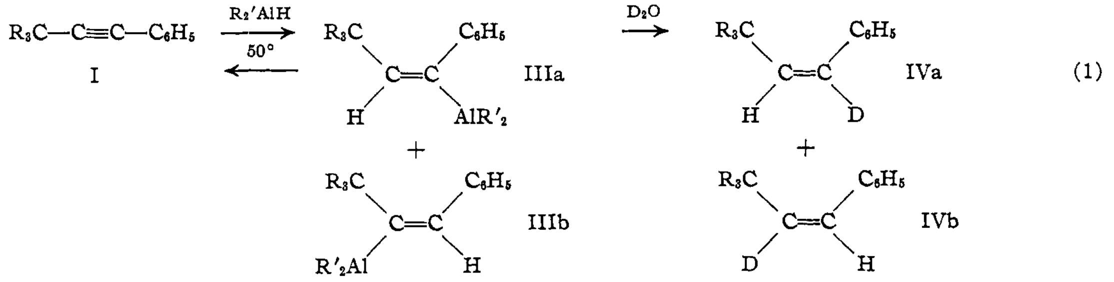
COMMUNICATIONS TO THE EDITOR

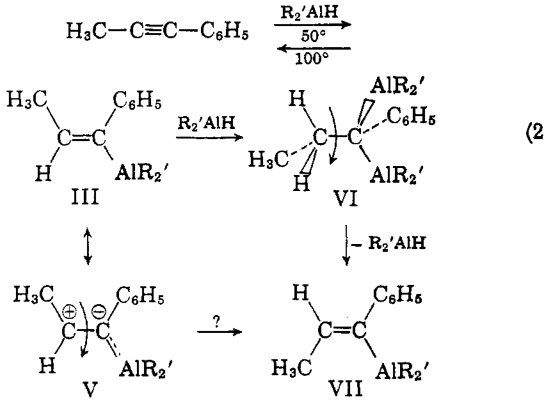
A Novel Carbon–Carbon Bond Scission and the Isomerization Mechanism of Vinylaluminum Compounds[1]

Sir:

Vinylaluminum derivatives, obtainable from the *cis*-addition of dialkylaluminum hydrides to internal alkynes[2] (eq. 1), offer the attractive possibility of studying *cis–trans* isomerization and hence of learning about potential p_π–p_π electronic effects between the aluminum atom and the vinyl group. The electronic character shown in V could promote the isomerization of III into VII (eq. 2) either intramolecularly or intermolecularly,[3] if the vinyl adduct alone can lead to isomerization. On the other hand, if diadducts, such as VI, are formed, the isomerization could pursue an addition–elimination pathway (eq. 2). The present study reports results obtained from the preparation and thermal behavior of vinylaluminum adducts of the 1-phenylpropyne system and thereby adduces unique support for the addition–elimination pathway of such vinylaluminum isomerizations.


(1)

Treatment of 1-phenylpropyne I (R = H) with a slight excess of diisobutylaluminum hydride II ($R' = i\text{-}C_4H_9$) at 50° and hydrolysis of the adducts with deuterium oxide gave 92% of *cis*-β-methylstyrene (IV) which by n.m.r. analysis was shown to be a 4:1 mixture of IVa and IVb. The remaining 8% was a 1:1 mixture of 1-phenylpropane and *cis,cis*-2,3-dimethyl-1,4-diphenylbutadiene-1,3.[4] The absence of *trans*-β-methylstyrene is significant. Indeed, the prolonged heating of adducts IIIa and IIIb at 50° and the reduction in pressure to 0.01 mm. allowed triisobutylaluminum to distil from the system. Despite this disproportionation of III, the hydrolysis of the residual vinylaluminum adduct yielded the same aforementioned hydrocarbons, but again no *trans*-β-methylstyrene. Only under conditions where the adducts III reverted to acetylene I and hydride II was isomerization observed. Thus, heating III at 100° under 0.01 mm. of pressure caused the evolution of 1-phenylpropyne and increased dramatically the amount of 1-phenylpropane and *trans*-β-methylstyrene obtained upon hydrolysis (ratio of *cis*-olefin:propane:*trans*-olefin = 4:4:3). This implies that adducts III decompose and the resulting hydride II enhances the amount of diadduct VI[5] (1-phenylpropane precursor). Since diisobutylaluminum hydride can be eliminated from III at 100°, it is also likely that VI can eliminate hydride at this temperature and hence be responsible for the observed *cis–trans* isomerization (eq. 2)


(2)

