Synthesis and Photolysis of 1,2,3,8-Tetrakis(trifluoromethyl)-cyclo-octatetraene

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Summary The title compound was derived from tetrakis-(trifluoromethyl)-5-thiabicyclo[2.1.0]pent-2-ene *via* Diels–Alder adduct formation with butadiene; its photolysis gave [2 + 2] reaction products.

Cyclo-octatetraene is an interesting compound since it is a non-aromatic alternate polyolefin and there is the possibility of three structural changes: bond shifting, ring inversion, and valence bond isomerization.[1] We were interested in the synthesis of 1,2,3,8-tetrakis(trifluoromethyl)cyclo-octatetraene (**5**) and its structural changes for comparison with nonfluorinated cyclo-octatetraene derivatives,[2] since perfluoroalkyl groups may stabilize unstable and strained ring systems sufficiently for their isolation at room temperature.[3] For this purpose, we used the adduct (**2**)[4] of the Dewar thiophen derivative (**1**) with butadiene as starting material.

Treatment of (**2**) with triphenylphosphine in pentane at room temperature gave the desulphurization product (**3**), m.p. 87—89 °C; $\nu_{C=C}$ ($CHCl_3$) 1725 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 5·91 (m, 3- and 4-H) and 2·56 (m, 2- and 5-H); ^{19}F n.m.r. ($CDCl_3$)† δ 0·0 (s, 6F) and 4·8 (s, 6F); *m/z* 378 (M^+). Compound (**3**) was brominated in carbon tetrachloride at room temperature to give the *trans*-dibromide (**4**), m.p. 49—51 °C; $\nu_{C=C}$ ($CHCl_3$) 1710 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 4·60 (m, 3-H), 4·36 (m, 4-H), and 2·92 (m, 2- and 5-H); ^{19}F n.m.r. ($CDCl_3$) δ − 1·8 (m, 3F), 1·6 (m, 3F), and 5·0 (s, 6F); *m/z* 536 (M^+). Dehydrobromination of (**4**) with 1,5-diazabicyclo-

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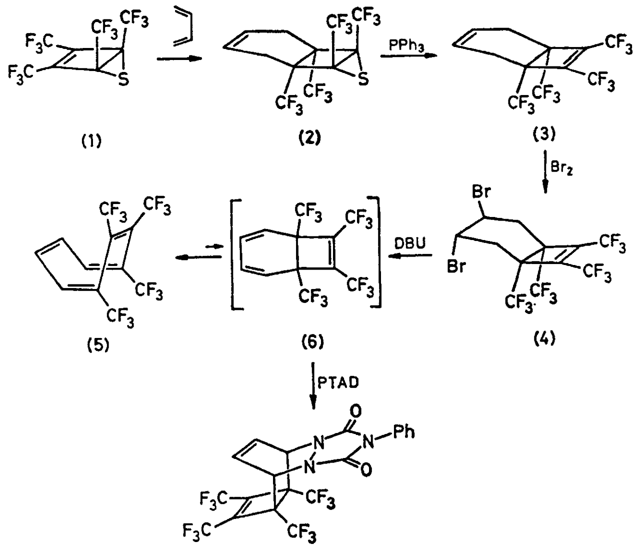
† α,α,α-Trifluorotoluene was used as an internal standard, since we were concerned only with CF_3 ^{19}F resonances; it resonates at 64 p.p.m. to higher field than $CFCl_3$, the most common standard for ^{19}F n.m.r. spectroscopy.

[5.4.0]undec-5-ene (DBU) in dichloromethane from 0 °C to room temperature gave the title compound (**5**) as sublimable colourless prisms; m.p. 66—68 °C; $\nu_{C=C}$ (CCl_4) 1650 cm^{-1}; ^{1}H n.m.r. (CCl_4) δ 6·77 (br. s) and 6·46 (br. s); ^{19}F n.m.r. (CCl_4) δ −4·2 (s, 6F) and −1·2 (s, 6F); M^+, *m/z* 376·010 (calc. 376·012). The absence of an absorption above 1700 cm^{-1} suggested that a cyclobutene double bond bearing trifluoromethyl groups was not present.‡ This was supported by the photoreaction of (**5**) described later. The bicyclo[4.2.0]octatriene (**6**), which presumably must be an intermediate in the conversion of (**4**) into (**5**), appears to be unstable owing to the steric repulsion of the CF_3 groups on the bridgehead and isomerizes to (**5**) by a disrotatory electrocyclic reaction. Although (**6**) could not be detected by ^{19}F n.m.r. spectroscopy, treatment of (**5**) with *N*-phenyltriazoline-3,5-dione (PTAD) gave the adduct (**7**), m.p. 215·5—216·5 °C; ν_{max} ($CHCl_3$) 1730 (C=O) and 1700 (C=C) cm^{-1}; ^{1}H n.m.r. [$(CD_3)_2CO$] δ 7·42, 6·81, and 5·82; ^{19}F n.m.r. [$(CD_3)_2CO$] δ 0·25 (m, 6F) and 1·29 (m, 6F); *m/z* 551 (M^+). Thus, the equilibrium between (**5**) and (**6**) markedly favours (**5**). These results are shown in Scheme 1.

