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SHORT COMMUNICATION

The Photochromism of Derivatives of 2,2'-Dichlorooctafluoro(bi-1-cyclobuten-1-yl)

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The reaction of dimethylarsine with 1,2-dichlorotetrafluorocyclobutene in the absence of solvent results in monosubstitution according to (1) [1]

$$(CH_3)_2AsH + Cl\overline{C{=}CCl(C}F_2)_2 \rightarrow (CH_3)_2As\overline{C{=}CCl(C}F_2)_2 + HCl \qquad (1)$$

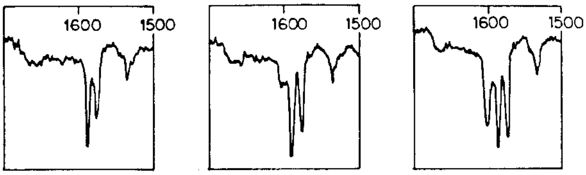
Disubstitution takes place when diphenylphosphine reacts with 2,2'-dichlorooctafluoro(bi-1-cyclobuten-1-yl) in ether solution to give the ditertiary phosphine **1** (equation (2)) [2]

$$2(C_6H_5)_2PH + Cl\overline{C{=}C(C}F_2)_2\ \overline{C{=}CCl(C}F_2)_2 \rightarrow$$

$$\mathbf{1} \qquad (C_6H_5)_2P\overline{C{=}C(C}F_2)_2\ C{=}CP(C_6H_5)_2(CF_2)_2 + 2HCl \qquad (2)$$

Compound **1** is unexpectedly photochromic in the solid state being red in the light and yellow in the dark [2].

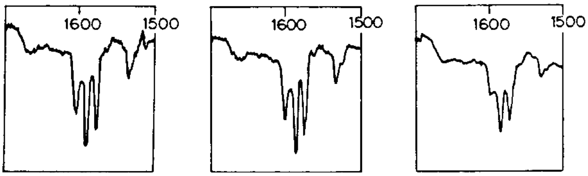
The Figure shows a portion of the infrared spectrum of **1**. The region selected is one of the two in the range 4000-250 cm^{-1} which changes when **1** is exposed to light. The yellow solid shows two weak bands in the ν(C=C) region at 1588 and 1576 cm^{-1} as expected for a 'butadiene' system. When the KBr disc is exposed to a small dose of sunlight it turns partly orange and a new band appears at 1602 cm^{-1}. Further exposure enhances the intensity of the band at 1602 cm^{-1} and turns the disc totally red. When the disc is placed in the dark the 1602 cm^{-1} band gradually disappears and the disc turns yellow again.



1, Before exposure

2.Exposed to sunlight
(7 min)

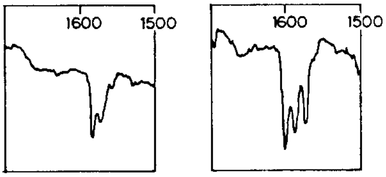
3.Exposed to sunlight
(32 min)



4.In the dark
(80 min)

5.In the dark
(12 x 60 min)

6.In the dark
(30 x 24 x 60 min)



7.In the dark
(48 x 24 x 60 min)

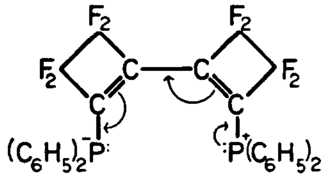
6.Same disc reexposed
to sunlight (40 min)

Figure. Partial infrared spectrum of **1** before and after exposure to sunlight.

The only other change in the infrared spectrum is the appearance of a weak new band at 895 cm^{-1} which also disappears when the disc is placed in the dark.

On this evidence it seems that the photochromism is associated with a structural change caused by electronic excitation. The phosphorus lone pairs seem to be involved since the bis-oxide of **1** is colorless and not photochromic [2].

The crystal structure of **1** [3] shows that the molecule has a cisoid arrangement of double bonds with the rings twisted by ∿35° away from planarity. The change in color from yellow to red indicates that there is more conjugation in the irradiated solid suggesting that rotation about the central C-C bond takes place affording more planar but sterically hindered molecules. A possible mechanism involving the phosphorus lone pairs is shown.



Here the excitation produces a C=C from the central C-C single bond which would encourage rotation to a more planar structure.

The presence of the phenyl groups should help to stabilize the charge transfer because of their ability to delocalize the negative charge. In our previous studies [4] we prepared the bis(cyclohexylphosphino) analogue $(C_6H_{11})_2PC{=}C(CF_2)_2\ C{=}CP(C_6H_{11})_2(CF_2)_2$ 2 in the belief that the more available lone pairs would enhance any photochromic behaviour. Unfortunately 2 although yellow is not photochromic thus the presence of phenyl groups may be essential. With this in mind we have attempted to prepare other diphenylphosphino derivatives such as $(CH_3)_2AsC{=}C(CF_2)_2\ C{=}CP(C_6H_5)_2(CF_2)_2$ 3 and $(C_6H_{11})_2PC{=}C(CF_2)_2\ C{=}CP(C_6H_5)_2(CF_2)_2$ 4. Our approach to 3 was based on the result that excess dimethylarsine reacts with 2,2'-dichlorooctafluoro(bi-1-cyclobuten-1-yl) at 60°C to give the disubstituted product $(CH_3)_2AsC{=}C(CF_2)_2\ C{=}CAs(CH_3)_2(CF_2)_2$ 5 [2]. Thus it could be expected that mixing dimethylarsine with the dichloro(bi-1-cyclobuten-1-yl) derivative in a 1:1 ratio would result in the formation of a tertiary arsine (c.f. equation (1)) which could then react with diphenylphosphine to displace the other chlorine atom affording 3. Unfortunately when the reaction is carried out at 25°C or -78° in ether or -78° in DMF [2,5] and diphenylphosphine is added at the same temperature only the symmetrical derivatives 1 and 5 are isolated.

Similar experiments in DMF solution [2,5] using first dicyclohexylphosphine followed by diphenylphosphine resulted in the production of both 1 and 2 rather than 4. Thus it seems that the best way to 'tune' the photochromic properties of compounds like 1 will be to substitute the aromatic rings attached to phosphorus. We hope to report on this aspect in the future.

It should be mentioned that phosphorus and/or fluorine compounds are not usually photochromic [6] and that solutions of 1 in methyl methacrylate can be polymerized to give yellow solids which will afford an image of an appropriate object when exposed to sunlight.

EXPERIMENTAL

A typical reaction is described below.

Attempted preparation of 2-dimethylarsino-2'-diphenylphosphino-octafluoro(bi-1-cyclobuten-1-yl) **3**

Dimethylarsine (0.22 g, 20.7 mmol) was condensed onto a frozen solution of 2,2'-dichlorooctafluoro(bi-1-cyclobuten-1-yl) (0.64 g, 20.1 mmol) in ether (12 ml) contained in a Carius tube. The mixture was warmed to -78°C and left for 20 h. A pale yellow solid precipitated. The mixture was slowly warmed to 20°C over 4 h, during which time the precipitate disappeared. The tube was opened and diphenylphosphine (0.39 g, 20.9 mmol) in ether (8 ml) was added using a syringe. The tube was cooled, evacuated, and left at -78°C for 24 h. This produced a deep yellow solution. After the solvent was removed from the tube (20°C) a yellow solid remained. This solid was dissolved in dichloromethane and chromatographed on a Florisil column. Elution with petroleum ether (b.p. 40°-60°C) gave a yellow solid which was separated into the known compounds [2] **1** (0.252 g, 39.0%) and **5** (0.166 g, 34.9%) by fractional recrystallization.

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