16b**, 357 (1961).

(11) G. Wilke and H. Müller, *Ann.*, **629**, 222 (1960).

(12) Although trimethylaluminum, triethylaluminum, and tri-*n*-butylaluminum are dimeric in benzene, triisopropylaluminum and triisobutylaluminum are monomeric. Apparently bulky substituents on the α carbon have the greatest influence on association (*cf.* ref 9). The general problem of the degree of association of the arylaluminum compounds considered here will receive further attention in this laboratory.

(13) A. N. Nesmeyanov and N. N. Novikova, *Bull. Acad. Sci. URSS, Classe Sci. Chim.*, 372 (1942); *Chem. Abstr.*, **39**, 1637 (1945).

(14) *Cf.* J. R. Surtees, *Rev. Pure Appl. Chem.*, **13**, 91 (1963), for a survey of arylaluminum compounds.

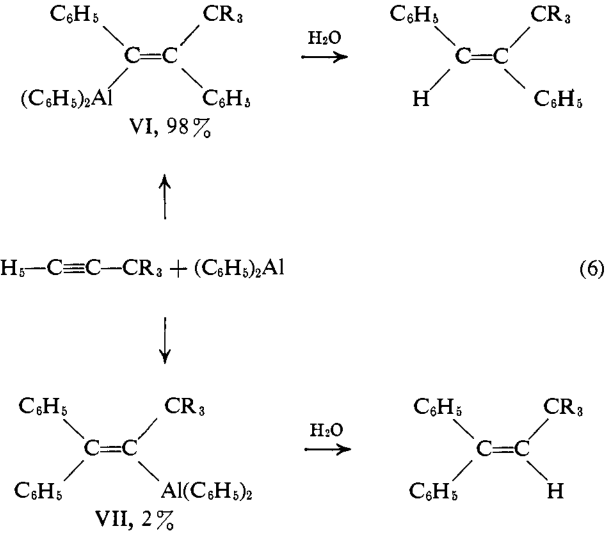
(15) Subsequent to our unsuccessful attempts to isolate pure diphenylaluminum hydride from ether solution, J. R. Surtees (*Chem. Ind.* (London), 1260 (1964)) has prepared this substance from triphenylaluminum and aluminum hydride etherate in benzene. We are investigating the action of this hydride source on tolane.

(16) K. Ziegler, H. G. Gellert, H. Martin, K. Nagel, and J. Schneider, *Ann.*, **589**, 91 (1954).

(17) Since the disproportionation occurred gradually during the purification, it is not certain whether the hydride formed is solely $(AlH_3)_x$ or whether some stable $(C_6H_5AlH_2)_x$ might be admixed with it.

(18) Terminal alkynes undergo facile metalation with triphenylaluminum with the formation of 1-alkinyldiphenylaluminum: J. J. Eisch and W. C. Kaska, *J. Organometal. Chem.*, **2**, 184 (1964).

triphenylaluminum, but the stereochemistry and direction of addition were most selective (eq 6, R = H). Exclusive *cis* addition of the phenyl–aluminum bond and a pronounced preference (36:1) for isomer VI over isomer VII characterized the reaction.



(6)

Chart I

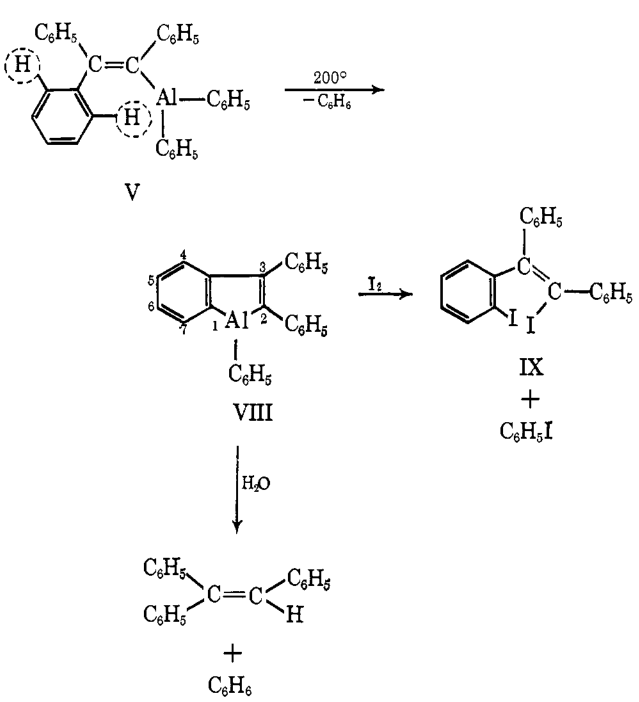
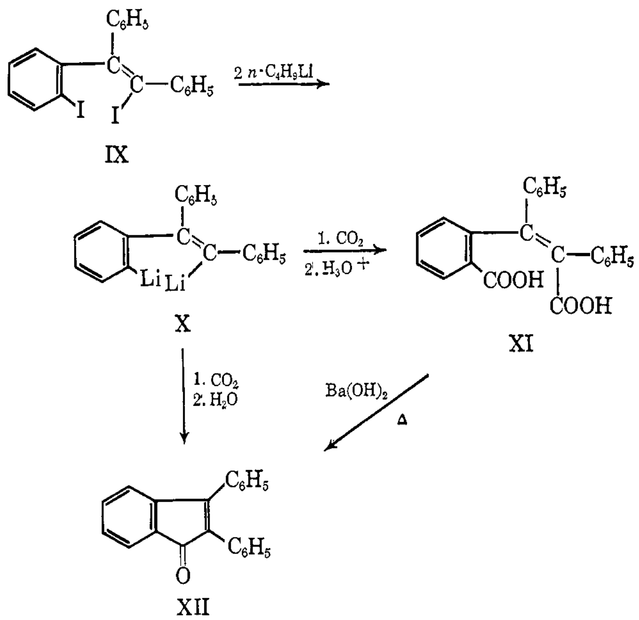


Chart II



Finally, the importance of steric factors in the addition of triphenylaluminum was revealed in the failure of 1,3,3,3-tetraphenyl-1-propyne to react under conditions (110°) more than adequate for diphenylacetylene or 1-phenylpropyne. Only at temperatures in excess of 200° did reaction finally occur, and then little selectivity in the direction of the phenyl–aluminum bond addition resulted. The hydrolysis products were the corresponding pentaphenylpropenes (eq 6, R = C_6H_5).

