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SYNTHESES WITH CYCLOBUTADIENES - 15.[1] PRISMANE / DEWAR BENZENE ISOMERIZATION - X-RAY CRYSTAL STRUCTURE OF TERT-BUTYL 3,4,5-TRI-TERT-BUTYL-2,6-BIS(TRIFLUOROMETHYL)PRISMANE-1-CARBOXYLATE

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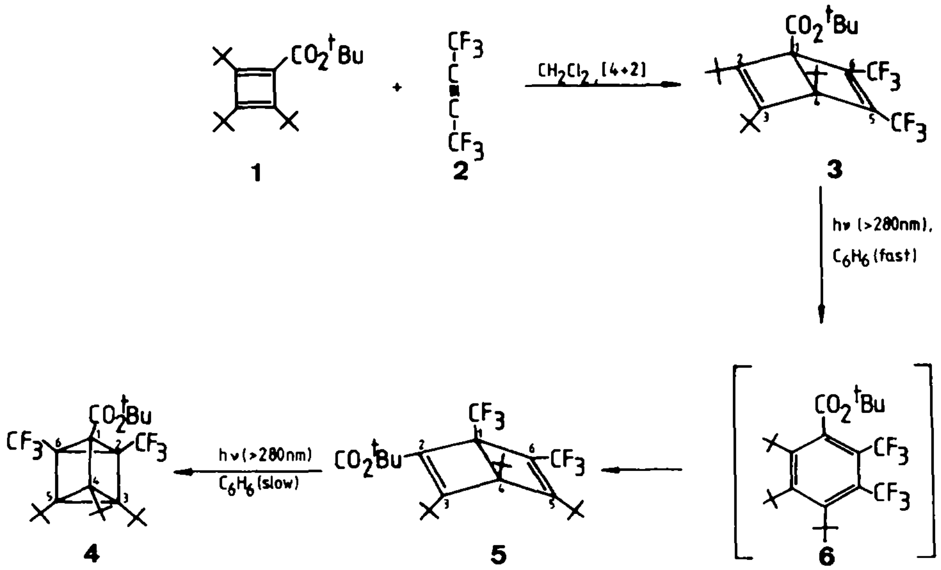
Abstract - The heavily substituted Dewar benzene derivatives 3 and 5 merely yield the carboxylic acids 7 and 9 by loss of isobutene when heated to 150-200 °C; isomerization to the benzoic acid 8 is not at all observed. Prismane derivative 4, which is obtained from 5 photochemically, behaves analogously at 150 °C, but the primarily formed acid 10 rearranges to the isomeric Dewar benzenecarboxylic acids 9 and 11 on prolonged heating at 150 °C. The Dewar benzenecarboxylic esters 12 and 13, obtained from 9 and 11 by esterification with diazomethane, are transformed into prismane 15 photochemically.

INTRODUCTION

Since more than 20 years, preparation and isomerization reactions of valence isomers of benzene derivatives were investigated intensively. The parent compounds - Dewar benzene [3], benzvalene [4] and prismane [5] - as well as a number of substituted derivatives have been synthesized and studied. It is obvious that the stability of one valence isomer of benzene relative to the others is strongly dependent on the nature of substituents as well as on the substitution pattern. With perfluoroalkyl groups, not only all of the isomers just mentioned [6,7] but also the bis(cyclopropenyl) isomer [8] have been isolated. Steric effects caused by tert-butyl groups exert a strong influence [9,10,11], which in the extreme case may thermodynamically favor the Dewar benzene over the aromatic structure [12].

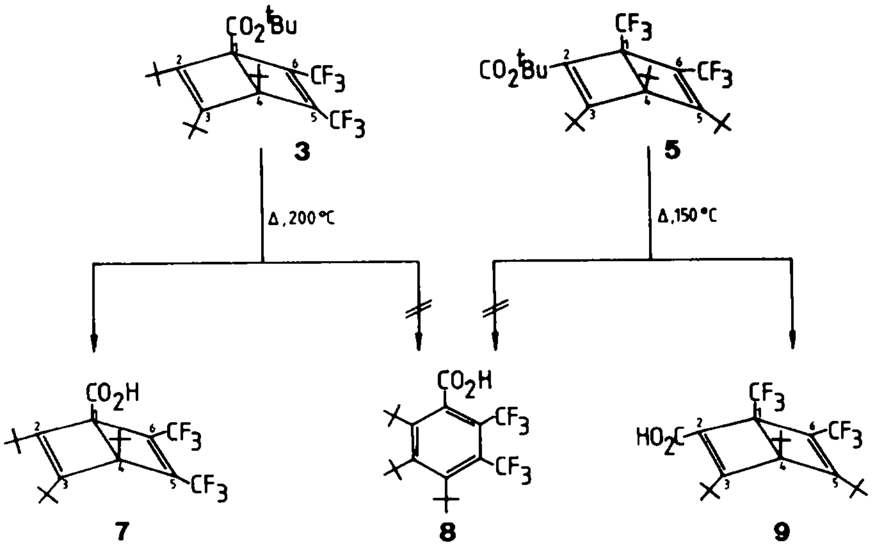
In the present paper, we report on isomerizations in a Dewar benzene / prismane system which carries both tert-butyl and trifluoromethyl substituents, namely Dewar benzenes 3 and 5 as well as prismane 4.



