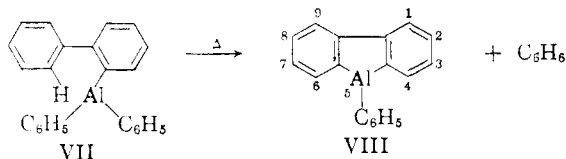
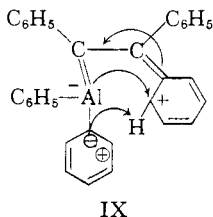


triphenylacrylic acid. Moreover, the metalative cyclization of VI to form the aluminole II gains support in our finding that certain *pseudoacidic hydrocarbons* such as fluorene and triphenylmethane are metalated by triphenylaluminum at 200° with the evolution of benzene. This leads us to postulate that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

To test the validity of the postulated cyclization (VI → II) *o*-biphenyldiphenylaluminum was prepared from *o*-biphenyllithium (VII) and diphenylaluminum chloride⁷ 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 C₁₈H₁₃Al: Al, 10.52. Found: Al, 10.12. Treatment of VIII with iodine gave iodobenzene and 2,2'-diiodobiphenyl.



In the light of the properties of certain α,β -unsaturated aluminum compounds⁸ 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



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

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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 sesquiodide 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 C₁₂H₁₀AlCl: 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 $(C_2H_5)_2Al-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-C_2H_5$, 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 BENZENE¹

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 e.v. whereas the electronic term of the first excited singlet state is 4.7 e.v. 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 biacetyl⁷ but there is dissociation.⁸

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

Benzene in the excited singlet state can provide enough energy upon collision either to dissociate biacetyl, to excite it to the second excited electronic 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 more⁹ 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 or 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 Duncan¹⁰ is 0.59×10^{-6} sec. and agrees well with the calculated radiative life.

(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. Fringsheim, "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.*, **85**, 1389 (1961).

Since the observed life should be the reciprocal of the sum of all first order rate constants it is at present impossible to tell what rate constant to use for the self-quenching of benzene vapor fluorescence. The effective cross section will be either about 0.04 or 0.15×10^{-16} cm.² depending on the assumption made.

If a mixture of benzene and biacetyl vapors is irradiated at 2537 Å. there is dissociation of the biacetyl sensitized by the benzene with a quantum yield of about 0.06, corresponding roughly to that in pure biacetyl at 3130 Å.⁸ Thus, as would be expected, not all of the electronic energy of the benzene is used to activate the biacetyl. There is also strong emission from the biacetyl and the ratio of phosphorescence to fluorescence is very high and may be infinity. This strongly suggests the presence of triplet state benzene molecules which transfer energy to normal biacetyl to produce excited triplet state molecules.

In a mixture of 20 mm. of benzene and 0.1 mm. of biacetyl the efficiency of the phosphorescent emission of the biacetyl is about 0.12. The benzene fluorescence efficiency under these conditions is about 0.22, *i.e.*, 78% of the absorbing benzene molecules do not fluoresce. If now one assumes that every benzene molecule which does not fluoresce goes to the triplet state by an intersystem cross-over and then is deactivated by biacetyl to produce triplet state biacetyl molecules the fraction of these which should phosphoresce is 0.15.⁵ Thus the expected phosphorescence efficiency from the biacetyl would be $0.78 \times 0.15 = 0.12$, in far better agreement with the found value than the data warrant.

The rate of the process benzene (triplet) + biacetyl = biacetyl (triplet) + benzene may not be estimated in the absence of knowledge of the mean life of the triplet state of benzene. Unless it is much less than a second the effective cross section for this reaction would be extremely small. If it is about the same as for other aromatic hydrocarbons¹¹ the effective cross section is reasonable.

The data strongly suggest, therefore, that in the gas phase every benzene molecule which absorbs at 2537 Å. either fluoresces or crosses over to a triplet state. The fates of the triplet state molecules are at present unknown in detail. They may do one of several things: (a) cross over to the ground state with ultimate loss of vibration energy by collision; (b) be destroyed on the walls; (c) undergo reaction to an intermediate which reverts ultimately to normal benzene. More work on this subject is needed.