In all of the preceding reactions of alkynes with triphenylaluminum it was observed that temperatures of approximately 200° caused the evolution of benzene from the reaction mixture. Since triphenylaluminum itself is fairly stable at this temperature,[19] it was reasoned that the vinylaluminum products (V–VII) might undergo an intramolecular metalative cyclization by virtue of the proximity of the *cis*-β-phenyl and the diphenylalumino groups. Inspection of a Stuart–Briegleb model of V reveals that the aluminum center is contiguous to the *ortho* position of the β-*cis*-phenyl group in several conformations (*cf.* Chart I). To test this hypothesis, the adduct of diphenylacetylene and triphenylaluminum (V) was heated up to 200° in diphenyl ether solution. After the copious evolution of benzene had ceased, a pale yellow arylaluminum compound (VIII) was isolated, whose aluminum analysis (7.4%) was consistent with that expected for the loss of benzene from V (7.5%). Although VIII yielded triphenylethylene and benzene upon hydrolysis, treatment with iodine was most helpful in labeling new carbon–metal bonds. Thus iodinolysis led to iodobenzene and a pale yellow iodo compound melting at 175° (IX). The nature and stereochemistry of IX as 1-iodo-*cis*-1,2-diphenyl-2(2-iodophenyl)ethene was demonstrated by its unambiguous transformation into the known 2,3-diphenylindone (XII, Chart II). Iodine–lithium exchange between IX and *n*-butyllithium resulted in an aryllithium compound X which upon carbonation produced both the indone XII and a dicarboxylic acid XI. Since the latter acid also produced the cyclic ketone XII upon heating with barium hydroxide, its structure as *cis*-1,2-diphenyl-2(2-carboxyphenyl)propenoic acid (XI) followed logically. The direct formation of the ketone XII in the carbonation step typifies a common side reaction of organolithium compounds, namely the reaction between the

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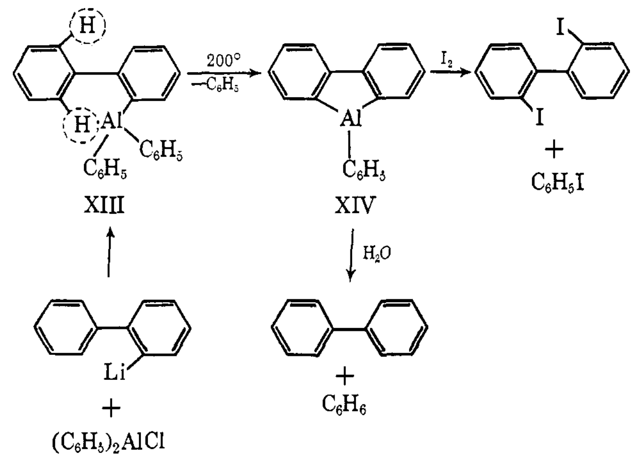
(19) Heating triphenylaluminum alone above 200° for extended periods caused decomposition with the evolution of benzene; *cf.* Eisch and Kaska, ref 18.

lithium carboxylate salts produced and the unconsumed lithium aryl.[20]

The nature of the degradation products from the new organoaluminum compound VIII strongly supports its structure as 1,2,3-triphenylbenzaluminole, the first reported example of an unsaturated aluminum heterocycle.[21] To explore the generality of the foregoing cyclization, *o*-biphenylyldiphenylaluminum (XIII) was chosen for possible ring closure to the dibenzaluminole system. This unsymmetrical aluminum aryl was prepared from *o*-biphenylyllithium and diphenylaluminum chloride (Chart III). Heating at 200° resulted in the evolution of benzene and some biphenyl. Apparently partial disproportionation of XIII to yield some bis-*o*-biphenylylphenylaluminum occurred, and its subsequent cyclization caused the elimination of biphenyl. However, recrystallization of the reaction mixture permitted the isolation of a new aluminum aryl whose aluminum analysis and iodinolysis support its identity as 5-phenyldibenzaluminole (XIV, Chart III). Treatment with iodine gave both iodobenzene and 2,2′-diiodobiphenyl. As is characteristic of triphenylaluminum itself, both 5-phenyldibenzaluminole (XIV) and 1,2,3-triphenylbenzaluminole (VIII) formed crystalline diethyl etherates which were stable up to 100° and were dissociated mainly at 200°.

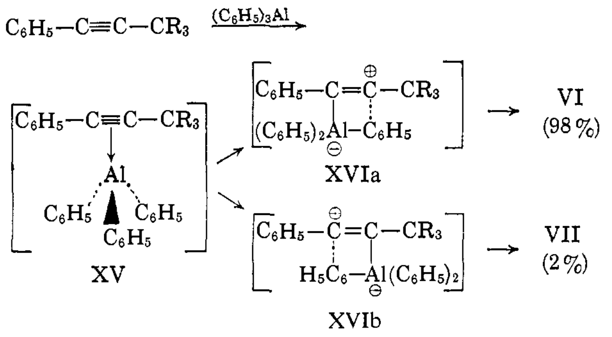
Chart III



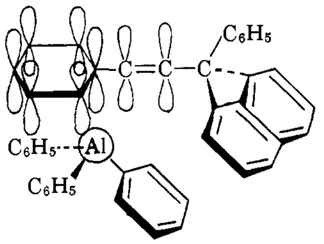
Discussion

The behavior of internal alkynes toward triphenylaluminum possesses at least three interesting facets. These are (a) the mechanisms of arylaluminum addition and cyclization, (b) the electronic character of the resulting vinylalanes, and (c) the preparative implications to the synthesis of vinylalanes and aluminoles, as well as to the arylation of alkynes. The present discussion will be confined to qualitative chemical evidence on the foregoing points. Current research is going forward to obtain quantitative data on the kinetics of such additions and metalations, on the spectroscopic and crystallographic properties of vinylalanes, and on the synthetic generality of these reactions.[22]