The bicyclic compound 3 is available by cycloaddition of hexafluoro-2-butyne (2) to the cyclobutadienecarboxylic ester 1. The two other starting materials were obtained by a photochemical Dewar benzene → Dewar benzene rearrangement via a benzene intermediate (3 → 6 → 5) and ring closure to give the prismane (5 → 4) on prolonged UV irradiation [10].

THERMAL BEHAVIOUR OF 3 AND 5

Loss of isobutene and formation of the bicyclic carboxylic acid 7 in a 77% yield is the only result when the Dewar benzene 3 is heated to 200 °C without a solvent. Compound 7 is characterized by the ν(O-H) absorption at 3300-2500 cm^{-1} in the IR spectrum as well as by the ^{1}H-NMR data δ = 1.19, 1.22, 1.26 (three tert-butyl groups) and 11.70 ppm (O-H). Only one singlet at δ = 102.3 for both CF_3 groups is seen in the ^{19}F-NMR spectrum. This was unexpected; in fact, the other Dewar benzene derivatives described in this paper, which also carry non-equivalent trifluoromethyl groups (9 and 12), show two quartets with a $^{5}J_{F,F}$ coupling constant of 9 Hz. That the ^{19}F magnetic equivalence of the CF_3 groups is accidental rather than caused by a symmetry element in the structure, is confirmed by the ^{13}C-NMR data: Besides the signals of the bridgehead carbons C-1 and C-4 ($\delta = 61.7, 74.1$), one finds four absorptions for the olefinic carbon atoms at $\delta = 145.4$ and 148.5 (quartets, $^{2}J_{C,F} = 35$ Hz, C-5/C-6) as well as $\delta = 152.3$ and 159.5 (C-2/C-3). The carboxylic carbon atom appears at $\delta = 178.3$. The δ-values of the carbon atoms in the bicyclic ring largely correspond to those in 3 [10].



Similar to 3, the isomeric Dewar benzene 5 suffers extrusion of isobutene to yield the Dewar benzenecarboxylic acid 9 at 150 °C in 1,1,2,2-tetrachloroethane. Thermal isomerization to the benzene derivative 8 could not be achieved. When the temperature is raised further, only uncontrolled decomposition occurs, as the case of the structurally related Dewar benzene-carboxylic ester 12 shows (200 °C, no solvent). In contrast, Dewar benzenes of type 5 bearing COOR or C≡N groups instead of CF_3 undergo isomerization to the corresponding aromatic compounds (8, COOR or CN instead of CF_3) already at 140 °C [10] (see discussion below).

The carboxylic function of 9 is recognized in the IR (ν(OH) at 3700-2500 cm^{-1}) as well as in the ^{1}H-NMR spectrum (δ = 8.80 ppm). The resonances of the tert-butyl groups appear at δ = 1.28, 1.33 and 1.34 ppm. In the ^{19}F-NMR spectrum, the two CF_3 groups give rise to two quartets at δ = 104.0 and 104.8 ($^{5}J_{F,F} = 9$ Hz). Further proof of the constitution of 9 is supplied by its formation during thermolysis of 4 as well as by its transformation into the prismane derivative 15 (see next paragraph).

THERMAL BEHAVIOR OF PRISMANE 4

When the prismane 4 is kept for two hours at 150^{0}C in 1,1,2,2-tetrachloroethane, about half of it is converted into prismanecarboxylic acid 10. In the ^{1}H-NMR spectrum, both 4 and 10 show one signal for the three C-CMe$_3$ groups ($\delta = 1.27$). The ester tert-butyl signal of 4 ($\delta = 1.43$) has disappeared in 10, and a OH absorption at $\delta = 10.85$ shows up instead. In the ^{19}F-NMR spectrum, the signal of the two equivalent CF$_3$ groups appears at slightly higher field ($\delta = 105.7$) than in 4 [10]. The ^{13}C-NMR spectrum shows only one signal for the pairs C-2/C-6 and C-3/C-5, resp., in agreement with the C_s symmetry of 10 [13].

