Journal of Fluorine Chemistry, *47* (1990) 175–178

Received: July 26, 1989; accepted: September 15, 1989

PRELIMINARY NOTE

Transannular Deactivation in Tetrafluoro[2.2]Paracyclophane. Electrophilic Reactivity of its Open-Chain Analog

ROBERT FILLER* and JOSEPH E. GADOMSKI

Department of Chemistry, Illinois Institute of Technology,
Chicago, Illinois 60616 (U.S.A.)

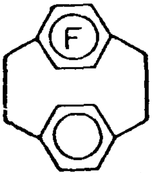
SUMMARY

The open-chain analog (3) which most closely resembles the structure of 4,5,7,8-tetrafluoro[2.2]paracyclophane (1) has been prepared. In contrast to (1), (3) undergoes acetylation of the phenyl ring. This observation provides further evidence that the failure of (1) to undergo electrophilic substitution can be attributed primarily to transannular deactivation of the phenyl by the tetrafluorophenyl ring and much less to an inductive effect through the sigma bond network.

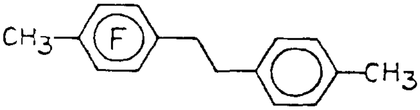
In an earlier paper [1] we reported on the properties and chemical reactivity of polyfluoro[2.2]cyclophanes. In particular, we noted the general lack of reactivity toward electrophilic substitution of the phenyl ring in 4,5,7,8-tetrafluoro[2.2]paracyclophane (1), although recently, we have shown that a stable monocation (σ-complex) of (1) is generated by ipso protonation in superacid media [2]. The deactivation was attributed to the decreased basicity of the phenyl ring, caused by transannular drain

0022-1139/90/$3.50

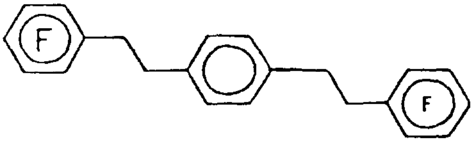
of π-electron density from C_6H_4 to C_6F_4. This explanation was bolstered by the diminution in stability of the charge-transfer complex of (1) with tetracyanoethylene (TCNE), relative to that of [2.2] paracyclophane. Moreover, we demonstrated that the open-chain analog 4,4'-dimethyl-2,3,5,6-tetrafluorobibenzyl (2), in which electronic effects must be transmitted through σ-bonds, did undergo acetylation at the 3'-position [1]. Although these observations seemed to provide convincing evidence of a trans-annular, internuclear interaction, our choice of (2) was challenged [3] as an adequate open-chain model of (1). We have now met this criticism by preparing the new compound (3), an analog whose structure most closely resembles (1) and hence, offers a rigorous test of reactivity.



(1)

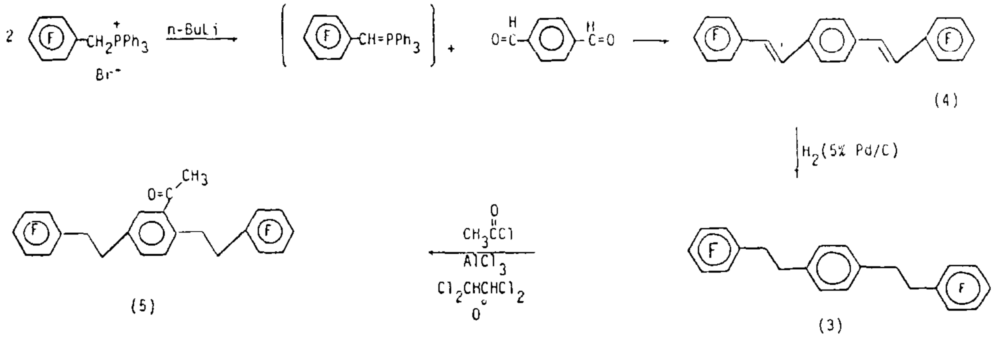


(2)



(3)

Compound (3) was obtained in two steps, a bis-Wittig reaction followed by catalytic hydrogenation of the resulting diene, as indicated in the Scheme.



SCHEME

The reaction of two equivalents of (2,3,4,5,6-pentafluorobenzyl)triphenylphosphonium bromide [1], prepared from pentafluorobenzyl bromide [4] and triphenylphosphine, with n-butyl lithium afforded the ylide, which reacted with one equivalent of terephthalaldehyde to give a 15% yield of the diene (4). No attempt was made to optimize the yield. Compound (4), previously unreported, is a yellow, crystalline material, m.p. 208-210°, which gave a correct elemental analysis and exhibited strong absorption at 352 nm, with a shoulder at 372 nm, in benzene solution. The trans, trans geometry was confirmed by proton magnetic resonance, which revealed two doublets at δ 7.45 and 7.10, J_{H-H} 17 Hz. Hydrogenation of (4), using 5% Pd/C, then provided a good yield of (3), m.p. 109-111°, with satisfactory analytical and spectroscopic data.

A small quantity of (3) was treated with acetyl chloride and anhydrous aluminum chloride in 1,1,2,2-tetrachloroethane solvent near 0 °, the conditions used previously with (1) and (2). The reaction was quenched after four hours to give an impure material which exhibited strong carbonyl absorption at 1710 cm^{-1}.

Although neither of the open-chain analogs (2) and (3) undergo acetylation as rapidly as [2.2] paracyclophane, tetrafluoro[2.2]paracyclophane (1) fails to react at all, even at higher temperatures. While the electron-withdrawing inductive effect of the fluorines may contribute to a limited degree to reduced reactivity, we conclude that the predominant cause of deactivation in (1) is the transannular drain of π-electron density from the phenyl ring [5]. These studies were stimulated by the original observation of the existence of a 1:1 complex between benzene and hexafluorobenzene [6].

1 R. Filler, G.L. Cantrell and E.W. Choe, J. Org. Chem., 52 (1987) 511.

2 K. Laali and R. Filler, J. Fluorine Chem., 43 (1989) 415.

3 S.I. Miller and P.Y. Johnson, Personal communication.

4a A.K. Barbour, M.W. Buxton, P.L. Coe, R. Stephens and J.C. Tatlow, J. Chem. Soc., (1961) 808.

b J.M. Birchall and R.N. Haszeldine, J. Chem. Soc., (1961) 3719.

5 R. Filler in J.F. Liebman, A. Greenberg and W.R. Dolbier, Jr. (eds.), 'Fluorine-Containing Molecules: Structure, Reactivity Synthesis and Applications', VCH Publishers, New York, 1988, p. 19.

6 C.R. Patrick and G.S. Prosser, Nature, 187 (1960) 1021.