The existing evidence on the mechanism of the addition of organoaluminum compounds to unsaturated hydrocarbons can be interpreted in terms of electrophilic attack by $R_2Al–R'$ ($R' = R, H$) on the π bond of the hydrocarbon.[23] Whether a metastable π complex (XV) intervenes is not established, but a four-center transition state with some positive charge development on carbon (XVI, eq 7) is in accord with three findings. First, the use of ether solvents (anisole, cineole), with which triphenylauminum forms complexes, retards or prevents altogether the addition reaction with alkynes.[22] It is understandable that $(C_6H_5)_3AlOR_2$ should be an inferior electrophile. Secondly, the observed *cis* addition to 1-phenylpropyne favors *cis* attack by aluminum and phenyl on the triple bond. Moreover, the preferential formation of VI over VIII (R = H) is consonant with the lower energy of transition state XVIa, compared with XVIb. Since a phenyl group is bulkier than a methyl group, attachment of the diphenylalumino group next to the phenyl must reflect the superior electron release of the methyl in XVIa in stabilizing the developing positive charge. Thus electronic considerations seem to outweigh steric factors. Thirdly, the low reactivity of 1,3,3,3-tetraphenylpropyne (R = C_6H_5 in XV–XVI) tends to weaken the case for an alternative transition state XVII wherein triphenylaluminum would attack the π cloud of the C_1 phenyl and hence favors isomer VI. If XVII were important, the steric hindrance occasioned by the trityl group should be far less severe than is observed.



(7)



XVII

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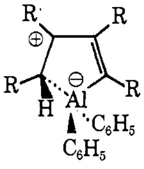
[20] H. Gilman and P. R. Van Ess, *J. Am. Chem. Soc.*, **55**, 1258 (1933).

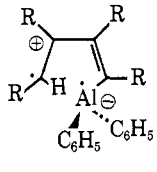
[21] The invaluable guidance of Dr. Leonard T. Capell of The Chemical Abstracts Service for his suggestions on nomenclature and numbering is acknowledged gratefully.

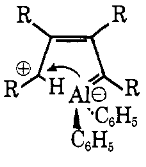
[22] J. J. Eisch, C. K. Hordis, M. F. Foxton, and J. Considine, The Catholic University of America, unpublished studies.

[23] J. J. Eisch, *J. Am. Chem. Soc.*, **84**, 3834 (1962).

The mechanism of the metalative cyclization of *cis*-β-phenylvinylaluminum systems is far from understood at this time. Although electrophilic metalation (XVIIIa) would form a consistent pattern with the preceding addition mechanism (eq 7), free-radical (XVIIIb) or nucleophilic (XVIIIc) alternatives cannot be dismissed readily. Structure XVIIIb implies a transition state where homolysis of phenylaluminum bonds is facilitated by charge transfer between the diphenylalumino group and the γ,δ double bond. Structure XVIIIc presupposes the operation of p_π–p_π interaction between aluminum and the appended butadienoid group. In support of an electrophilic view (XVIIIa) is the behavior of triphenylaluminum toward acidic hydrocarbons. Although phenylacetylene and indene have about the same acidity toward carbanions, only phenylacetylene is metalated readily in warm benzene by triphenylaluminum.[24] A transition state similar to XVIIIa is easily envisaged for alkynes, but not for attack on the CH_2 group of indenes. On the debit side for electrophilic attack is the high temperature required (200°). Indeed, at this temperature saturated benzylic hydrogens (*e.g.*, in fluorenes) begin to be attacked by triphenylaluminum.[22] Moreover, between 200 and 300°, autodecomposition of aluminum aryls themselves becomes serious. The possible significance of radical (XVIIIb) and nucleophilic (XVIIIc) alternatives can only be decided by current experiments designed to detect radical intermediates and to evaluate p_π–p_π effects in these systems.


XVIIIa


XVIIIb


XVIIIc

Finally, the preparative advantages of the addition and cyclization reactions should be emphasized. A general approach to arylated vinylalanes and aluminoles is now available. Further, there is the real possibility that these organometallics can serve, in turn, as starting materials for the preparation of other novel systems. For example, interaction of V with tolane could yield pentaphenylbutadienylaluminum products; likewise, the benzaluminole VIII could insert tolane leading to ring expansion to benzaluminepins (*cf.* IV).[25] As a complement to these organometallic syntheses, the chemistry involved permits the stereospecific preparation of valuable hydrocarbons or their iodides by high-yielding cleavage reactions. The *cis* arylation of alkynes and the preparation of 1,4-diiodobutadienes are two most promising fruits of this study.

Experimental Section

Manipulation of Arylaluminum Compounds. All operations involved in the preparation and purification of organoaluminum compounds were conducted under an atmosphere of dry, oxygen-free nitrogen. The glassware used in such procedures was dried scrupulously at 150° and flushed copiously with pure nitrogen before use. Transfer of air- and moisture-sensitive solids was accomplished in a Plexiglas inert atmosphere chamber (Manostat).[26] The aprotic organic solvents used as reaction media were all of reagent grade. Liquid alkanes were treated with potassium permanganate and then with concentrated sulfuric acid to ensure the absence of unsaturates. Routinely the solvents were refluxed over sodium slices for 1 day, then distilled, and finally redistilled from lithium aluminum hydride directly into the reaction vessel.