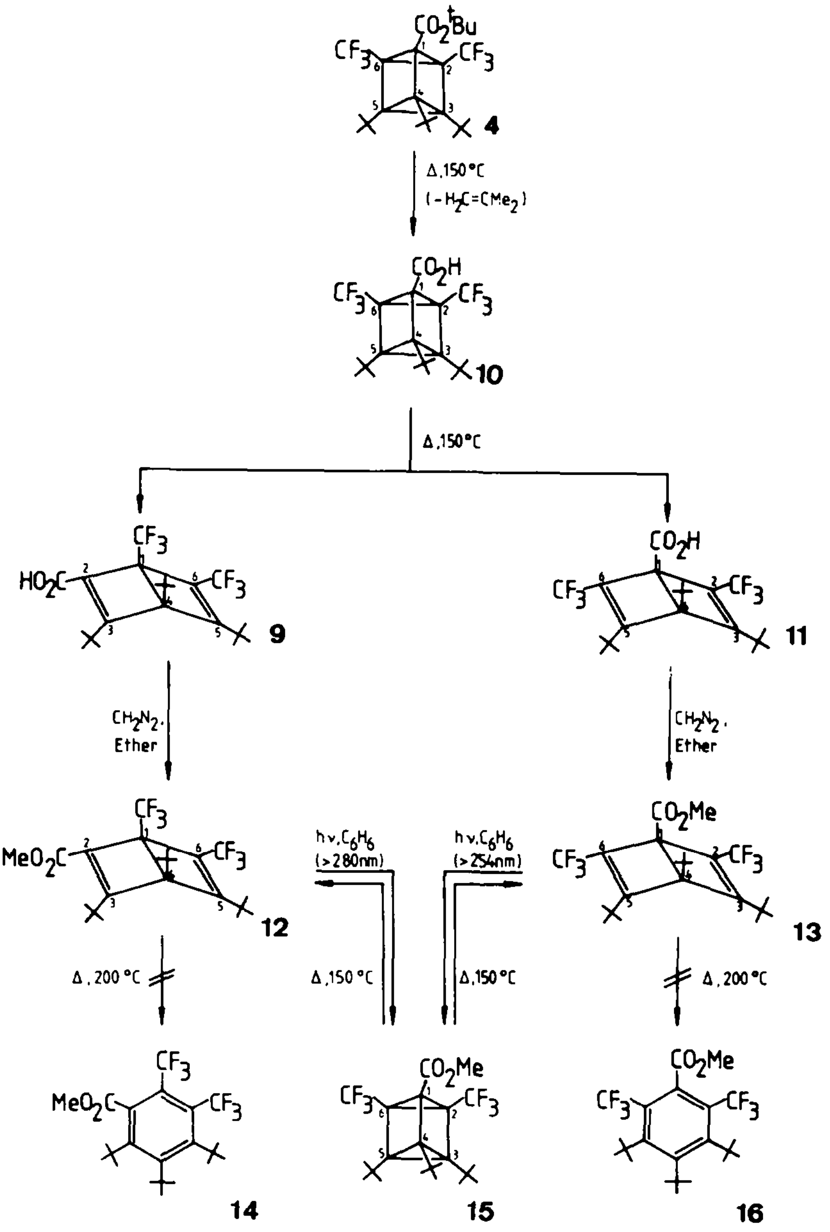
Prolonged heating (70 h at $150\,^{0}$C) converts prismane 4 via intermediarily formed 10 into a mixture of the two isomeric Dewar benzenecarboxylic acids 9 and 11 (ca. 1:1 by ^{19}F-NMR integration), which could neither be separated by chromatography (flash chromatography or MPLC with ether/pentane mixtures) nor by crystallization.

Therefore, the mixture of acids 9 and 11 was converted into the esters 12 and 13 by treatment with diazomethane (which does not undergo [3+2] cycloaddition to the C=C bonds for steric reasons). Column chromatography furnished 41% of 12 and 34% of 13. From these experiments, no hints were obtained that thermolysis of prismane 4 would produce the isomeric benzene derivatives; this contrasts with the behavior of those prismanes which carry COOR or CN rather than CF$_3$ substituents [10] (see below for discussion).

In agreement with its constitution, Dewar benzene 12 shows three tert-butyl signals in the ^{1}H-NMR spectrum ($\delta = 1.27$, 1.31 and 1.32 ppm) and two CF$_3$ quartets ($\delta = 103.8$ and 105.2, $^{5}J_{F,F} = 9$ Hz) in the ^{19}F-NMR spectrum. The bicyclic skeleton is recognized by the ^{13}C-NMR data which resemble very much those of 5 [10]: The bridgehead carbons appear at $\delta = 58.4$ (q, $^{2}J_{C,F} = 33$ Hz, C-1) and $\delta = 81.9$ (C-4); at lower field, one finds C-6 ($\delta = 132.1$, q, $^{2}J_{C,F} = 37$ Hz) and C-2 ($\delta = 135.1$) and finally C-3/C-5 ($\delta = 172.2$, 173.0) which are deshielded because of the acceptor groups in β-position.

The Dewar benzene isomer 13 has C_s symmetry which becomes obvious from the reduced number of signals in the ^{1}H- ($\delta = 1.23$, 1.33, tert-butyl), ^{19}F- ($\delta = 104.3$) and ^{13}C-NMR spectra. The olefinic carbons in the bicyclic skeleton give rise to only two signals [$\delta = 134.6$, q, $^{2}J_{C,F} = 38$ Hz (C-2/C-6) and $\delta = 171.9$ (C-3/C-5)], which can be assigned based on the F/C coupling.

Contrary to the situation in **12**, no such coupling exists for C-1 ($\delta = 53.4$) and C-4 ($\delta = 79.2$); the assignment of C-4 to the low-field signal follows from experience.



Even at 200 °C in diphenyl ether, the Dewar benzenecarboxylic esters 12 and 13 do not furnish the isomeric benzene derivatives 14 and 16, resp.. While 12 suffers decomposition, compound 13 can be recovered almost quantitatively even after 20 h at this temperature.

Irradiation of Dewar benzene 12 (benzene, $\lambda > 280$ nm) produces prismane 15 in 74% yield besides some unchanged starting material. Under the same conditions, the isomer 13 does not undergo intramolecular [2+2] cycloaddition. However, the isomerization 13 → 15 can be brought about at $\lambda > 254$ nm (70% yield of 15). ^{1}H- and ^{19}F-NMR data of 15 compare well with those of 4. A further proof of the structure of 15 is supplied by quantitative thermal re-isomerization into a 3:2 mixture of Dewar benzene derivatives 12 and 13 (150 °C in $Cl_2DC\text{-}CDCl_2$, carried out in an NMR tube).

