After preparation of this manuscript, there appeared an article[9a] describing the isolation of certain *Pleiocarpa* alkaloids with properties similar to those of aspidofractine (XA). Subsequent correspondence with Prof. H. Schmid (Zürich) and Dr. A. R. Battersby (Bristol) revealed that they had arrived independently at skeleton A for their alkaloids. Direct comparison of kopsinine[9] and XI, kopsinyl alcohol[9] and XII, and synthetic N-formylkopsinine and aspidofractine (X) established the identity of the two series. As reported elsewhere,[10] the British and Swiss investigators have been able to prove chemically the C-21 attachment of the carbomethoxy group; their other studies as well as our results mutually support the novel skeleton A for this group of alkaloids.

All of the substances recorded in this communication gave satisfactory elementary analyses and correct mass spectral molecular ion peaks. We are indebted to the National Institutes of Health (grants 2G-682 and A-4257) and to the Rockefeller Foundation for financial aid, and to Prof. K. Biemann for a stimulating discussion.

[9] (a) W. G. Kump and H. Schmid, *Helv. Chim. Acta*, **44**, 1503 (1961); (b) W. D. Crow and M. Michael, *Australian J. Chem.*, **8**, 129 (1955).

[10] W. D. Kump, D. J. Le Count, A. R. Battersby and H. Schmid, *Helv. Chim. Acta*, **45**, in press (1962).

[11] The contents of this paper were first reported at the Golden Jubilee Phytochemistry Symposium of the University of Hong Kong, September 12, 1961.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD, CALIFORNIA
CARL DJERASSI[11]
T. GEORGE
N. FINCH
H. F. LODISH
H. BUDZIKIEWICZ

INSTITUTO DE QUIMICA AGRICOLA
MINISTERIO DA AGRICULTURA
RIO DE JANEIRO, BRAZIL
B. GILBERT

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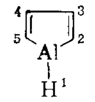
THE NOVEL SYNTHESIS OF ALUMINOLES BY THE METALATIVE CYCLIZATION OF UNSATURATED ORGANOALUMINUM COMPOUNDS

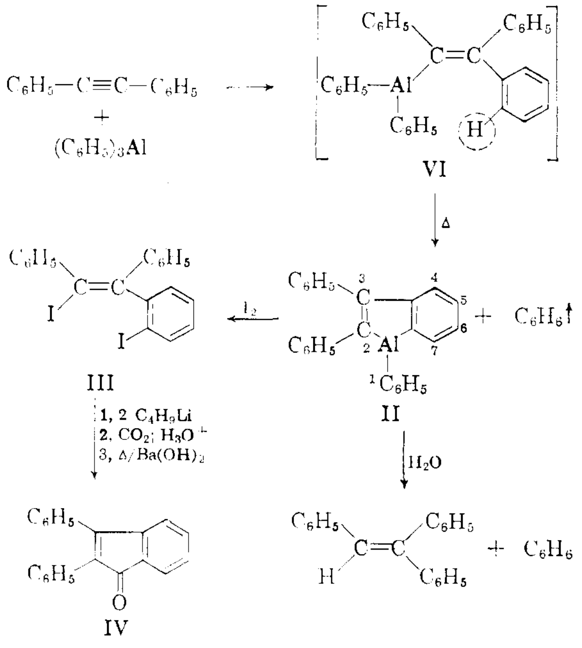
Sir:

We wish to report the novel cyclization of certain unsaturated organoaluminum compounds, leading to the formation of the unsaturated, five-membered aluminum heterocyclic system shown in I. Representing the first reported example of an aluminum heterocycle, I may be designated as the aluminole nucleus.[1] Interaction of triphenylaluminum with diphenylacetylene in a melt at 200° led to the evolution of benzene (identified as its *m*-dinitro derivative) and the deposition of a yellow solid (II). The reaction proceeded more smoothly in phenyl ether solution. After washing II with benzene and recrystallizing from toluene the pale yellow solid II melted at 285–288°.[2] *Anal.* Calcd. for $C_{26}H_{19}Al$: Al, 7.53. Found: Al, 7.40. Upon hydrolysis II yielded benzene and triphenylethylene. Treatment of II with iodine provided iodobenzene and a pale yellow, iodine-containing solid III, m.p. 174–175°. The latter product was shown to be 1-iodo-*cis*-1,2-diphenyl-2-(2-iodophenyl)ethene by the results of analysis (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) and its transformation into the known 2,3-diphenylindone (IV).[3] The latter conversion was effected by treating III with two equivalents of *n*-butyllithium in ether to exchange the iodine for lithium.[4] Carbonation of the resulting dilithio compound produced the diacid V, 3-(2-carboxyphenyl)-*cis*-2,3-diphenylpropenoic acid, m.p. 208–210° (*Anal.* Calcd. for $C_{22}H_{16}O_4$: neut. equiv., 172. Found: neut. equiv., 173) and some IV. Heating the diacid V with $Ba(OH)_2$ also afforded IV (mixture m.p. with authentic 2,3-diphenylindone undepressed). This therefore proves both the structure of III and the *cis*-relationship of the two phenyl groups about the ethylenic linkage. By heating diphenylacetylene with triphenylaluminum in phenyl ether solution at 200° and then treating with iodine pure yields of 65% of this interesting and otherwise difficultly accessible diiodo compound have been achieved.[5]



I

Thus the course of the formation and structure-proof of 1,2,3-triphenylbenzaluminole (II) can be viewed as shown



Although the adduct VI has not been isolated as yet, there can be no doubt that reactive aryl organometallics are able to add across the C≡C linkage. We have observed, for example, that the heating of diphenylacetylene with phenyllithium in ether solution and subsequent carbonation yields

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[1] The authors are grateful for the guidance of Dr. Leonard T. Capell of Chemical Abstracts Service in the choice of suitable nomenclature for this novel system.

[2] Due to the sensitivity of organoaluminum compounds to oxidation and hydrolysis all operations were conducted under an atmosphere of dry, oxygen-free nitrogen.

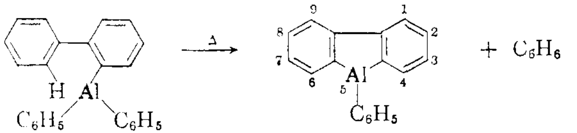
[3] C. F. Koelsch, *J. Am. Chem. Soc.*, **54**, 2045 (1932).

[4] *Cf.* R. G. Jones and H. Gilman, "Organic Reactions," John Wiley and Son, Inc., New York, N. Y., Chap. 7, 1951.

[5] Utilization of such an appropriate intermediate for the synthesis of the benzocyclobutadiene system is under consideration in this Laboratory.

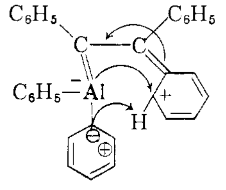
triphenylacrylic acid. Moreover, the metalative cyclization of VI to form the aluminole II gains support in our finding that certain *pseudoacidic hydrocarbons* such as fluorene and triphenylmethane are metalated by triphenylaluminum at 200° with the evolution of benzene. This leads us to postulate that the encircled hydrogen in VI has *pseudoacid character*.[6]

To test the validity of the postulated cyclization (VI → II) *o*-biphenylyldiphenylaluminum was prepared from *o*-biphenylyllithium (VII) and diphenylaluminum chloride[7] and then heated at 200°. After benzene evolution slackened, the resulting solid was recrystallized from xylene to yield colorless 5-phenyldibenzaluminole (VIII), m.p. 225–230°; *Anal.* Calcd. for $C_{18}H_{13}Al$: Al, 10.52. Found: Al, 10.12. Treatment of VIII with iodine gave iodobenzene and 2,2'-diiodobiphenyl.



VII VIII

In the light of the properties of certain α,β-unsaturated aluminum compounds[8] it is suggested that this novel cyclization of such α,β-unsaturated systems as VI and VII can be ascribed to the π-electron withdrawal from the vinylogous β-position (*ortho*) by the available aluminum orbital. Such π-electron polarization would enhance both the "acidic" character of the *ortho* proton of the benzene ring and the nucleophilic character of the attacking phenyl group (IX).[9]



IX

Further chemical and physical consequences of electronic effects in unsaturated organoaluminum compounds are receiving our attention.