Measurements. Melting points were determined by means of a Hershberg apparatus and are uncorrected. The melting points of organoaluminum samples were measured on samples in sealed capillary tubes. Infrared spectra were obtained on a Perkin-Elmer recording spectrophotometer, Model 21. Anhydrous, degassed mineral oil was used to prepare mulls of organoaluminum compounds directly in the drybox. The nuclear magnetic resonance spectrum of triphenylaluminum was recorded in benzene-d_6 with the traces of C_6H_6 acting as an internal standard. Either a Varian V-4300C at 56.3 or 60 Mc or a Varian A-60 instrument was employed in obtaining the following spectra. The nmr chemical shifts are reported on the δ scale (ppm downfield from tetramethylsilane). Finally, most quantitative product data were procured by means of a Barber-Colman gas chromatograph, Model 10, which has a strontium-90 ionization source.

Diphenylmercury. The procedure of Bachmann was modified to obtain high yields of pure product.[27] Phenylmagnesium bromide (prepared from 75.8 g (3.13 g-atoms) of magnesium and 162 g (1.04 moles) of bromobenzene in 550 ml of anhydrous tetrahydrofuran) was filtered and then diluted with 450 ml of anhydrous benzene. Over a 2-hr period 150 g (0.416 mole) of solid mercuric bromide was introduced into the Grignard solution. After a total reflux period of 120 hr the reaction mixture was hydrolyzed with saturated ammonium chloride. The biphasic system was separated and the aqueous layer extracted with 2–100-ml portions of benzene and with 200 ml of chloroform. The combination of all organic layers, drying over anhydrous calcium sulfate, and evaporation of solvent gave 125 g (85%) of colorless needles, mp 123–125°. Traces of phenylmercuric bromide, possibly deleterious to the preparation of triphenylaluminum, were removed by the treatment of this product with hydrazine hydrate in ethanol.[28] Diphenylmercury thus treated was free of halogen and melted at 123.5–125.5° (70% over-all yield).

Triphenylaluminum. In an adaptation of published procedures, a modified Dreikugel-Apparatur,[29,30] provided with ground-glass joints, was used for the preparation of ether-free triphenylaluminum.[29b] The reaction flask (A) was a three-necked, 500-ml, round-bottomed flask; the side necks were at a 45° angle with respect to the center neck. The one side neck was provided with a ₸24/40 outer joint (neck A-1), while the other two necks were ₸24/40 inner joints (A-2, center, and A-3). Flask B was a 300-ml flask equipped with a 24/40 inner joint on its center neck (B-1) and a 24/40 outer joint on its 45° side neck (B-2). Finally flask C was a 500-ml flask equipped with 24/40 inner joints on its center (C-2) and 45° side necks (C-1). The flasks were interconnected *via* the following joints: A-1 → B-1; B-2 → C-1. Joints A-3 and C-2 were provided with three-way stopcocks for evacuation or for admission of nitrogen. Center neck A-2 was attached to a short reflux condenser which was surmounted by a gas inlet. When flask A was upright, a solution in flask A could be refluxed with little distillation of vapors into flask B.

Flask A was charged with 61.6 g (0.174 mole) of diphenylmercury, 21.8 g (0.80 g-atom) of aluminum chips (ingots from Aluminum Foils, Inc., of 99.992% minimum purity), and 300 ml of anhydrous xylene. Flask B, disposed at an angle to flask A, was provided with

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(24) See Eisch and Kaska, ref 18.

(25) J. J. Eisch, unpublished studies.

(26) Detailed descriptions of the nitrogen purification train, glass apparatus used for the reactions and purification of organoaluminum compounds, and general manipulation procedures have been published: (a) see ref 1; (b) W. C. Kaska, Doctoral dissertation, University of Michigan, 1963.

(27) W. E. Bachmann, *J. Am. Chem. Soc.*, **55**, 2830 (1933).

(28) H. Gilman and M. M. Barnett, *Rec. Trav. Chim.*, **55**, 563 (1936).

(29) (a) S. Hilpert and G. Grüttner, *Ber.*, **45**, 2828 (1912); (b) E. Krause and P. Dittmar, *ibid.*, **63**, 2401 (1930); (c) H. Gilman and K. E. Marple, *Rec. Trav. Chim.*, **55**, 135 (1936).

(30) E. Krause and H. Polack, *Ber.*, **59**, 777 (1926).

10 g of aluminum chips. The contents of flask A were heated at reflux for 4 days and then the hot solution was decanted carefully into flask B. Care was taken that the mercury in flask A was not carried over. Then the mixture in flask B was heated at reflux for 2 days. The clear hot solution was poured into flask C, and approximately 200 ml of solvent was distilled into flask B. Cooling of flask C deposited white crystals of triphenylaluminum. Flasks A and B were disconnected under nitrogen and replaced by another flask like flask B (B′). Flask B′ was used to receive the mother liquor from flask C. Recrystallization of the solid in flask C was effected by distilling over the necessary xylene from flask B′. This recrystallization could be repeated several times by transfer of hot solvent and mother liquor between flasks B′ and C. Finally the product could be recrystallized from toluene to give the highest melting product, mp 240–242°.[22] If the product from xylene was dried directly under vacuum, it melted at 227–241°, with preliminary shrinking.

Anal.[31] Calcd for $C_{18}H_{15}Al$: Al, 10.41. Found: Al, 10.18.

The product reacted readily with ethyl ether to yield colorless needles of triphenylaluminum etherate, mp 129–129.5°, from ethyl ether.[32] Treatment of triphenylaluminum with tetrahydrofuran and with dioxane led to the exothermic formation of etherates also; a solid complex with cineole was formed upon heating.