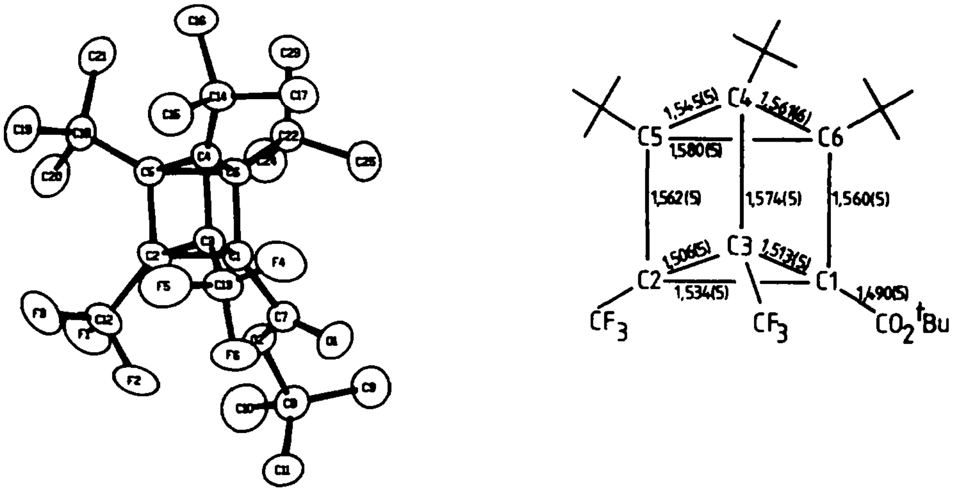
DISCUSSION

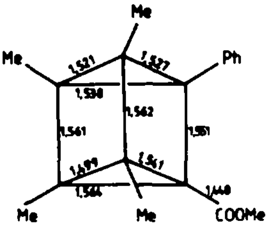
The photochemical behavior of the trifluoromethyl-substituted Dewar benzenes 3, 5, 12 and 13 parallels that of other derivatives which have COOR [10,11] or C≡N [10] rather than CF_3 substituents. However, their thermal behavior has been found to be quite different. All Dewar benzenes mentioned in this paper (3,5,7,9,11,12,13) resist to thermal isomerization to the corresponding benzene derivatives. We assume that the substitution pattern in 6,8,14 and 16 renders the benzene structure thermodynamically unfavorable. Compared to a methyl group, the much higher bulkiness of a trifluoromethyl group [14] has to be taken into account. Furthermore, dipole-dipole interaction between the neighboring CF_3 groups in 6,8 and 14 causes an electronic destabilization [15]. A third destabilizing factor is due to the vicinity of three tert-butyl groups which in the benzenes (6,8,14,16) would be forced to assume a more or less eclipsed arrangement around the benzene ring. A comparable situation holds for hexakis(perfluoroalkyl)benzenes [16,17] and 3,4,5,6-tetra-tert-butylphthalic acid dimethylester [12], both of which are transformed into the corresponding Dewar benzene isomers at elevated temperature.

In summary, the combined influence of CF_3 and ^{t}Bu substituents accounts for the fact that prismanes 4 and 15 are transformed into Dewar benzenes rather than benzene derivatives thermally. Of course, this result suggests that bicyclic intermediates are also involved in other [10,11] thermal prismane → benzene isomerizations.

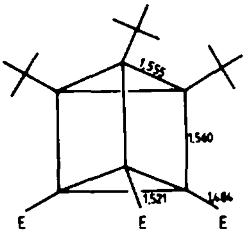
MOLECULAR STRUCTURE OF PRISMANE **4**

The molecular structure of prismane **4** has been determined by X-ray crystal structure analysis (Fig. 1). The structures of only three other prismane derivatives have been published so far, two of which were obtained by X-ray diffraction (**17** [11] and **18** [18]) and one by electron diffraction methods (**19** [19]). The bond lengths in the tetracyclic skeleton of all four fully substituted prismanes are compiled in Fig. 1. Not unexpectedly, prismane **4** shows the highest distortions. Similar to **18**, bond lengths in the ^{t}Bu-substituted cyclopropane ring are longer than in the other three-membered ring. The two longest bonds in each ring are opposite to each other (C1-C2 and C5-C6). The geometry around the C1-C7 bond is such that the ester group is not in a bisecting conformation relative to the cyclopropane ring C1-C2-C3 (torsion angle O1-C7-C1-midpoint of C2-C3: 81.4 °) - this situation parallels the one found in **18** [18] and contrasts with that in **17** [11] - and consequently does not influence the bond lengths in the ring by its π-acceptor properties [20]. Therefore, the shortening of the C2-C3 bond relative to C2-C1 (C3-C1 and C2-C3 are equal within their esd's) is probably due to the σ acceptor property of the CF_3 groups which is expected to shorten the adjacent bonds and to lengthen the distal one [21]. However, no simple reason is seen for the different bond lengths of C1-C3 and C2-C3 which both have the same substitution pattern. The values of the exocyclic bond angles display the dominating influence of unfavorable steric interactions between the three tert-butyl groups [C16-C21 3.391(8), C16-C23 3.483(9), C21-C23 3.480(8)Å, van der Waals radius between methyl groups 4.0 Å [22]]. Obviously, some steric strain is relieved by a distortion of the bond angles which renders the angles between the substituents and the cyclopropane ring larger than those between the substituents and the bonds to the second three-membered ring. As a consequence, the reverse distortion appears at C1, C2, C3, but only to an extent which approximately maintains the van der Waals distance between the two CF_3 groups [F2-F6 2.572(4) Å, van der Waals radius of F: 1.35 Å [22]]. The same type of bond angle distortion has already been noted in **18** [18].



