

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

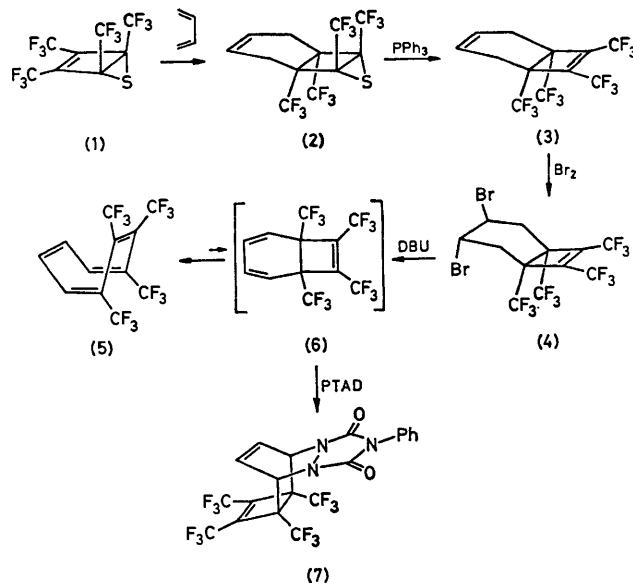
room temperature.³ For this purpose, we used the adduct (**2**)⁴ of the Dewar thiophen derivative (**1**) with butadiene as starting material.

Treatment of (**2**) with triphenylphosphine in pentane at room temperature gave the desulphurization product (**3**), m.p. 87—89 °C; $\nu_{C=C}$ (CHCl₃) 1725 cm⁻¹; ¹H n.m.r. (CDCl₃) δ 5.91 (m, 3- and 4-H) and 2.56 (m, 2- and 5-H); ¹⁹F n.m.r. (CDCl₃)[†] 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; $\nu_{C=C}$ (CHCl₃) 1710 cm⁻¹; ¹H n.m.r. (CDCl₃) δ 4.60 (m, 3-H), 4.36 (m, 4-H), and 2.92 (m, 2- and 5-H); ¹⁹F n.m.r. (CDCl₃) 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-

[†] α,α,α -Trifluorotoluene was used as an internal standard, since we were concerned only with CF₃ ¹⁹F resonances; it resonates at 64 p.p.m. to higher field than CFCl₃, the most common standard for ¹⁹F 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; $\nu_{C=C}$ (CCl₄) 1650 cm⁻¹; ¹H n.m.r. (CCl₄) δ 6.77 (br. s) and 6.46 (br. s); ¹⁹F n.m.r. (CCl₄) 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 CF₃ groups on the bridgehead and isomerizes to (5) by a disrotatory electrocyclic reaction. Although (6) could not be detected by ¹⁹F 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} (CHCl₃) 1730 (C=O) and 1700 (C=C) cm⁻¹; ¹H n.m.r. [(CD₃)₂CO] δ 7.42, 6.81, and 5.82; ¹⁹F n.m.r. [(CD₃)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.

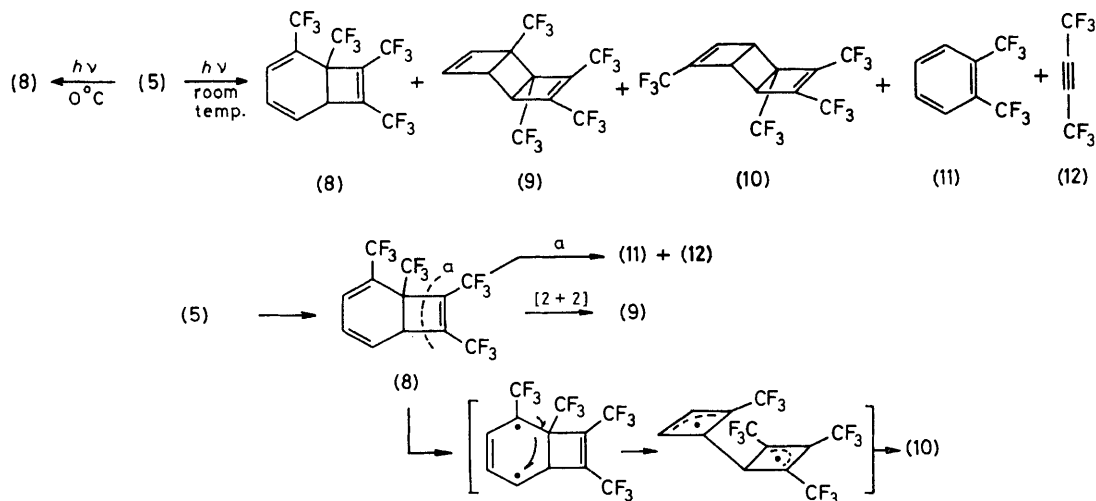
We next examined the photoisomerization of (5). Irradiation of a solution of (5) in pentane at room temperature with a high-pressure mercury lamp for 65 h gave a mixture of compounds (8)–(11). Compound (10), insoluble in pentane, was filtered off (*ca.* 5%). Preparative g.l.c. (SE. 30; 60 °C) of the 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; $\nu_{C=C}$ (CCl₄) 1710 and 1615 cm⁻¹; ¹H n.m.r. (CCl₄) δ 6.80 (m, 1H), 6.15 (m, 2H), and 3.95 (br, 1H); ¹⁹F n.m.r. (CCl₄) 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; $\nu_{C=C}$ (CCl₄) 1710 cm⁻¹; ¹H n.m.r. (CDCl₃) δ 6.66, 6.43, 3.55, and 3.46; ¹⁹F n.m.r. (CDCl₃) δ 0.0 (br), 1.3 (br, s),



SCHEME 1

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; ¹H n.m.r. [(CD₃)₂CO] δ 7.32, 4.37, 3.28, and 3.04; ¹⁹F n.m.r. [(CD₃)₂CO] δ 0.27 (sept.), 0.9 (q), 1.3 (m), and 1.9 (qq); m/z 376 (M^+). The ¹⁹F 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

† 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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