The infrared spectrum of triphenylaluminum suspended in mineral oil displayed prominent bands at 650 (m), 670 (w), 690 (s), 700 (s, b), 730 (s), 1000 (s), 1025 (m), 1055 (s), 1090 (s, b), 1200 (m), 1255 (m), 1430 (s), 1570 (w), and 1585 (m) cm^{-1}. The far-infrared spectrum showed bands at 325 (s), 345 (w), 465 (m, b), and 475 (s, v, b). The etherate absorbed at 685, 705, 730, 775, 840, 895, 1000, 1025, 1090, 1155, 1200, 1255, 1400, 1430, and 1580 cm^{-1}.

Diphenylaluminum Chloride. Smaller amounts of this chloride could be prepared by mixing the triphenylaluminum and anhydrous aluminum chloride in a 2:1 formula weight ratio directly in a one-piece distillation apparatus.[33] After the reaction melt was held at 200° for 4 hr, distillation afforded colorless diphenylaluminum chloride, bp 150–155° (0.15 mm). However, a better yield in larger runs was realized by the following procedure.

A yellow melt of 9.0 g (0.035 mole) of triphenylaluminum and 2.32 g (0.0174 mole) of anhydrous aluminum chloride (Baker reagent with 0.005% iron) was held at 185–190° for 6 hr. The cooled reaction mass was dissolved in benzene and the solution filtered through a glass frit of medium porosity (10–15 μ). Excess benzene was removed by distillation and dry heptane was distilled into the benzene filtrate to achieve a slight turbidity. Upon cooling the product separated as colorless needles, mp 135–148°, 9.8 g (86% yield). Recrystallization from a benzene-pentane pair provided pure diphenylaluminum chloride, mp 148–150° (pink at 137°, deep red melt at 150°).

Anal. Calcd for $C_{12}H_{10}AlCl$: Al, 12.45; Cl, 16.37. Found: Al, 12.41; Cl, 16.28 (Volhard).

The infrared spectrum in mineral oil suspension exhibited characteristic bands at 670 (m), 695 (s), 705 (s), 735 (s), 1000 (s), 1090 (s), 1100 (s), 1175 (w), 1200 (w), 1260 (m), 1310 (w), 1345 (w), 1430 (s), 1570 (w), and 1590 (m) cm^{-1}.

Attempted Isolation of Diphenylaluminum Hydride. The preparation of this hydride (unknown at the time of the following experiment) was achieved in solution according to the method of Ziegler and co-workers.[34] Unfortunately, however, the reaction was too slow in benzene, and disproportionation vitiated its isolation from ether solution.

A solution of 7.0 g (0.032 mole) of diphenylaluminum chloride in 125 ml of dry ether was stirred under reflux with 0.27 g (0.034 mole) of lithium hydride (95–98%) for 4 days. The cooled mixture was filtered from the copious gray precipitate and the ethereal filtrate (F_1) evaporated to dryness. The resulting solid was treated with benzene and filtered through a porous glass frit (solid S_1 and filtrate F_2). After removal of benzene, filtrate F_2 left a solid S_2, which was recrystallized several times from ethyl ether. Colorless needles melting at 128–129° were obtained. By its infrared spectrum and a mixture melting point this substance proved to be triphenylaluminum etherate.

Solid S_1 was free of halogen (Volhard) and of lithium (flame test). Hydrolysis gave a copious gas evolution. Its infrared spectrum displayed a broad Al–H absorption centered at 1780 cm^{-1},[35] and bands characteristic of the phenyl group at 1430 and 1630 cm^{-1}. The wide melting range of 113–123° was improved by recrystallization from ethyl ether. Each time, however, an insoluble gray solid S_3 had to be filtered off (filtrate F_3). Solid S_3 was an Al–H material, since it evolved gas upon hydrolysis. Filtrate F_3 gave solids whose melting range and infrared spectra gradually approached those of $(C_6H_5)_3Al\cdot O(C_2H_5)_2$. The prominent Al–H band in the 1800-cm^{-1} region became weaker with each recrystallization and filtration.

Reaction of Diphenylacetylene with Triphenylaluminum. A. Iodinolysis. A mixture of 3.56 g (0.02 mole) of diphenylacetylene,[36] 5.16 g (0.02 mole) of triphenylaluminum, and 10 ml of anhydrous diphenyl ether was heated to 200° to attain solution. The solution gradually became orange, and a volatile liquid could be condensed out into an attached cold trap, as the bath temperature was maintained at 200 ± 2°. (The liquid was shown to be benzene by spectral measurements and by conversion to *m*-dinitrobenzene, mp 88.5–90°.) During a 12-hr heating period the golden solution finally solidified. The cooled solid mass was diluted with dry benzene, and slowly a solution of 15.3 g (0.0601 mole) of iodine in benzene was introduced. After the exothermic reaction had subsided, the iodine had been almost all consumed. The benzene solution was poured into ice–water and the organic layer was separated. After washing with 10% sodium bisulfite and sodium bicarbonate solutions, the organic extracts were dried over anhydrous calcium sulfate. The crude yellow solid remaining after evaporation of solvent was recrystallized from an ethanol-benzene pair. The pale yellow cubic crystals weighed 7.3 g (72%) and melted at 169–172°. An analytical sample melted at 174–175°.

Anal. Calcd for $C_{20}H_{14}I_2$: C, 47.27; H, 2.78; I, 49.95. Found: C, 47.26; H, 2.90; I, 49.80.

1-Iodo-*cis*-1,2-diphenyl-2-(2-iodophenyl)ethene (*cf.* below for structure proof) displayed the following infrared bands: 640 (m), 670 (m), 690 (s), 720 (m), 738 (s), 768 (s), 790 (m), 841 (m), 958 (s), 1015 (s), 1030 (m), 1080 (m), 1160 (m), 1225 (m), 1450 (s), 1490 (m), 1580 (m), and 1600 (m) cm^{-1}.

B. Hydrolysis. The reaction was conducted on one-half the amounts given above for 6 hr at 200–205°. The product was diluted with benzene and cautiously treated with water. The slurry was then poured into 6 *N* hydrochloric acid and worked up in the foregoing manner. After removal of the organic solvent, the residue was distilled at 0.5 mm to provide 1.75 g (68%) of triphenylethylene, bp 154–156°. Upon chilling, the viscous liquid crystallized. Recrystallization from ethanol formed acicular needles, mp 67.5–69°. Mixture melting point and spectral comparisons established its identity.