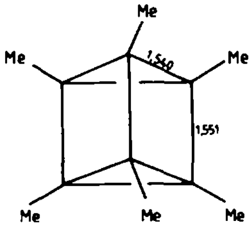


17[11]



(E = COOMe)

18[18]



19[19]

Fig. 1 Top: ORTEP plot and bond distances [Å] in the tetracyclic framework. - Bottom: Bond lengths [Å] in other prismane derivatives. **18** has C_s symmetry, **19** has D_{3h} symmetry.

Table 1. Positional and thermal parameter of non-hydrogen atoms in **4**.
Esd's are in parentheses. $B_{eq} = 4/3\cdot\Sigma_i\Sigma_j B_{ij}\cdot\underline{a}_i\cdot\underline{a}_j$

Atom	X	Y	Z	B_{eq}[Å^2]	Atom	X	Y	Z	B_{eq}[Å^2]
F1	0.1759(2)	0.3597(3)	0.7176(3)	8.2 (1)	C10	0.4010(4)	0.4654(6)	0.8796(5)	7.7(2)
F2	0.2078(2)	0.3281(3)	0.5979(2)	7.40(9)	C11	0.4210(3)	0.4467(6)	0.7257(4)	6.1(2)
F3	0.0891(2)	0.2813(4)	0.5931(3)	9.8 (1)	C12	0.1661(3)	0.2770(5)	0.6475(4)	5.3(1)
F4	0.2693(2)	0.0525(4)	0.5141(2)	8.08(9)	C13	0.2305(3)	0.0483(5)	0.5329(3)	4.9(1)
F5	0.1575(2)	0.0541(4)	0.4652(2)	8.2 (1)	C14	0.1764(3)	-0.2082(5)	0.6510(3)	4.2(1)
F6	0.2686(2)	0.1531(3)	0.5202(2)	6.83(8)	C15	0.1126(4)	-0.2000(6)	0.5515(4)	6.7(2)
01	0.4061(2)	0.1561(4)	0.6951(2)	5.41(9)	C16	0.1409(3)	-0.2875(5)	0.7124(4)	6.3(2)
02	0.3610(2)	0.2760(3)	0.7915(2)	3.87(7)	C17	0.2515(3)	-0.2793(5)	0.6468(4)	6.3(1)
C1	0.2835(3)	0.0999(5)	0.7193(3)	3.5 (1)	C18	0.0995(3)	0.0467(5)	0.7764(3)	4.1(1)
C2	0.1943(3)	0.1430(4)	0.6801(3)	3.7 (1)	C19	0.0197(3)	0.0357(7)	0.6941(4)	6.3(2)
C3	0.2252(3)	0.0410(5)	0.6293(3)	3.6 (1)	C20	0.1037(3)	0.1784(6)	0.8255(4)	6.3(1)
C4	0.2015(2)	-0.0692(4)	0.6873(3)	3.2 (1)	C21	0.1026(3)	-0.0556(6)	0.8513(4)	6.4(1)
C5	0.1701(3)	0.0363(4)	0.7391(3)	3.5 (1)	C22	0.3220(3)	-0.0551(5)	0.8736(3)	4.3(1)
C6	0.2621(3)	-0.0079(4)	0.7796(3)	3.4 (1)	C23	0.2986(3)	-0.1802(6)	0.9118(4)	6.2(2)
C7	0.3576(3)	0.1795(5)	0.7327(3)	3.7 (1)	C24	0.3326(4)	0.0522(7)	0.9467(3)	6.4(2)
C8	0.4259(3)	0.3768(5)	0.8145(3)	4.6 (1)	C25	0.4031(3)	-0.0801(6)	0.8618(4)	6.4(2)
C9	0.5072(3)	0.3151(6)	0.8636(4)	6.8 (2)					

Table 2. Bond distances and bond angles in **4**.

Bond distances [Å]

F1	C12	1.321(5)	C1	C7	1.490(5)	C8	C9	1.500(7)
F2	C12	1.325(5)	C2	C3	1.506(5)	C8	C10	1.511(7)
F3	C12	1.315(5)	C2	C5	1.562(5)	C8	C11	1.497(7)
F4	C13	1.325(5)	C2	C12	1.487(5)	C14	C15	1.531(7)
F5	C13	1.333(5)	C3	C4	1.574(5)	C14	C16	1.521(6)
F6	C13	1.316(5)	C3	C13	1.493(5)	C14	C17	1.528(7)
01	C7	1.199(4)	C4	C5	1.545(5)	C18	C19	1.518(6)
02	C7	1.318(4)	C4	C6	1.561(5)	C18	C20	1.531(6)
02	C8	1.488(4)	C4	C14	1.538(5)	C18	C21	1.531(7)
C1	C2	1.534(5)	C5	C6	1.580(5)	C22	C23	1.522(6)
C1	C3	1.513(5)	C5	C18	1.534(5)	C22	C24	1.524(7)
C1	C6	1.560(5)	C6	C22	1.522(5)	C22	C25	1.517(6)

Selected bond angles [°]

