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CYCLOADDITION OF 2-PHENYLISOBUTENYLIDENECYCLOPROPANE *via* A DIRADICAL INTERMEDIATE. REACTION WITH 1,1-DICHLORO-2,2-DIFLUOROETHYLENE (1)

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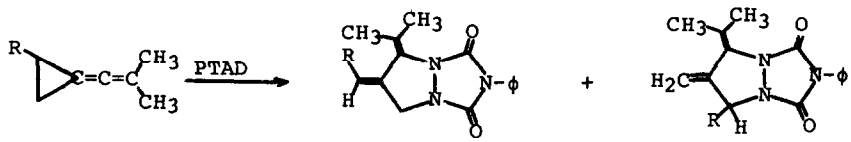
In a study of cycloaddition reactions of cyclopropane-containing compounds we have observed that alkenylidenecyclopropanes (1) react rapidly with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) to form adducts of the general structures 2 and 3. We proposed that the cycloaddition reactions occurred *via* concerted $[(_\pi 2 + _\pi 2 + _\sigma 2) + _\pi 2]$ pathways in which both double

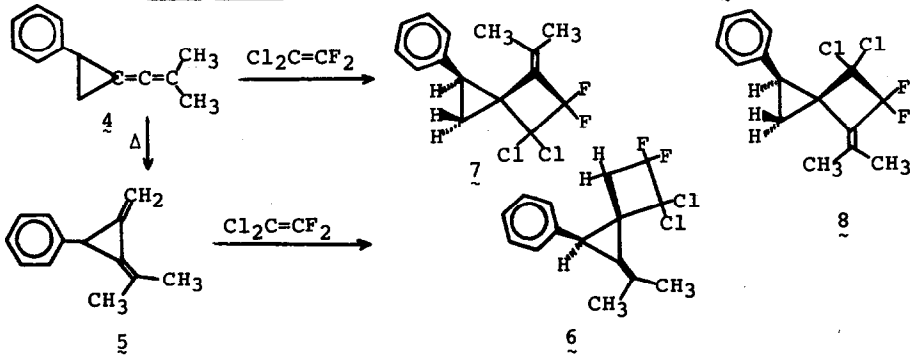


1 2 3

bonds of the allene moiety were involved in the reaction (2). The results of MO calculations (2b) provided a basis for understanding the highly reactive nature of 1. In order to evaluate the possibility that 2 and 3 were formed *via* dipolar or diradical intermediate pathways, studies were undertaken of cycloaddition reactions of alkenylidenecyclopropanes with chlorosulfonylisocyanate (3) and 1,1-dichloro-2,2-difluoroethylene (1122). The course of the reactions with chlorosulfonylisocyanate provided a distinct contrast with that observed with PTAD indicating that dipolar intermediates were not involved in the reactions with PTAD (3). We wish now to present our results on the reaction of 2-phenylisobutenylidenecyclopropane (4) with 1122.

The reaction of 1.05 g of 4 with 3 ml of 1122 in a sealed tube at temperatures above 105° for four days quantitatively produced adduct 6 (by nmr analysis) along with apparently polymeric 1122. Chromatographic

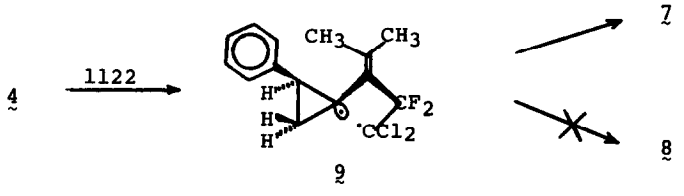
separation on alumina (elution with 5% benzene-hexane) gave pure 6: bp (molecular still) 93-95° (0.30 mm); ^{1}H nmr ($CDCl_3$) δ 1.95 (d, J = 1.9 Hz, 3H), 2.05 (d, J = 2.1 Hz, 3H), 2.38 and 2.58 (XY portions of an ABXY system, $J_{HH(XY)}$ = 13.8 Hz, $J_{HF(AX)} = J_{(AY)} = J_{(BX)} = J_{(BY)}$ = 11.5 Hz, 2H), 3.20 (m, 1H), 7.27 (m, 5H); ^{19}F nmr ($CDCl_3$) δ (CCl_3F internal standard) +100.8 and +102.2 (AB portions of an ABXY system, J_{FF} = 178 Hz); mass spectrum m/e 302.0439 (calcd for $C_{15}H_{14}Cl_2F_2$, 302.0441). The structure of 6 is based on its nmr spectrum, which notably lacks the typical AXY pattern expected for the cyclopropyl hydrogens of three-membered ring retained adducts 7 and 8, and the fact that 5, formed by the thermally induced rearrangement of 4 (4), reacts fairly rapidly with 1122 to produce 6. The stereochemistry of the adduct is tentatively assigned on the basis that attack on the C_1-C_4 double bond of 4 occurs at the face opposite the phenyl group (vide infra) which should also happen with 5.



4 5 6 7 8

When the reaction of 4 with 1122 is carried out at 95° (13 days) 4 reacts quantitatively to produce a mixture of adducts 6 and 7. Chromatographic separation on alumina with elution with 4% benzene-hexane gave pure fractions of 6 and 7 (32 and 60% isolated yields respectively). The structure and stereochemistry of 7 is clearly evident from its ^{1}H nmr spectrum [($CDCl_3$) δ 0.68 (t, J = 3.4 Hz, 3H), 1.76 (t, J = 2.7 Hz, 3H), 1.86 (m, XY portion of an AXY system, 2H), 3.05 (dd, A portion of an AXY system with

J_{AX} = 8.2 Hz, J_{AY} = 9.6 Hz, 1H), 7.30 (s, 5H)], ^{19}F nmr spectrum [δ +98.1 (m)], and mass spectrum (m/e 302.0439). The presence of the AXY system demonstrates the presence of the three-membered ring, while the low-field methyl triplet indicates the presence of the isopropylidene group. The high-field methyl triplet (δ 0.68) represents the "inside" methyl group of the isopropylidene function which experiences extensive shielding by the phenyl group owing to its position directly into the face of the aromatic ring, thus defining the stereochemistry of 7. Adduct 7 is formed by attack on the face of the C_1-C_4 double bond opposite the phenyl group, consistent with the high degree of facialselectivity exhibited in other reactions of 4 involving attack on the C_1-C_4 double bond (5), producing the diradical 9 which collapses to 7 before extensive inversion, rotation and collapse to the stereoisomeric adduct 8. (Adduct 8 can also be formed by synfacial attack on 4 followed by collapse of the diradical intermediate prior to inversion or rotation).



Very small amounts (<2% each) of apparently two other 1:1 adducts (by mass spectrometry) were formed, but could not be completely separated from 7, and, thus, definitive nmr spectra could not be obtained.

The results reported herein indicate that the reactions of PTAD with 1 do not occur via diradical intermediates. We are extending these studies to other substituted alkenylidenecyclopropanes and other radical addition reagents.

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