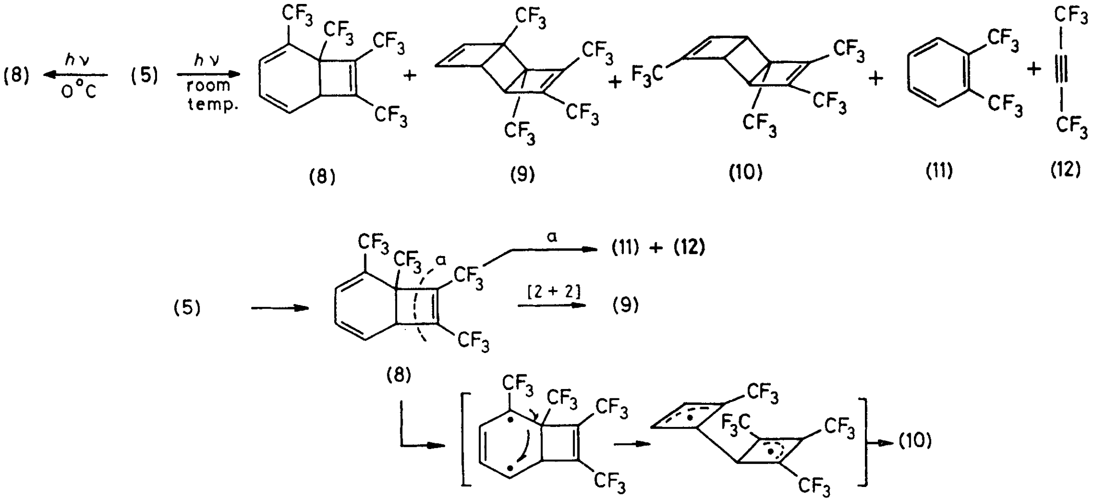


(**7**)

SCHEME 1

We next examined the photoisomerization of (**5**). Irradiation of a solution of (**5**) in pentane at room temperature with a high-pressure mercury lamp for 65 h gave a mixture of compounds (**8**)—(**11**). Compound (**10**), insoluble in pentane, was filtered off (*ca.* 5%). Preparative g.l.c. (SE. 30; 60 °C) of the filtrate led to the separation of (**8**), (**9**), and (**11**), in estimated yields (g.l.c.) of 6, 57, and 5% respectively. Compound (**11**) was identified as 1,2-bis-(trifluoromethyl)benzene by comparison with an authentic sample. The structure of (**8**) was determined from the following data: colourless oil; $\nu_{C=C}$ (CCl_4) 1710 and 1615 cm^{-1}; ^{1}H n.m.r. (CCl_4) δ 6·80 (m, 1H), 6·15 (m, 2H), and 3·95 (br, 1H); ^{19}F n.m.r. (CCl_4) δ −0·8 (q), −0·4 (sept.), 0·8 (m), and 9·8 (qq); *m/z* 376 (M^+). The structures of (**9**) and (**10**) were tentatively assigned from the following data: (**9**), colourless oil; $\nu_{C=C}$ (CCl_4) 1710 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ 6·66, 6·43, 3·55, and 3·46; ^{19}F n.m.r. ($CDCl_3$) δ 0·0 (br), 1·3 (br, s), 2·6 (q), and 6·48 (m); *m/z* 376 (M^+); (**10**), m.p. 163—165 °C: $\nu_{C=C}$ (KBr) 1710 and 1660 cm^{-1}; ^{1}H n.m.r. [$(CD_3)_2CO$] δ 7·32, 4·37, 3·28, and 3·04; ^{19}F n.m.r. [$(CD_3)_2CO$] δ 0·27 (sept.), 0·9 (q), 1·3 (m), and 1·9 (qq); *m/z* 376 (M^+). The ^{19}F n.m.r. spectrum of the reaction mixture also suggested the presence of hexafluorobut-2-yne (**12**). When this photolysis was carried out at 0 °C, only (**8**) was obtained. These results suggest that (**8**) was formed initially, and the other products were formed from it through [2 + 2] ring-closure or elimination, or a free-radical intermediate as shown in Scheme 2. A more detailed study on the photochemical mechanism is in progress.

Compound (**8**) was stable at room temperature and no isomerization to the cyclo-octatetraene form was observed,



SCHEME 2

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‡ All the compounds with a trifluoromethyl-substituted cyclobutene unit that we have synthesized so far show an absorption above 1700 cm^{-1}. For example, 5-azabicyclo[2.1.0]pent-2-enes show an absorption in the 1700—1720 cm^{-1} region: Y. Kobayashi, A. Ando, K. Kawada, and I. Kumadaki, *J. Org. Chem.*, 1980, **45**, 2966.

in interesting contrast with the fact that the bond-shift isomer (**5**) of tetrakis(trifluoromethyl)cyclo-octatetraene was stable and that no bicyclo-octatriene form was observed even by ^{19}F n.m.r. spectroscopy. Paquette *et al.*[5] synthesized two bond-shift isomers of tetramethylcyclo-octatetraene and reported that the 1,2,3,4-tetramethylcyclo-octatetraene was in equilibrium with a small amount of the bicyclo-octatriene isomer. This difference due to the substituents may be attributed to the electronic effect of the CF_3 groups or to the difference in the bulk of CF_3 and CH_3 groups.

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