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COMPOUNDS CONTAINING LOCALIZED CARBON-PHOSPHORUS DOUBLE BONDS I. DIELS-ALDER REACTION OF 3-METHYL-2-PHOSPHANAPHTHALENE WITH HEXAFLUOROBUTYNE-2.

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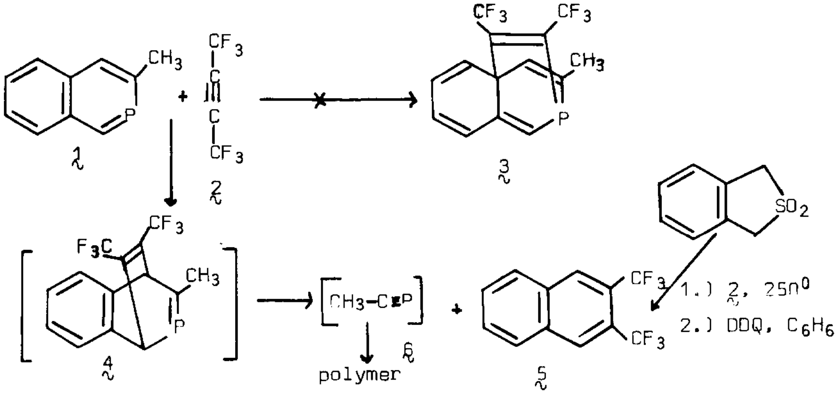
Elements of the second and higher rows of the periodic table do usually not form stable multiple bonds by pπ-pπ overlap[1] . Stabilization of such bonds can be achieved by delocalization, as exemplified by an increasing number of phosphaaromatic systems[2] . The first compound with an isolated phosphorus carbon multiple bond was phosphaacetylene, H-C≡P, which polymerized even at -130^0 C[3]. More recently stable compounds have been prepared containing P=N[4] or substituted P=C[5] or As=C[6] bonds, and also simple molecules containing the P=C bond and having a half life of several seconds have been obtained[7].

With the intention of generating P=C bonds by a novel approach, we studied the Diels-Alder reaction between 3-methyl-2-phosphanaphthalene (1)[8] and hexafluorobutyne-2 (2). Whereas phosphabenzene and its derivatives yielded Diels-Alder adducts with the phosphorus atom as bridgehead[9], this mode of reaction was highly improbable for 1, as it would lead to 3 in which both rings have lost their aromaticity. Rather, addition to position 1 and 4 was predicted to give 4, which contains an isolated P=C bond.

The reaction was performed both in the gas phase (evacuated ampoule, 50 min, 250^0 C) and in solution (cyclohexane, 115-150^0 C, 48 hours); besides tarry material, 2,3-bis(trisfluoromethyl)naphthalene (5) was isolated in about 30% yield. Apparently, 4 had undergone a retro Diels-Alder reaction to 5 splitting off the unstable 1-phosphapropyne (6), which polymerized under these reaction conditions. A similar course of reaction has recently been described for arsabenzenes by Ashe[10] . The structure of 5 (m.p. 81-$82{,}5^0$ C; ^{1}H NMR (D_6-aceton) : δ (ppm), 8,72 (s.2H), 8,35 and 7,95 (d of d, 4H, J=3Hz); UV (cyclohexane), λ (nm), (log ε): 228 (3,32), 265 (3.25), 275 (3.25), 305 (2.62), 312 (2.54), 320 (2.69); $C_{12}H_6F_6$:

calcd. C 54.56%, H 2.29%, m/e= 264.03871, found C 54.11%, H 2.79% m/e: 264.03876; mass spectrum m/e (%): 264 (100) $(5)^{+\cdot}$; 245 (19) $(5\text{-F})^{+\cdot}$; 214 (19), $(5\text{-CF}_2)^{+\cdot}$, 195 (22), $(5\text{-CF}_3)^{+\cdot}$ was confirmed by an independent synthesis.



Apparently, 4 is thermally too unstable to survive the conditions of its formation; experiments to intercept 4 with cyclopentadiene or water were not fully conclusive so far.

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