NOVEL FORMATION OF [5]PARA-1-AZACYCLOPHANES

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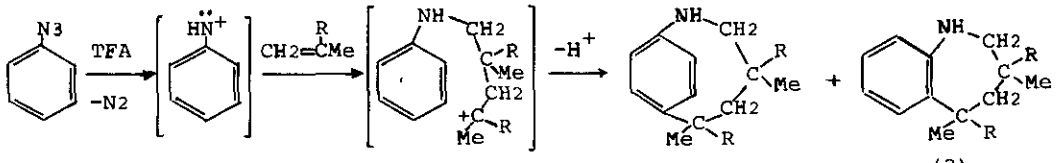
The reaction of phenyl azide with 2-methylpent-1-ene in the presence of trifluoroacetic acid (TFA) of 60% v/v at *ca.* 90°C gave *cis*- and *trans*-[5]*para*-1-azacyclophanes (1a)(10%)and (1b)(trace) and *cis*- and *trans*-[5]*ortho*-1-azacyclophanes (2a)(2%) and (2b)(2%). Further, the reaction using 2-methylbut-1-ene instead of 2-methylpent-1-ene afforded the corresponding *cis*- and *trans-para*isomers (1c)(12%) and (1d)(3%) and *cis*- and *trans-ortho*isomers (2c)(2%) and (2d)(1%). I.R. spectra of (1) show 820 cm^{-1}(*p*-substituted Ph). Phenyl protons (AB q, 6.4–7.15 ppm) of (1) are somewhat shielded as compared with those (6.4–7.5 ppm) of (2) because of a decreased ring-current by a distorted benzene ring of (1). The chemical shifts of protons of C(2)–H2 and C(4)–H2 for (1) are almost the same as those for the corresponding isomers of (2), respectively, since the protons are located on the nearby edge of distorted benzene ring. U.V. spectra of (1a) exhibit a shift of absorption maxima of *ca.* 250 and *ca.* 300 nm to longer wavelength relative to (2a). ^{13}C-n.m.r. of C(2),C(4), and C(5) of (1a) appear at the nearly identical fields with those of (2a), respectively. This suggests the idea that the bond angles C-C-C and N-C-C involving the bridging atoms of (1) are similar to those of the usual seven-member compounds. Elemental analysis and m/z [259(M^+), 244(M^+-Me), 216(M^+-Pr)] of (1a) well support the structure.



(1) R=Pr or Et (2)

The feasible formation of (1) comes from the fact that the transition state of an intramolecular Friedel-Crafts reaction giving (1) does not have a great strain; the transition state is similar to a σ-complex which is formed in the reaction, and the strain is not large in extent because the *para*-carbon atom attacked by the reaction is changed from sp^2 to sp^3 hybridization which is favorable to the intramolecular *para*-cyclization.