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2,2'-DIHALO-BIS(PERFLUOROCYCLOALKENES): Part II. REACTION WITH PYRIDINE

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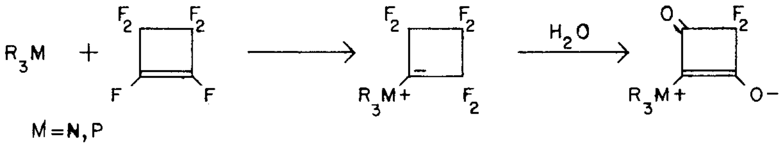
SUMMARY

Pyridine reacts with 2,2'-dichloro(perfluorobicycloalken-1-yl) under hydrolytic conditions to give the pyridinium betaine of a 1,3-diene. Hydrolysis of the allylic fluorines occured exclusively in the cyclobutenyl ring bearing the oxygen anion. The intermediate ylide, if indeed formed at all, was too unstable to isolate and identify.

INTRODUCTION

Stable ammonium and phosphonium ylides have been isolated from the reaction of perfluorocycloalkenes with tertiary amines [1] and phosphines [2,3]. Under protic solvent conditions with a trace of added water the initially formed ylides rapidly hydrolyze to ammonium [1,4] and phosphonium [2,5] betaines.



In previous publications we have described the synthesis of 2,2-dihalo-(perfluorobicycloalken-1-yl)s [6,7] and their reactions with secondary

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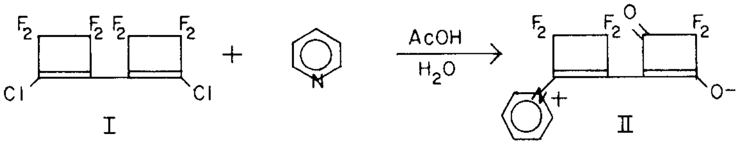
phosphines and arsines [8,9]. We wish to report here on the isolation of an unusual ammonium betaine of a 1,3-diene formed through the reaction of pyridine with 2,2'-dichloro-(perfluorobicyclobuten-1-yl) I.



RESULTS

The fluorocarbon I was added to an excess of pyridine in acetic acid containing a small amount of added water. The reaction mixture was heated then all solvents removed and the residue purified to a light yellow solid II. Elemental analysis and a mass spectrum parent ion at 321 amu indicated a molecular formula $C_{13}H_5NO_2F_6$ for II. Fragmentation ions in the MS pattern clearly showed the loss of F, CF_2, CO and the presence of the pyridinium ion at 79 amu. The most prominent features in the ir spectrum of II were a strong absorption at 1171 cm^{-1} and a very strong-broad absorption at 1640 cm^{-1}. Previous workers [2,10] have characterized these bands as diagnostic of the O=C-C=C-O - system. The proton n.m.r. spectrum showed a broad multiplet pattern between 8.3-9.0 ppm which was quite similar in shape and position to the published spectra for the aryl proton of pyridinium inner salts [11].

Assignment of the resonances of the six fluorine atoms was reasonably straight forward for the ^{19}F n.m.r.. The spectrum appeared as two multiplets at -109.6 and -113.1 ppm and a singlet at -118.9 ppm. Integration indicated equal areas in each absorption group. The two multiplet patterns were reminiscent of the AA'BB' patterns found in tetrafluorocyclobutenes where the 1,2-positions are substituted by different groups and their chemical shift values are well within the reported ranges found in substituted bis(perfluorocyclobutenes) [12].

The ^{19}F singlet at -118.9 ppm closely corresponds to the reported values for the $-CF_2-$ group bridging the two carbonyl groups in 4,4-difluoro-2-(triphenylphosphoranylidene)-cyclobutane-1,3-dione (-118.4 ppm) [2] or in (3,3-difluoro-2,4-dioxocyclobutyl) pyridinium betaine (-120.7 ppm) [1].

A report on the reaction of triphenylphosphine with 2,2'-dihalo-bis (perfluorocyclobutenes) is in preparation.

EXPERIMENTAL

Crystals of I (0.30 g, 0.94 mmol) were added to a solution of pyridine (1.5 g, 19 mmol), water (.05 g) and acetic acid (8.0 g) to give a bright lemon yellow coloration. The solution turned dark reddish brown after heating to 102°C for 5 hours. All liquids were then removed under high vacuum and the residue dissolved in a few ml of aqueous acetone (1:1). After two treatments with decolorizing charcoal the solvent volume was reduced to 3 ml giving 0.12 g of a light tan solid. A third treatment with decolorizing charcoal gave 1-[2-(3,3-Difluoro-2-hydroxy-4-oxo-1-cyclobuten-1-yl)-3,3,4,4-tetrafluoro-1-cyclobuten-1-yl]pyridinium hydroxide, inner salt nc II as a light yellow powder: mp (dec) 195-196°C [Found: C, 48.4; H, 1.56; N, 4.10; M^+, 321. $C_{13}H_5NO_2F_6$ requires: C, 48.6; H, 1.57; N, 4.36; M, 321]. Spectral data included: i.r. (KBr pellet) 1771 s, 1640 vs br, 1485, 1440, 1370, 1335, 1298, 1275, 1215 s, 1150 s, 1120 s, 1100 sh, 1058 s, 1205, 910, 872, 845, 785, 755, 745, 675, 665, 548 and 522 s cm^{-1}; 'H n.m.r. showed multiplet 8.3-9.0 ppm; ^{19}F n.m.r. δ multiplets at -109.6 (2F) and -113.1 ppm (2F) and a singlet at -118.9 ppm (2F).

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