Unique support for the isomerization of III into VII as proceeding by an addition–elimination pathway (III → VI → VII), rather than by the unaided thermal isomerization of III (V → VII) comes from the behavior of 1,3,3,3-tetraphenylpropyne (I, $R = C_6H_5$) toward diisobutylaluminum hydride. The novel carbon–carbon bond scission observed in this case is very informative concerning the isomerization mechanism. Heating the acetylene with a sight excess of this hydride in toluene and subsequent hydrolysis of the aluminum products yielded 60% of triphenylmethane, 40% of *cis*-1,3,3,3-tetraphenylpropene[4] and ethylbenzene. No 1,1,1,3-tetraphenylpropane or *trans*-1,3,3,3-tetraphenylpropene could be detected. To establish the bonding sites of aluminum, a reaction run identical with the foregoing was worked up by treatment with deuterium oxide. N.m.r. analysis revealed that the resulting triphenylmethane[4] was deuterated to an extent of >90% on its α-carbon atom. In addition, the *cis*-1,3,3,3-tetraphenylpropene[4] contained 56% of its deuterium on the vinyl carbon atom α to the phenyl and 44% of the deuterium on the other vinyl carbon atom. Therefore, the following cleavage scheme can be formulated. The proposed diadduct intermediate (IX) appears unable to undergo rotation about the central carbon–carbon bond without suffering elimination of $R_2'AlH$ (pathway a, regenerating only the *cis*-adduct) or of $(C_6H_5)_3C—AlR_2'$ (pathway b, leading to carbon–carbon bond scission). Hence, the *trans*-adduct is prevented from forming and isomerization is not observed. As to an isomerization pathway involving the

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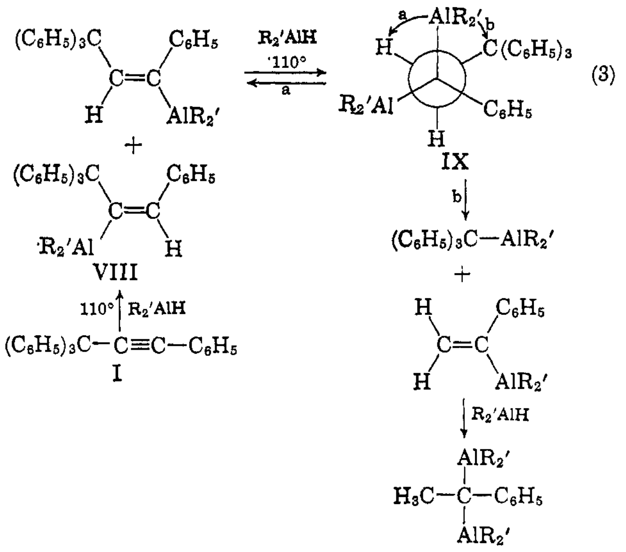
[1] Paper III in the series: Organometallic Compounds of Group III. Previous papers: J. J. Eisch, *J. Am. Chem. Soc.*, **84**, 3605, 3830 (1962).

[2] *Cf.* G. Wilke and H. Müller, *Chem. Ber.*, **89**, 444 (1956); *Ann.*, **629**, 222 (1960), for the preparative utility of such *cis*-reductions.

[3] Since vinylaluminum compounds are highly associated, intermolecular bridging of the vinyl group through the α-carbon atom might also be considered an isomerization pathway (*cf.* G. Wilke and H. Müller, *ibid.*, **629**, 224 (1960)).

[4] The structures of all new compounds encountered in this investigation are supported by acceptable elemental analyses, molecular weight estimates and infrared and n.m.r. spectroscopic data.

[5] The tendency for diadducts of terminal alkynes and dialkylaluminum hydrides to yield geminal dialuminum structures, as shown in VI, is established by the deuteration studies of G. Wilke and H. Müller, *Ann.*, **618**, 267 (1958).



cis-adducts directly (*cf.* V), it can be stated that adducts VIII show no such isomerization tendency at 110°.

Further studies bearing upon the behavior of vinylaluminum compounds and the possible role of p_π–p_π effects are under consideration in this Laboratory.

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Influence of Cumene Hydroperoxide upon the Inhibited Oxidation of Cumene

Sir:

Considerable effort has been devoted to distinguishing between the conflicting oxidation inhibition mechanism of Bolland and ten Have,[1] which postulates simple hydrogen abstraction from aromatic amine and phenol inhibitors, and that of Boozer and Hammond,[2] which postulates rapid reversible complex formation between alkylperoxy radical and inhibitor. Recent electron spin resonance studies[3] indicating nil complex formation between cumylperoxy radicals and pyridine or triphenylamine have prompted us to reinvestigate alternative proposals which give kinetic results similar to the Boozer–Hammond proposal.

