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REACTION OF TETRAKIS(TRIFLUOROMETHYL)FURAN AND ITS PHOTO-ADDUCT

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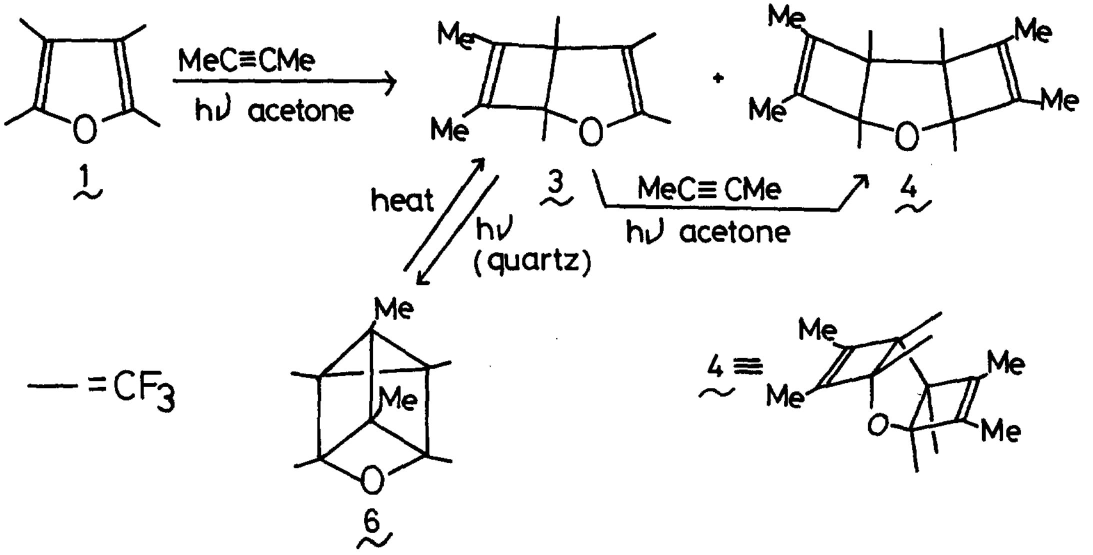
Our recent study concerning the synthesis of valence-bond isomers of hexakis(trifluoromethyl)oxepin$^{1)}$ led to the synthesis of tetrakis(trifluoromethyl)furan$^{2)}$ (1), which was synthesized by two other groups by a different route at almost the same time.$^{3)}$ This furan derivative (1) is considered to be an interesting molecule, because of the possibility of the isolation of valence-bond isomer(s), same as in the case of tetrakis(trifluoromethyl)thiophene$^{4)}$ (2). Though we tried to obtain the isomer(s) of 1, none of the isomers was obtained under the same photoreaction condition employed in the case of 2. On the other hand, acetone-sensitized reaction of 1 in the presence of dimethylacetylene for 30 hr gave two products; 1,3,4,5-tetrakis(trifluoromethyl)-6,7-dimethyl-2-oxabicyclo[3.2.0]hepta-3,6-diene (3) and 1,3,6,7-tetrakis(trifluoromethyl)-4,5,8,9-tetramethyl-2-oxatricyclo[5.2.0.0^{3,6}]nona-4,8-diene (4). 3: Yield$^{5)}$ 15%, colorless oil; IR (CCl_4) cm^{-1}: 2960 (ν C-H), 1690 (cyclobutene double bond), 1670 (enol ether double bond), 1140-1240 (ν C-F); ^{19}F-NMR$^{6)}$ (CCl_4) ppm; 10.8 (q. J=11.66), 4.6 (m.), 3.1 (q. J=10.5), -6.4 (m.) (relative intensity 1:1:1:1); ^{1}H-NMR (CCl_4) δ: 1.88 (br. m.), 1.95 (br. m.) 1:1 respectively, MS, m/e 394 (M^+). 4: Yield$^{5)}$ 12%, colorless crystals, mp 134-5°; IR (Nujiol) cm^{-1}: 1700 (cyclobutene double bond), 1160-1210 (ν C-F); ^{19}F-NMR ($CDCl_3$) ppm: 10.9, -1.9 (equal intensity; ^{1}H-NMR ($CDCl_3$) δ: 1.75 (broad signal); MS, m/e 448 (M^+). The stereochemical structure of 4 is speculated to be an anti-form because 4 failed to give any [$\pi 2s + \pi 2s$] product under direct or sensitized irradiation. The ratio of yields of 3 and 4 depends on the concentration of demethylacetylene. When the ratio of 1 and dimethylacetylene is about 1:1, the ratio of 3 and 4 is nearly 1:1. In this case, conversion of 1 to 3 and 4 was about 50% (calculated from ^{19}F-NMR spectrum). In the presence of a large excess of dimethylacetylene, 4 is obtained exclusively in a good yield. These facts indicate that 3 is formed first and then 4 is formed from 3. This was also ascertained by the NMR spectrum checked during irradiation. The bicyclo compound (3) so obtained is a partial substitution of trifluoromethyl groups in hexakis(trifluoromethyl)-2-oxabicyclo[3.2.0]hepta-3,6-diene$^{1)}$ (5) by methyl groups. Although 5 is photochemically innert to direct irradiation at room temperature, 3 is smoothly converted to compound (6), which shows m/e 394 (M^+) in mass spectrum. In the ^{19}F-NMR spectrum, signals of two kinds of trifluoromethyl groups were observed with equal intensity and two nonequivalent methyl signals were observed in ^{1}H-NMR spectrum. These spectral data show that the compound (6) must be the isomer of 3. Absorbtion bands of the olefinic region were not observed in the IR spectrum of 6, and 6 reproduced 3 by thermolysis (140°). Therefore, we concluded that the compound (6) is a $[\pi 2s + \pi 2s]$ product of 3, which is the first example of an oxygen containing tetracyclic-system; 1,3,4,5-tetrakis(trifluoromethyl)-6,7-dimethyl-2-oxatetracyclo[3.2.0.0^{3,7}.0^{4,6}]heptane. 6: Yield 66%, colorless oil, purified by bulb-to-bulb distillation 55-60° (bath temp.) at 14 mmHg; IR (CCl_4) cm^{-1}: 2960, 2920 (ν C-H), 1150-1250 (ν C-F); ^{19}F-NMR (CCL_4) ppm: 11, -3 (equal intensity); ^{1}H-NMR (CCl_4) δ: 1.4, 1.7 (broad signals, equal intensity); MS, m/e 394 (M$^+$).



Thermal cleavage of 6 must be paid a little attention because cleavage of the four-membered ring would take place preferentially over that of the C-C and C-O bond in the oxetane ring. We are now investigating the reaction of 6 with a transition metal complex.

References and Notes

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5) 3 and 4 were separated by using Varian GC Model 705, 100°, 10-m column with 15% DEGS on Chromosorb W. Satisfactory high resolution mass spectra were obtained for the new compounds.
6) Benzotrifluoride as an internal standard; upfield signals are positive.

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