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MICHIGAN JOHN J. EISCH
ANN ARBOR, MICHIGAN WILLIAM C. KASKA

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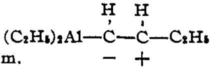
[6] Previous workers have been unable to metalate active hydrogen compounds such as 1-alkynes (G. Wilke and H. Müller, *Ann.*, **629**, 222 (1960)) or dibenzofuran (H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **67**, 1033 (1945)) with aluminum *alkyls*. The latter authors did obtain a 1% yield of dibenzofuran-2-carboxylic acid by heating dibenzofuran with ethylaluminum sesquiiodide for 72 hr. at 210° and then carbonating the product.

[7] Diphenylaluminum chloride was prepared from triphenylaluminum and aluminum chloride, m.p. 145–148°; *Anal.* Calcd. for $C_{12}H_{10}AlCl$: Al, 12.45; Cl, 16.37. Found: Al, 12.41; Cl, 16.28.

[8] *Cf.* G. Wilke and H. Müller, *Ann.*, **629**, 222 (1960), for physical data supporting the formulation  $(C_2H_5)_2Al-\underset{-}{\overset{H}{C}}-\underset{+}{\overset{H}{C}}-C_2H_5$, for the π-bond in diethyl-1-butenylaluminum.

[9] Our current studies on the n.m.r. spectra of arylaluminum systems tend to support such π-unshielding of *ortho* (β-vinyl) protons.

THE TRIPLET STATE OF BENZENE[1]

Sir:

The first excited triplet state of benzene has been identified through emission from a glassy matrix and possibly through weak absorption from the ground state.[2,3] The electronic energy term is probably about 3.6 ev. whereas the electronic term of the first excited singlet state is 4.7 ev. Fluorescence from benzene has been observed and self quenching is small.[4]

Biacetyl when illuminated at 4358 Å. and at 4050 Å. both fluoresces and phosphoresces. The efficiency of the latter is about 0.15,[5] a value which is also reached at 3650 Å. at relatively high pressures. The ratio of phosphorescence to fluorescence at room temperature is about 60:1.[6] When illuminated at 3130 Å. and shorter wave lengths there is very little emission from biacetyl[7] but there is dissociation.[8]

The dissociation energy of biacetyl is not known very exactly but should be at least 3 ev.

Benzene in the excited singlet state can provide enough energy upon collision either to dissociate biacetyl, to excite it to the second excited electron state, or to excite it to the first excited electronic state provided sufficient energy appears as vibration or kinetic energy. Benzene in the triplet state can provide enough energy to excite the first excited singlet or triplet states of biacetyl but has barely enough energy to dissociate the biacetyl.

It has been shown to be probable that biacetyl excited to the first singlet state undergoes an inter-system cross-over to the triplet state to the extent of 99% or more[9] even though the phosphorescence efficiency is only 0.15. Hence about 85% of these triplet state molecules revert to the ground state without either emission of dissociation at room temperature.

The fluorescence efficiency of pure benzene vapor has been measured at pressures of 2 mm. and higher. A plot of $1/Q$ (the inverse of the absolute fluorescence efficiency) *vs.* concentration gives a straight line with an intercept of 0.258. In other words, extrapolation to zero pressure shows that three-quarters of the molecules still fail to fluoresce although it is known that they do not dissociate. On the other hand the radiative life measured by Donovan and Duncan[10] is 0.59×10^{-6} sec. and agrees well with the calculated radiative life.

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[1] This work was supported by Contract Number AF49(638)-679 with the Office of Air Research.

[2] See R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956), who has given references to earlier work.

[3] J. von Kowalski, *Physik. Z.*, **12**, 956 (1911); G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 236 (1944); D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949); H. Sponer, Y. Kanda and L. A. Blackwell, *Spectrochim. Acta*, **16**, 1135 (1960); Y. Kanda and H. Shimada, *ibid.*, **17**, 7 (1961).

[4] P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publishers, New York, N. Y., 1949, p. 265.

[5] G. M. Almy and P. R. Gillette, *J. Chem. Phys.*, **11**, 188 (1943).

[6] H. Okabe and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **79**, 801 (1957).

[7] *Cf.* J. Heicklen, *ibid.*, **81**, 3863 (1959).

[8] W. E. Bell and F. E. Blacet, *ibid.*, **76**, 5332 (1954).

[9] H. L. J. Bäckström and K. Sandros, *Acta. Chem. Scand.*, **14**, 48 (1960).

[10] J. W. Donovan and A. B. F. Duncan, *J. Chem. Phys.*, **35**, 1389 (1961).