One such proposal by Bickel and Kooyman[4] suggests that data supporting the complex mechanism might be explained by a reversible reaction between intermediate inhibitor radical and hydroperoxide as shown in reactions 1 and 2. Hammond and Nandi[5] tested this possi-

$$RO_2\cdot + IH \longrightarrow RO_2H + I\cdot \qquad k_1 \qquad (1)$$

$$I\cdot + RO_2H \longrightarrow IH + RO_2\cdot \qquad k_2 \qquad (2)$$

bility by studying the influence of cumene hydroperoxide upon the oxidation rate of cumene at 70° when inhibited with several inhibitors including phenol. No effect was observed and this explanation was discarded. In contrast, we observe a significant accelerating effect of cumene hydroperoxide upon both phenol and diphenylamine inhibited oxidation rates of cumene initiated by azobisisobutyronitrile (AIBN) at 57.2°. Figure 1 presents initial phenol inhibited rates as a function of the concentration of added cumene hydroperoxide to the one-half power. On the other hand, inhibited oxidation rates with the highly hindered phenols, 2,6-*t*-butyl phenol and 2,6-*t*-butyl cresol, are uninfluenced by cumene hydroperoxide at the highest concentrations included in Fig. 1. In Fig. 2, inhibited rates are plotted against the inverse square root of phenol concentration for zero added hydroperoxide and for a hydroperoxide concentration of 0.012 *M*.

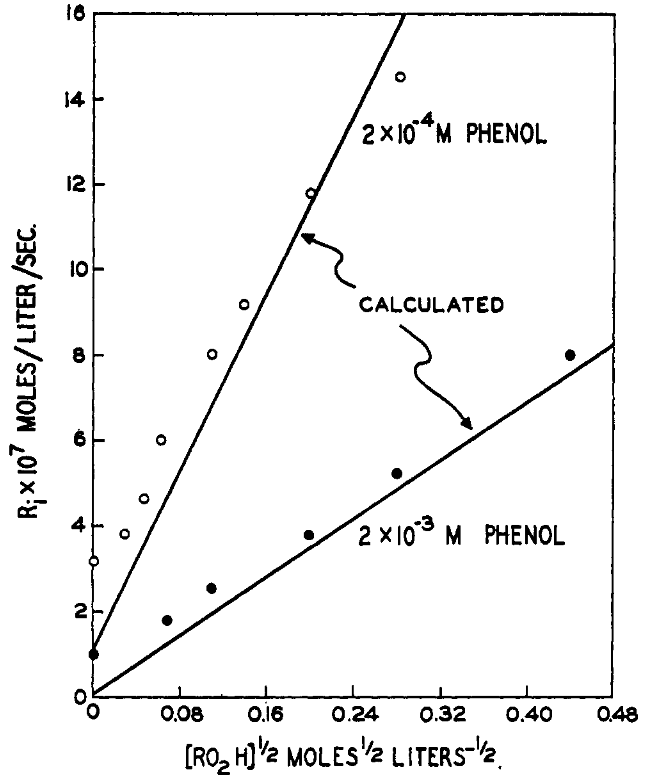

Fig. 1.—Phenol inhibited oxidation rates of cumene *vs.* square root of added cumene hydroperoxide: 5.68 *M* cumene; 8 × 10^{-3} *M* AIBN; 57°; 1 atm. of O_2; chlorobenzene diluent.

Reactions 1 and 2 together with 3 give a moderately

$$RO_2\cdot + I\cdot \longrightarrow RO_2I \qquad k_3 \qquad (3)$$

good account of the experimental results as shown by the calculated curves in Fig. 1 and 2. These curves are due to the appropriate rate expression (4) where k_p and k_i are the known propagation and initiation rate constants, and using $k_1 = 4 \times 10^3$ l. mole^{-1} sec.$^{-1}$ and $k_2/k_3 = 5.7 \times 10^{-5}$. This expression calls for inverse first

$$R_i = \frac{k_p[RH]k_i[AIBN]}{4k_1[IH]}\left\{1 + \left(1 + \frac{8\,k_1k_2[RO_2H][IH]}{k_i[AIBN]k_3}\right)^{1/2}\right\} \qquad (4)$$

power dependence of the oxidation rate upon inhibitor concentration at zero hydroperoxide. If the mechanism is to apply, the observed inverse square root dependence must arise from hydroperoxide formed by reaction during the determination of the initial rate. By oxygen absorption measurement, the hydroperoxide generated during this period is approximately 10^{-3} *M* in all cases, and this value was used in (4) for the calculated curve. Treatment of starting cumene with activated silica reduced contaminating hydroperoxide to undetectable levels, less than 5 × 10^{-4} *M*. The concentration ranges covered in Fig. 1 and 2 are the maximum permissible except for the higher inhibitor concentration of Fig. 1. Limitations are imposed by the inhibited rate approaching the uninhibited rate (32

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[1] J. L. Bolland and P. ten Have, *Trans. Faraday Soc.*, **43**, 201 (1947).

[2] C. E. Boozer and G. S. Hammond, *J. Am. Chem. Soc.*, **76**, 3861 (1954).

[3] J. R. Thomas, *ibid.*, **85**, 591 (1963).

[4] A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 2215 (1956).

[5] G. S. Hammond and U. S. Nandi, *J. Am. Chem. Soc.*, **83**, 1217 (1961).