C7	02	C8	122.1(3)	C2	C3	C4	90.3(3)	C5	C4	C6	61.2(2)
C2	C1	C3	59.2(2)	C2	C3	C13	128.1(4)	C5	C4	C14	136.3(3)
C2	C1	C6	90.5(3)	C4	C3	C13	134.2(4)	C6	C4	C14	135.6(3)
C2	C1	C7	128.3(3)	C3	C4	C5	89.3(3)	C2	C5	C4	89.3(3)
C3	C1	C6	90.9(3)	C3	C4	C6	88.6(3)	C2	C5	C6	88.7(3)
C3	C1	C7	128.8(3)	C3	C4	C14	124.6(3)	C2	C5	C18	125.2(3)
C6	C1	C7	133.4(3)	C5	C4	C6	61.2(2)	C4	C5	C6	59.9(2)
C1	C2	C3	59.7(2)	C5	C4	C14	136.3(3)	C4	C5	C18	135.3(3)
C1	C2	C5	91.2(3)	C6	C4	C14	135.6(3)	C6	C5	C18	136.5(3)
C1	C2	C12	124.9(4)	C2	C5	C4	89.3(3)	C1	C6	C4	89.6(3)
C3	C2	C5	91.2(3)	C2	C5	C6	88.7(3)	C1	C6	C5	89.6(3)
C3	C2	C12	127.8(4)	C2	C5	C18	125.2(3)	C1	C6	C22	122.8(3)
C5	C2	C12	135.4(4)	01	C7	C1	123.8(4)	C4	C6	C5	58.9(2)
C1	C3	C2	61.1(3)	02	C7	C1	109.7(3)	C4	C6	C22	137.6(3)
C1	C3	C4	90.9(3)	C3	C4	C6	88.6(3)	C5	C6	C22	137.1(3)
C1	C3	C13	127.1(3)	C3	C4	C14	124.6(3)	01	C7	02	126.6(4)

EXPERIMENTAL PART

Melting points: Copper block (uncorrected).- Elemental analyses: Perkin-Elmer Elemental Analyzer 240.- IR spectra: Beckman IR-20 A, Perkin-Elmer 710 B.- ^{1}H-NMR spectra: Varian EM 390, TMS as internal standard.- ^{13}C-NMR spectra: Bruker WP 200, TMS as standard.- ^{19}F-NMR spectra: Varian EM 390, hexafluorobenzene as standard.- Photolyses: High-pressure mercury lamp Philips HPK 125 W, Pyrex glass vessel ($\lambda > 280$ nm); low-pressure mercury lamp Hanau TNN 15/32, 15 W, Quartz glass vessel ($\lambda > 254$ nm).- Column chromatography: Silica gel ICN Biomedicals, 32-63 µm; column dimensions 30 x 4.2 cm; flash chromatography [23] was done at 0.4 - 0.7 bar.- Preparative MPLC: Column (46 x 2.6 cm) filled with 150 g of silica gel Li Chroprep ^{R} Si 60, 15-25 µm (Merck); Büchi 681 chromatography pump.- All solvents had been dried and distilled. The petrolether used had a boiling point range of 30-75 °C. The syntheses of **3**-**5** [10] have been published before.

2,3,4-Tri-tert-butyl-5,6-bis(trifluoromethyl)bicyclo[2.2.0]hexa-2,5-diene-1-carboxylic acid (7). Dewar benzene **3** [10] (1.45 g, 3.00 mmol) is placed in a Schlenk tube which is kept for 1.5 h at 200 °C in an oil bath. Flash chromatography of the resulting brown oil (110 g of silica gel, 1.5 l of ether-petrolether (1:7) yields:

a) 90 mg (6%) of unchanged Dewar benzene **3**, identified by its IR spectrum;

b) 980 mg (77%) of Dewar benzene **7** as a colorless oil which crystallized on short standing, mp. 183 °C.- IR(KBr): 3300-2500 (OH), 1695, 1680 cm^{-1} (C=O).- ^{1}H-NMR(CDCl$_3$): δ = 1.19, 1.22, 1.26 (each s, each 9H, ^{t}Bu), 11.70 (broad, 1H, COOH).- ^{19}F-NMR(CDCl$_3$): δ = 102.3 (s, 6F, CF$_3$).- ^{13}C-NMR(CDCl$_3$): δ = 29.1, 30.7, 31.8 [C($\underline{C}$H$_3$)$_3$], 34.0, 34.6, 35.0 [$\underline{C}$(CH$_3$)$_3$], 61.7 (C-1), 74.1 (C-4), 119.8, 120.0 (each q, $^1J_{C,F}$ = 273 Hz, $\underline{C}$F$_3$), 145.4, 148.5 (each q, $^2J_{C,F}$ = 35 Hz, C-5/C-6), 152.3, 159.5 (C-2/C-3), 178.3 ($\underline{C}$O$_2$H).- $C_{21}H_{23}F_6O_2$ (426.44) calc. C, 59.15; H, 6.62. Found C, 59.2; H, 6.67.