(11) G. Porter and F. J. Wright, *Trans. Faraday Soc.*, **51**, 1205 (1955).

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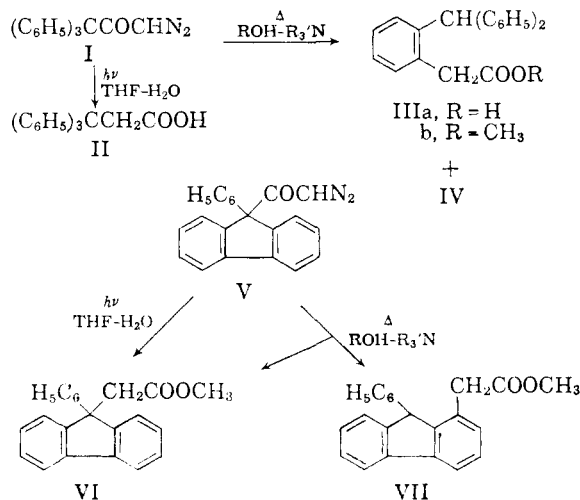
ABNORMAL ACIDS FROM THE ARNDT-EISTERT SYNTHESIS

Sir:

Because of brevity, convenience and structural reliability of the product, the Arndt-Eistert syn-

thesis has become the standard method for converting an acid into its higher homolog. Wolff rearrangement of the intermediate diazoketone derived from diazomethane or higher diazohydrocarbons can be made to go satisfactorily in nearly all cases by one of the improved rearrangement procedures,^{1,2,3} often in excellent yield. We are now reporting an example in which this rearrangement not only failed to go normally, but gave abnormal acid derivatives isomeric with the expected product.

Triphenylacetyldiazomethane (I, m.p. 162.5–164.5° dec.; C₂₁H₁₈N₂O, found: C, 80.3; H, 5.12; diazo N, 96% of calcd.), prepared in excellent yield from the acid chloride, failed⁴ to undergo normal rearrangement by the silver oxide-methanol, silver benzoate-triethylamine-methanol,² or even the tertiary amine-high boiling alcohol (at 180°) procedure,¹ which in our hands has never failed otherwise. In all cases in which nitrogen was evolved the product was not the normal rearranged ester, and failed to give the acid II on hydrolysis. With pyridine and benzyl alcohol at 110° and then hydrolysis, I gave 40% of the isomeric acid IIIa (m.p. 207.5–208.5°; C₂₁H₁₈O₂, found: C, 83.65; H, 5.76). The structure of IIIa was established by Arndt-Eistert synthesis from triphenylmethane-*o*-carboxylic acid and preparation from I by a second sequence. Heating I with boron trifluoride



in ether gave 90–100% of 1,1-diphenyl-2-indanone (m.p. 129–130.5°, 120.5–121.5°; $\lambda_{\text{max}}^{\text{EtOH}}$ 262, 267, 276 and 303 m μ , ϵ 1720, 1850, 1630 and 545; $\lambda_{\text{max}}^{\text{CHCl}_3}$ 5.77 μ ; C₂₁H₁₆O, found: C, 88.4; H, 5.91), which was cleaved to IIIa by potassium hydroxide at 190°.

Heating triphenylacetyldiazomethane (I) with 1-hexanol and N-ethylmorpholine, followed by alkaline hydrolysis and esterification, gave 35% of the abnormal methyl ester IIIb (m.p. 79.5–80.5°; C₂₂H₂₀O₂, found: C, 83.4; H, 6.27) and 18% of a second abnormal ester IV (m.p. 178.5–179°;

(1) A. L. Wilds and A. L. Meader, Jr., *J. Org. Chem.*, **13**, 763 (1948).

(2) M. S. Newman and P. F. Beal, *J. Am. Chem. Soc.*, **72**, 5163 (1950).

(3) L. Horner, E. Spietschka and A. Gross, *Ann.*, **573**, 17 (1951).

(4) John Van Den Berghe, Ph.D. Thesis, University of Wisconsin, 1952.