

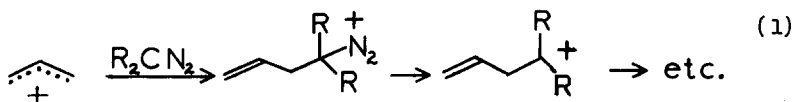
A NEW SYNTHESIS OF HOMOALLYLIC CATIONS

H. W. Whitlock and M. R. Pesce (1)

Department of Chemistry, The University of Wisconsin,
Madison, Wisconsin

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Previous work on the homologation of carbonium ions (2,3) suggested the possibility of a new synthetic route to homoallylic cations, namely the reaction between allylic cations and diazo compounds (eq. 1). The reaction system



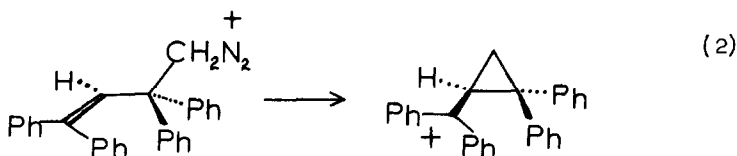
chosen for study was that of 1,1,3,3-tetraphenylallyl perchlorate (4) (I) and diazomethane. Although nitrogen was vigorously evolved when ethereal diazomethane was added to a slurry of perchlorate I in ether at 0°, only 1,1,3-triphenylindene, resulting from cyclization (4) of I, could be isolated. After a number of attempts it was found that formation of the indene could be suppressed if freshly prepared and rapidly dried perchlorate I was added to an excess of ethereal diazomethane at 0°. By extensive chromatography and recrystallization, the oily reaction mixture was then resolved into two components. The first component, m.p. 178-180° was isolated in 6-10% yield. Its structure was tentatively assigned as 1,1,4,5-

tetraphenyl-1,3-pentadiene (V) (a 2:1 diazomethane-perchlorate salt adduct) on the basis of its elemental analysis and absorption of two moles of hydrogen on catalytic hydrogenation, and on spectroscopic and mechanistic grounds. The second component, isolated in 20-40% yield, was identified as 1,1,4,4-tetraphenyl-1,3-butadiene (IV). No other crystalline materials, in particular 1,1,3,4-tetraphenyl-1,3-butadiene (III), could be isolated. The usual simple carbonium ion mechanism, showing the likely intermediates in this reaction, is advanced in Figure 1. Consistent with this scheme is the observation that diphenyl(2,2-diphenylcyclopropyl)-carbinol (VI) is smoothly dehydrated under acidic conditions to afford 1,1,4,4-tetraphenyl-1,3-butadiene (5).

The observation that, within the limits of the rather poor material balance of isolated products, 2,2-diphenylvinyl migration (path a) occurs to the exclusion of phenyl migration (path b) is reasonable. The transition states for the two possible paths of rearrangement of cation II presumably involve only partial bonding between the methylene and the migrating group. Any charge donation by the migrating group in the transition state, however, should clearly favor diphenylvinyl migration (developing benzhydryl cation) over phenyl migration (developing phenonium ion). That this effect could override the compression of the energy scale

for this presumably highly exothermic reaction is suggested by a comparison of the cation localization energies for electrophilic substitution of benzene (6) ($I_R^+ = 2.54\beta$), the para position of aniline (6) ($I_R^+ = 2.40\beta$), and the 2-position of 1,1-diphenylethylene ($I_R^+ = 1.51\beta$).

Stereochemical factors are also consistent with 2,2-diphenylvinyl migration. If rearrangement of II is faster than rotation around the carbon-carbon σ -bonds, it is seen that the geometry of II is such as to favor interaction of the double bond and the methylene group (eq. 2).



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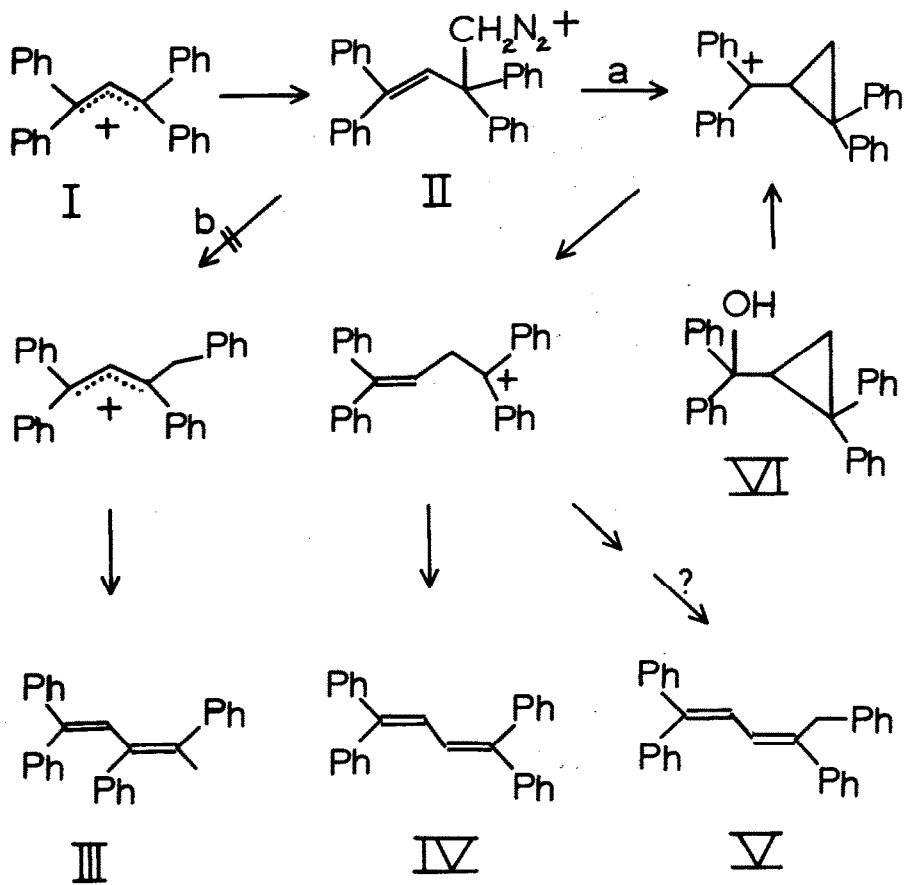


Fig.