3,4,5-Tri-tert-butyl-2,6-bis(trifluoromethyl)tetracyclo[2.2.0^{2,6}.0^{3,5}]hexane-1-carboxylic acid (10). The solution of prismane **4** [10] (230 mg, 0.48 mmol) in 1,1,2,2-tetrachloroethane (2 ml) is placed in a Schlenk tube which is kept at reflux for 2 h (oil bath temperature 150 °C). The solvent is removed by Kugelrohr distillation, and the oily residue is separated by MPLC with 1 l of ether-petrolether (1:15) and 500 ml of ether:

a) 100 mg (43%) of unchanged prismane **4**, identified by IR-comparison;

b) 110 mg (54%) colorless crystals of prismanecarboxylic acid **10**, mp. 227 °C (recryst. from petrolether at -30 °C).- IR(KBr): 3600-2500 (OH), 1710 cm^{-1} (CO).- ^{1}H-NMR(CDCl$_3$): δ = 1.27 (s, 27 H, ^{t}Bu), 10.85 (broad, 1H, COOH).- ^{19}F-NMR(CDCl$_3$): δ = 105.7 (s, 6F, CF$_3$).- ^{13}C-NMR (CDCl$_3$): δ = 30.2, 30.5 (2x) [C($\underline{C}$H$_3$)$_3$], 31.6(2x), 32.8 [$\underline{C}$(CH$_3$)$_3$], 44.6 ($^2J_{C,F}$ = 43 Hz, C-2/C-6), 45.5 (C-1), 60.1 (C-3/C-5), 61.1 (C-4), 122.5 ($^1J_{F,C}$ = 273 Hz, CF$_3$), 169.6 ($\underline{C}$O$_2$H).- $C_{21}H_{33}F_6O_2$ (426.44) calc. C, 59.15; H, 6.62. Found C, 58.9; H, 6.85.

Thermal isomerization of prismane **4** into Dewar benzenecarboxylic acids **9** and **11**. The solution of prismane **4** [10] (1.50 g, 3.11 mmol) in 1,1,2,2-tetrachloroethane (4 ml) is kept at reflux for 70 h (oil bath temperature 150 °C). The solvent is removed by Kugelrohr distillation (80 °C/0.01 Torr) and the oily brown residue is separated by flash chromatography on silica gel (110 g, 1 l of ether as eluent). A colorless oil consisting of **9** and **11** (1.21 g, 91%) is obtained, which crystallized on short standing.- ^{1}H-NMR($CDCl_3$): $\delta = 1.29, 1.32, 1.34, 1.36$ (each s, each 9H, ^{t}Bu).- ^{19}F-NMR($CDCl_3$): $\delta = 104.0, 104.8$ [each q, $^5J_{F,F} = 9$ Hz, each 3F, CF_3 (**9**)], 104.6 [s, 6F, CF_3 (**11**)].

Esterification of Dewar benzenecarboxylic acids **9** and **11** with diazomethane. To a solution of the mixture of isomers **9** and **11** (1.21 g, 2.84 mmol) in 10 ml of methanol-water (10 : 1), a freshly prepared ethereal solution of diazomethane is added in portions, until gas evolution has ceased [24]. The solvent is evaporated at 30 °C/15 Torr and the remaining oil is subjected to flash chromatography on 110 g of silica gel with 2 l of ether-petrolether (1:50). This procedure furnishes 490 mg of Dewar benzenecarboxylic ester **12**, 380 mg of a mixture of **12** and **13**, and 220 mg of Dewar benzenecarboxylic ester **13**. The mixture of **12** and **13** is separated by MPLC with ether-petrolether (1:50), and the corresponding batches of the two isomers are combined:

a) Methyl 3,4,5-tri-tert-butyl-1,6-bis(trifluoromethyl)bicyclo[2.2.0]hexa-2,5-diene-2-carboxylate (**12**): 560 mg (41%) of a colorless oil which crystallizes on short standing to give colorless platelets, mp. 121 °C (recryst. from EtOH at -30 °C).- IR(KBr): 1725 (C=O), 1635 cm^{-1} (C=C).- UV(hexane): λ_{max} (lg ε) = 229 (3.41), 254 nm (3.08).- ^{1}H-NMR($CDCl_3$): $\delta = 1.27, 1.31, 1.32$ (each s, each 9H, ^{t}Bu), 3.77 (s, 3H, OCH_3).- ^{19}F(NMR)($CDCl_3$): $\delta = 103.8$, 105.2 (each q, $^5J_{F,F} = 9H$, each 3F, CF_3).- ^{13}C-NMR($CDCl_3$): $\delta = 30.5, 30.7, 31.0$ [$C(\underline{C}H_3)_3$], 31.5, 33.5, 34.9 [$\underline{C}(CH_3)_3$], 51,8 (OCH_3), 58.4 ($^2J_{C,F} = 33$ Hz, C-1), 81.9 (C-4), 120.9 ($^1J_{C,F} = 271$ Hz, CF_3), 125.3 ($^1J_{C,F} = 278$ Hz, CF_3), 132.1 ($^2J_{C,F} = 37$ Hz, C-6), 135.1 (C-2), 164.3 ($\underline{C}O_2CH_3$), 172.2, 173.0 (C-3/C-5).- $C_{22}H_{30}F_6O_2$ (440.47) calc. C, 59.99; H, 6.86. Found C, 60.1; H, 6.96.