C. Structure Proof of Iodo Derivative. A solution of 3.00 g (0.059 mole, assumed) of the foregoing iodo compound in 30 ml of dry benzene and 20 ml of dry ether was prepared under nitrogen at 25°. With stirring 5.9 ml of 2.0 *N* *n*-butyllithium (0.012 mole) solution in hexane–heptane was added over a 10-min period. After an additional 10 min of stirring, Gilman's color test II indicated the absence of *n*-butyllithium.[37] The solution was poured onto a slurry of solid carbon dioxide in anhydrous ether. Upon warming to room temperature the ether was extracted with portions of 5% potassium hydroxide solution. The aqueous extracts were boiled to expel ether, cooled, and acidified with dilute hydrochloric acid. The precipitated acid weighed 0.82 g (40%, mp 199–201° dec). Recrystallizations from ethanol and from 1-propanol furnished colorless granules of *cis*-1,2-diphenyl-2-(2-carboxyphenyl)propenoic acid (*cf.* below), mp 208–210° dec.

Anal. Calcd for $C_{22}H_{16}O_4$: equiv wt, 172.2. Found: equiv wt, 173.5.

Removal of solvent from the ether layer left about 2.6 g of red, viscous oil. Repeated recrystallization from petroleum ether (bp 65–75°) eventually gave fine red needles, mp 151.5–153°. Mixture melting point and infrared spectral comparison showed this to be 2,3-diphenylindone.[38]

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[31] H. L. Watts, *Anal. Chem.*, 30, 967 (1958).

[32] G. Wittig and D. Wittenberg, *Ann.*, **606**, 13 (1957).

[33] See ref 26b, Appendix.

[34] Subsequent to this work, Surtees[15] has prepared diphenylaluminum hydride (mp 156–157.5°) from triphenylaluminum and aluminum hydride etherate in benzene.

[35] G. Schomberg and E. G. Hoffmann, *Z. Elektrochem.*, **61**, 1110 (1957), assign the Al–H stretch to the 1675–1900-cm^{-1} region of the infrared spectrum.

[36] A. C. Cope, D. S. Smith, and R. J. Cotter, *Org. Syn.*, **34**, 42 (1954).

[37] H. Gilman and J. Swiss, *J. Am. Chem. Soc.*, **62**, 1847 (1940).

[38] C. F. Koelsch, *ibid.*, **54**, 2045 (1932).

Pyrolysis of the diacid with barium hydroxide and work-up with aqueous hydrochloric acid left a red precipitate. Recrystallization of this solid provided red needles, mp 152–153°, which also proved to be 2,3-diphenylindone.

D. Isolation of 1,2,3-Triphenylbenzaluminole. A mixture of 2.67 g (0.015 mole) of tolane, 3.87 g (0.015 mole) of triphenylaluminum, and 7.5 ml of dry diphenyl ether was heated at 200° for 8 hr. Dry benzene (25 ml) was distilled into the reaction suspension and the liquid phase was decanted. The remaining light yellow solid was washed five times with benzene and then was dried over night under high vacuum. A hydrolyzed sample was found to contain 7.26% of aluminum. Attempted recrystallization from toluene was not completely successsful; also all solid did not dissolve. The insoluble residue was combined with the previous solid (7.26% Al), and this light yellow solid was washed with benzene repeatedly. A melting point of 285–288°, slight softening below 285°, was observed. Aluminum analyses gave constant values, even after further washing with benzene and vacuum drying.

Anal. Calcd for $C_{26}H_{19}Al$: Al, 7.53. Found: Al, 7.28 ± 0.04 (five analyses). A portion of this 1,2,3-triphenylbenzaluminole was treated with an excess of iodine in dry benzene and worked up according to the procedure of part A. Iodobenzene was detected in the volatile fraction. The same solid fraction remaining after evaporation of the organic liquid was triturated with petroleum ether (bp 30–60°) and the resulting solid recrystallized from ligroin (bp 90-100°). The pale yellow solid melted at 169–171°. Further recrystallization provided the above-mentioned diiodo compound, mp 174–175°.

Another portion of the heterocycle was dissolved in 175 ml of anhydrous diethyl ether. Upon partial evaporation of the ether, colorless, cubic crystals separated from the solution, mp 121–126°. This etherate decomposed upon heating since above 126° crystals began to regrow. At 135° the mass resolidified completely. Consequently, a sample of the etherate was heated for 12 hr at 150° and for 2 hr at 175° under 0.01 mm pressure. The resulting pale yellow solid melted at 283–286° (preliminary softening).

Anal. Calcd for $C_{26}H_{19}Al$: Al, 7.53. Found: Al, 7.40.

The infrared spectrum exhibited peaks at 700 (s) (C_6H_5), 740 (s) (C_6H_5Al), 770 (m), 782 (m), 800 (m), 977 (m), 1020 (m), 1090 (m), 1300 (m), 1435 (s), 1445 (s), 1580 (s) (C=C conjugated with C_6H_5), and 1600 (m) cm^{-1}.

Reaction of 1-Phenylpropyne with Triphenylaluminum. Gentle warming of a mixture of 14.8 g (0.057 mole) of triphenylaluminum and 6.08 g (0.058 mole) of 1-phenylpropyne caused an exothermic reaction. Thereupon the yellow mass was heated for 5 hr at 60° and for 7 hr at 90°. As the solidified mass was then heated at 150–160° for 3 hr, the product remelted and benzene was evolved. The cooled reaction product was dissolved in pentane and then was hydrolyzed. The glc analysis of the hydrolyzed products on a 3-ft column of 5% silicon gum rubber on firebrick revealed two companion peaks in a ratio of 1:36. The first peak was identified as 1,1-diphenylpropene by comparison of its nmr spectrum and glc retention time with an authentic sample.[39] The second component was isolated by recrystallizing the crude reaction product from ethanol. Colorless plates of *trans*-1,2-diphenylpropene, mp 81–85°, were obtained.

