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NEW SYNTHESIS OF 1,2-BISMETHYLENECYCLOBUTANES BY [2+2] CYCLOADDITION REACTION OF 1,1-DIPHENYL-4,4-BIS(TRIFLUOROMETHYL)-BUTATRIENE WITH ELECTRON-RICH ALKENES

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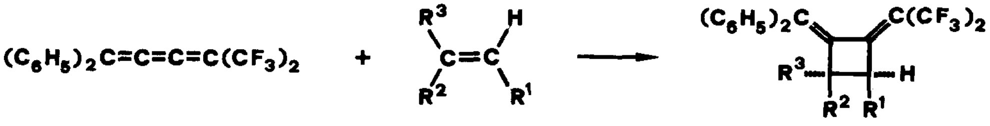
Abstract: *The title compound* 1 *undergoes thermal* $[_{\pi}2_{s}+_{\pi}2_{s}]$ *cycloaddition reactions with 1,1-dimethoxyethylene or enamines to produce 1,2-bismethylenecyclobutanes of type* 3.

Butatrienes display an interesting position-selective behavior towards cycloaddition reactions. For example, recently it has been established that several substituted butatrienes react with 1,3 dipoles like diazomethane[1] or 1,3-dithiolylium-4-olates[2,3] at one of the terminal double bonds exclusively and not at the central one. In connection with this study, we wish to report preliminary results on [2+2] cycloaddition reactions which position-specifically take place at the central double bond of the title butatriene. To our knowledge there is no report on thermal [2+2] cycloaddition reactions of butatrienes to CC double bonds except photochemical dimerization of tetraarylbutatrienes[4].



1 **2** **3**

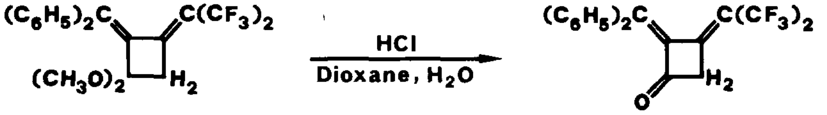
As we now found, the reaction of 1,1-diphenyl-4,4-bis(trifluoromethyl)butatriene[5] (1) in the presence of excess 1,1-dimethoxyethylene (2a) at 100-110°C proceeds with regiospecific formation of the 1,2-bismethylenecyclobutane derivative 3a in 63% yield as pale yellow needles (table 1).

Table 1. 1,2-Bismethylenecyclobutanes 3 from 1 and 2

2,3	R^1	R^2	R^3	3	
				yield [%][a]	mp. [°C]
a	H	CH_3O	CH_3O	63	134.5-135.5
b	H	$(CH_3)_2N$	$(CH_3)_2N$	54	>158[b]
c	$-(CH_2)_3-$		morpholino	69	152-153
d	$-(CH_2)_4-$		morpholino	68	154-155[b]

a) Analytically pure. b) dec.

The absence of an allenic infrared vibration and of an allenic carbon in the ^{13}C NMR spectrum as well as the following spectroscopic data are consistent with the constitution 3a: IR, 1662, 1649 cm^{-1} (C=C); ^{1}H NMR (C_6D_6), δ 2.93 (s, 2 CH_3O), 3.03 (mc, CH_2), 6.93-7.50 (m, 2 C_6H_5); ^{19}F NMR (C_6D_6), δ -58.42 (qt, $^{4}J_{FF}$ = 7.34 Hz, $^{5}J_{HF}$ = 2.51 Hz, CF_3), -62.05 (qt, $^{4}J_{FF}$ = 7.34 Hz, $^{5}J_{HF}$ = 1.66 Hz, CF_3); MS, *m/e* 428 (38%, M^+). On acid catalyzed hydrolysis, 3a is converted to the cyclobutanone derivative 4 in 64% yield (mp. 143-145°C dec; IR, 1758 cm^{-1} (C=O); MS, *m/e* 382 (100%, M^+)).



3a **4**

In a similar way, 1 combines with the enamines 2b-d even at 20-100°C to produce the 1,2-bismethylenecyclobutane derivatives 3b-d of table 1. Their constitutions are also in agreement with elemental analyses and spectroscopic data.

Furthermore, the solvent influence on the cycloaddition rate constant is relatively small as evidenced by k(acetonitrile)/k(hexane) = 208 for the reaction of 1 with 1-morpholinocyclohexene (45°C). Since this is a very much smaller solvent dependence than reported for the cycloaddition reaction of tetracyanoethylene with enol ethers involving a zwitterionic intermediate, where k(acetonitrile)/k(cyclohexane) values of up to 29 000 have been found[6], we interpret our reactions as a concerted cycloaddition. In principle, this concerted [2+2] cycloaddition reaction can mechanistically proceed either as a $[_{\pi}2_s + _{\pi}2_a]$ process at the central isolated CC double bond of 1, or as a $[_{\pi}2_s + _{\pi}2_s]$ one involving the central carbon atoms of the 1,3-diene system in 1, followed by 90° rotations of the terminal carbons. Because, the frontier atomic orbital coefficients at the carbons of the central isolated CC double bond of 1 are zero, we prefer the above-mentioned concerted $[_{\pi}2_s + _{\pi}2_s]$ process. - Further studies are in progress.

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