b) Methyl 3,4,5-tri-tert-butyl-2,6-bis(trifluoromethyl) bicyclo [2.2.0]hexa-2,5-diene-1-carboxylate (**13**). Yield 470 mg (34%), colorless crystals, mp. 169 °C (recryst. from petrolether at -30 °C).- IR(KBr): 1725 (C=O), 1640 cm^{-1} (C=C).- UV(hexane): λ_{max} (lg ε) = 222 nm (3.41).- ^{1}H-NMR($CDCl_3$): $\delta = 1.23$ (s, 9H, ^{t}Bu), 1.33 (s, 18H, ^{t}Bu), 3.75 (s, 3H, OCH_3).- ^{19}F-NMR($CDCl_3$): $\delta = 104.3$ (s, 6F, CF_3).- ^{13}C-NMR($CDCl_3$): $\delta = 29.9$, 30.8(2x) [$C(\underline{C}H_3)_3$], 34.8, 34.9(2x) [$\underline{C}(CH_3)_3$], 52.3 ($^1J_{C,H} = 147$ Hz, OCH_3), 53.4 (C-1), 79.2 (C-4), 121.1 ($^1J_{C,F} = 272$ Hz, CF_3), 134.6 ($^2J_{C,F} = 33$ Hz, C-2/C-6), 170.1 ($\underline{C}O_2CH_3$), 171.9 (C-3/C-5).- $C_{22}H_{30}F_6O_2$ (440.47) calc. C, 59.99; H, 6.86. Found C, 60.0; H, 6.95.

Methyl 3,4,5-tri-tert-butyl-2,6-bis(trifluoromethyl)tetracyclo[$2.2.0.0^{2,6}.0^{3,5}$]hexane-1-carboxylate (**15**). a) By photolysis of Dewar benzene **12**: The solution of **12** (340 mg, 0.77 mmol) in 40 ml of benzene is irradiated ($\lambda > 280$ nm) for 30 h at room temperature. The solvent is evaporated (30°C/15 Torr), and the residue is recrystallized several times from petrolether (-30 °C). One obtains 250 mg (74%) of **15** as colorless crystals, mp. 195°C. The mother liquor contains **15** and **12** in a 1:6 ratio (by ^{1}H-NMR spectroscopy).- IR(KBr) of **15**: 1730 cm^{-1} (C=O).- ^{1}H-NMR(CDCl$_3$): δ = 1.30 (s, 9H, ^{t}Bu), 1.33 (s, 18H, ^{t}Bu), 3.79 (s, 3H, OCH$_3$).- ^{19}F-NMR(CDCl$_3$): δ = 105.2 (s, 6F, CF$_3$).- $C_{22}H_{30}F_6O_2$ (440.47) calc. C, 59.99; H, 6.86. Found C, 60.1; H, 6.78.

b) By photolysis of Dewar benzene **13**: The solution of **13** (30 mg) in CDCl$_3$ (0.3 ml) is irradiated at room temperature in an NMR tube with light of λ > 254 nm. According to ^{19}F-NMR monitoring, the maximum concentration of prismane **15** is reached after 24 h (ca. 70%). On prolonged irradiation, increasing amounts of decomposition products are formed. Prismane **15** was identified by an increase of signal intensity on addition of an independently synthesized sample of **15**.

Thermal behavior of Dewar benzenes **12** and **13**

The solution of **12** (30 mg) in diphenylether (0.3 ml) in an NMR tube is kept at 200 °C (oil bath temperature) for 22 h. Monitoring of the reaction by ^{1}H- and ^{19}F-NMR spectroscopy indicates unspecified decomposition, but gives no hint to the eventual formation of benzene derivative **14**.

A similar experiment with **13** shows mostly unchanged starting material after 20 h. On further heating, unspecified decomposition products increase. The formation of benzene derivative **16** was not observed.

Thermal isomerization of prismane **15** to the Dewar benzenes **12** and **13**

The solution of prismane **15** (30 mg) in Cl$_2$DC-CDCl$_2$ in an NMR tube is heated to 150 °C. According to ^{1}H- and ^{19}F-NMR spectroscopy, quantitative isomerization to the isomeric Dewar benzene derivatives **12** and **13** (3:2) has taken place after 110 h.

X-Ray crystal structure analysis of **4** [25]

Crystal data: $C_{25}H_{36}O_2F_6$, $M_r = 482.6$, monoclinic, space group P $2_1/c$, $a = 17.554(3)$, $b = 10.271(3)$, $c = 15.099(8)$ Å, $\beta = 110.40(2)$ °, $Z = 4$, $D_x = 1.256$ g cm^{-3}. Data collection: Crystal dimensions ca. 0.6 · 0.4 · 0.4 mm, diffractometer Enraf-Nonius CAD 4 (Mo-K$_\alpha$, monochromatized ω/2θ scan, scan width 0.80 + 0.35 tan θ, scan speed 1.1-4.0 ° min^{-1} depending on intensity), 3317 independent reflections with $2.00 \leqslant \theta \leqslant 22.50$ °. An average intensity loss of 13.9% was observed for three monitoring reflections ($5\,4\,\bar{1}$, 1 4 6, 2 5 2) which was accounted for by linear data correction. No absorption correction was applied (μ(Mo-K$_\alpha$) = 1.019 cm^{-1}). Structure solution and refinement: The structure was solved with MULTAN 82 and refined by full-matrix least-squares methods. All hydrogen atoms were located in a ΔF map and refined with B = 7.0 Å^2. The 2 0 0 reflection was discarded because of $F_o \ll F_c$. $R = 0.0627$, $R_w = (\Sigma\Delta F^2/\Sigma F_o^{\,2})^{1/2} = 0.0571$ (2356 reflections having $I > 2\sigma(I)$, unit weights, 442 variables, shift/error ratio < 1.83). Positional and thermal parameters of nonhydrogen atoms are given in Table 1, bond distances and angles in Table 2. Further data have been deposited [26].

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26 The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.