Anal. Calcd for $C_{15}H_{14}$: C, 92.76; H, 7.31. Found: C, 92.82; H, 7.25.

Reaction of 1,3,3,3-Tetraphenylpropyne with Triphenylaluminum. To learn whether sterically hindered alkynes would undergo this addition, tetraphenylpropyne was investigated. A solution of 5.34 g (0.016 mole) of the alkyne and 4.0 g (0.016 mole) of triphenylaluminum in 35 ml of dry toluene was held at 100° for 24 hr. Usual hydrolytic work-up gave a 98% recovery of pure alkyne.

In a second attempt the same quantities of reactants were heated without solvent at 180–250° for 3 hr. The dark brown melt evolved benzene during this time. Hydrolytic work-up in benzene gave an oily solid, after evaporation of the dried organic layer. After several unsuccessful recrystallization attempts, the product was chromatographed on a column of alumina and eluted with a 10:1 mixture of petroleum ether (bp 30–60°) and benzene. The first fractions yielded a solid A which crystallized from absolute ethanol as colorless needles, mp 166.5–167°.

Anal. Calcd for $C_{33}H_{26}$: C, 93.80; H, 6.20. Found: C, 93.66; H, 6.21.

Successive chromatographic fractions were united and recrystallized from glacial acetic acid. Colorless cubic crystals of solid B, mp 136–137°, were obtained.

Anal. Calcd for $C_{33}H_{26}$: C, 93.80; H, 6.20. Found: C, 93.60; H, 6.29

The infrared spectra of solids A and B are similar, but distinguishable. Noteworthy are the bands at 720 (B) and 730 (A) cm^{-1}, assignable to vinyl C–H out-of-plane deformations. Their relatively simple nmr spectra tend to rule out the possibility of disubstituted benzene units: (solid B) phenyl peaks at δ 6.57, 7.00, and 7.07, vinyl peak at 6.82; (solid A) phenyl peaks at 7.21 and 7.25, vinyl peak at 7.07 ppm. Evidence indicates these solids are the expected pentaphenylpropenes. From limited nmr and melting point correlations, solid A is probably 1,1,3,3,3-pentaphenylpropene and solid B is *trans*-1,2-diphenyl-3,3,3-triphenylpropene. The single nmr phenyl signal of 1,3,3,3-tetraphenylpropyne at 7.1 suggests that the closely grouped phenyl peaks of solid A might stem from a related structure.

Synthesis of 5-Phenyldibenzaluminole. A. Preparation of 2-Biphenylyldiphenylaluminum. A suspension of 0.81 g (0.12 g-atom) of lithium pieces in 30 ml of anhydrous diethyl ether at reflux was treated with 4.5 g (0.019 mole) of 2-bromobiphenyl in 60 ml of solvent. The rate of addition was adjusted to maintain spontaneous reflux (95 min). After an additional reflux period of 60 min, the dark red-brown solution was poured into a suspension of Dry Ice in ether. Usual work-up yielded 97% of 2-phenylbenzoic acid, mp 108–110° (lit.[40] 114°).

A solution of 2-biphenylyllithium in diethyl ether was prepared according to the foregoing procedure. The solution was filtered to remove the excess lithium metal, and the solvent was then evaporated under reduced pressure. The tan-colored lithium reagent was suspended in 30 ml of dry toluene and then treated with a solution of 4.05 g (0.019 mole) of diphenylaluminum chloride in 30 ml of toluene. The tan color was discharged promptly and a copious white precipitate was formed. Complete reaction was ensured by allowing the mixture to stir for 3 hr at 60°. The cooled suspension was filtered through a sintered glass frit of medium porosity to give a clear, light yellow solution. Evaporation of volatile organic material by warming under reduced pressure resulted in a viscous yellow oil. This 2-biphenylyldiphenylaluminum would not crystallize, but a fair purity was assured by the fact that a test portion was found to be free of ionic halogen.

B. Cyclization of 2-Biphenylyldiphenylaluminum and Iodinolysis. The foregoing noncrystallizable oil was brought up to 200° over a 1-hr period under reduced pressure, in order to remove solvated ether. The liquid mass was held at 200–215° for 8 hr. Initially benzene was evolved as well as some biphenyl; toward the end the mass finally solidified. No melting occurred when the mass was heated to 240° briefly. After an additional 10 hr at 150°, the product was treated with excess iodine in hexane–toluene solution. The hydrolyzed organic layer was washed successively with a 10% sodium bisulfite solution, a 10% sodium bicarbonate solution, and water. Removal of solvent yielded 2.95 g of colorless solid, mp 96–100° (39%). Recrystallization from absolute ethanol gave 2.05 g (27%) of 2,2′-diiodobiphenyl, mp 108.5–109.5°, as proved by mixture melting point and spectral comparison with an authentic sample.

C. Isolation of 5-Phenyldibenzaluminole. In another preparation 2-biphenylyllithium (prepared from 4.7 g (0.024 mole) of 2-bromobiphenyl and 1.0 g (0.144 g-atom) of lithium in 45 ml of anhydrous diethyl ether) was filtered and analyzed for aryllithium. A slight deficiency in equivalents of diphenylaluminum chloride was employed (4.05 g, 0.0188 mole). The toluene suspension of reagents was heated under reflux for 2 hr and then stirred at room temperature for 12 hr. Filtration through a sintered disk and removal of toluene gave a yellow oil free of halogen. Heating of this 2-biphenylyldiphenylaluminum at 200–250° for 18 hr caused the evolution of benzene and biphenyl until finally the residual mass solidified. The cooled solid product was washed with hexane several times to remove any biphenyl. Dissolution in warm xylene, filtration, and concentration of the xylene solution yielded colorless cubic crystals. After several recrystallizations from xylene the product melted at 225–230° (slight preliminary softening). Recrystallization from diethyl ether yielded a white, microcrystalline powder (note: triphenylaluminum etherate crystallizes easily as needles), mp 132–134°. The melt had a few suspended particles above 134°, and at 190° some solid reappeared. For removal of solvated ether this substance was heated up to 180° over a 1-day

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[39] D. J. Cram and F. A. A. Elhafez, *J. Am. Chem. Soc.*, 74, 5828 (1952).

[40] H. Gilman and K. Oita, *J. Org. Chem.*, 20, 864 (1955).

period under a pressure of 0.02 mm and held there for 1 day. Some slight sublimation was noted.

Anal. Calcd for $C_{18}H_{13}Al$: Al, 10.52. Found: Al, 10.12.

A portion of the etherate was treated with iodine in hexane. Usual work-up yielded a semisolid organic residue. By infrared spectral comparison, the supernatant liquid was shown to be mainly iodobenzene and 2,2′-diiodobiphenyl, with some traces of 2-iodobiphenyl. The isolated solid was principally 2,2′-diiodobiphenyl (mp 109–109.5°, from ethanol). The detection of 2′-iodobiphenyl points to the possibility of some uncyclized 2-biphenylyldiphenylaluminum (8.06%). In other runs conducted at 200° for shorter periods, the aluminum analyses ranged from 8.0 to 8.8%. Alternatively, the presence of some 5-(2-biphenylyl)dibenzaluminole (8.11%) might explain the origin of the 2-iodobiphenyl and the low analyses in certain cases.

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Electron Transfer through Organic Structural Units. III. Chain Branching and Nitro and Thia Substitution in Bridging Groups for Oxidation–Reduction Reactions[1]

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Abstract: The reactions of 30 carboxylatopentaamminecobalt(III) complexes (containing a variety of straight-chain, branched-chain, and aromatic ligands) with Cr^{2+} have been studied. A number of the acyclic ligands have alkylmercapto substituents, whereas most of the aromatic ligands are nitro derivatives. The specific rates for reduction of the acyclic derivatives have been found to be much more sensitive to steric crowding than are benzoato derivatives; α substitution is particularly effective in retarding reduction, the triethylacetato complex (VII, k = 0.0024 l. mole^{-1} sec^{-1}) being more resistant to reduction than any other carboxylato complex reported. The α-NH_3^+ substituent, as found in the complexes of the amino acids at low pH values, is also strongly rate retarding. The moderate increases in reduction rates observed when α,β unsaturation is introduced into acyclic ligands also appears to be steric, rather than electronic, in origin, and no special effects are noted on incorporating a second double bond in conjugation with the first (XVII). Conjugative enhancement of reduction, sometimes attributed to remote attack, is, as in earlier studies, confined to complexes derived from readily reducible ligands. Rate enhancement (from five- to fiftyfold) resulting from substitution of a sulfur atom α or β to the coordinated carboxyl appears to be general. Reductions of the nitro derivatives, which involve changes not only at coordinated cobalt, but also at the NO_2 groups, are complex and have not been separated into clean-cut kinetic steps. The very fast reduction of the nitro group of the *o*-nitrobenzoato complex is accompanied by some "leak through" of reducing capacity, resulting in a much more rapid reduction of Co(III) than would result from preliminary reduction of NO_2 to an amino group. With the *p*-nitro complex in 1.2 *M* $HClO_4$, release of Co(II) is delayed until 1.5–2.0 equiv of Cr^{2+} have been added (but, nevertheless, represents a very rapid reduction), whereas with the *m*-nitro isomer, 4 equiv of Cr^{2+} must be added before Co^{2+} appears. Leak through during the fast stages in these reactions is taken as a strong indication of reduction of coordinated Co(III) *via* remote attack at the nitro group or at a group derived from it by reduction. The nitro group (in the *ortho* sequence) and the nitroso group (in the *para* sequence) appear to be the principal "bridging" substituents. In addition, the reduction of the 3-nitro-4-methylbenzoato complex appears to involve a small degree of "*meta*-oriented remote attack" at the nitroso stage. The striking spectral changes occurring during the early stages of these reductions are considered. Evidence is cited (in the *p*-nitro reduction) for an intensely colored Cr(III)-bound nitro radical cation lying apart from the principal reduction sequence and also for a nitroso radical cation; both of these are observed in 1.2 *M* acid, but are destroyed in 0.024 *M* acid.

The specific rates at which pentaamminecobalt(III) complexes containing organic ligands are reduced with Cr^{2+} cover a range of over nine powers of ten when the structure of the organic group is suitably modified. Earlier research in this area[2,3] touched upon the following points, which probably involve less striking rate differences, but which, nevertheless, appear to warrant further investigation. (a) Although the reductions of benzoatopentaamminecobalt(III) complexes were found to be retarded only slightly by steric crowding,[3b] the sensitivity of noncyclic carboxylato complexes to steric effects was not examined. (b) Carbon–carbon unsaturation in the carboxylato ligand was shown to facilitate reduction of Co(III) in cases where the free ligand acid was readily reduced by Cr(II), but the picture with regard to nonreducible olefinic ligands was not clear.[2] (c) Substitution of an α-benzylmercapto group in the acetato complex resulted in a significant (greater than tenfold) acceleration of reduction, whereas α-alkoxy groups are generally slightly retarding.[2] However, only a single sulfur

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[1] This research was sponsored by the Stanford Research Institute Research and Development Fund. Support is gratefully acknowledged.

[2] E. S. Gould, *J. Am. Chem. Soc.*, **87**, 4730 (1965).

[3] (a) R. T. M. Fraser, *ibid.*, **84**, 3436 (1962); (b) E. S. Gould and H. Taube, *ibid.*, **86**, 1318 (1964).