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THERMAL CYCLOADDITION OF CARBONYL COMPOUNDS TO A STABLE CYCLOBUTADIENE [1]

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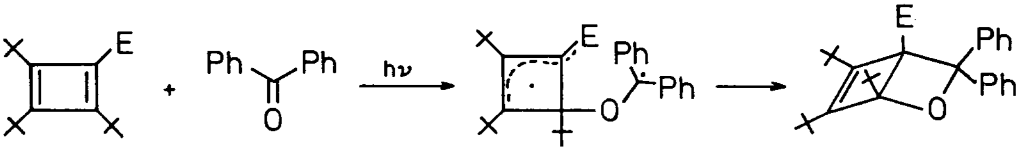
Summary: In contrast to acid chlorides which undergo addition to 1 to form cyclobutene derivatives 4, aldehydes react with the same antiaromatic starting compound 1 to give the [4+2]-cycloaddition product 5. Activated ketones such as 1,1,1-trifluoroacetone, biacetyl, and acetyl cyanide undergo a clean cycloaddition reaction to tricyclic compounds (1 + 6a-c → 9a-c), whereas trioxoindane yields a bicyclic product (1 + 6d → 8d).

Previously only one example of a light-induced cycloaddition of a ketone to a cyclobutadiene had been reported. Benzophenone reacts with t-butyl 2,3,4-tri-t-butylcyclobutadiene-1-carboxylate (1)[2] to produce the 2-oxabicyclo[2.2.0]hexene 3[3] under photolytic conditions.



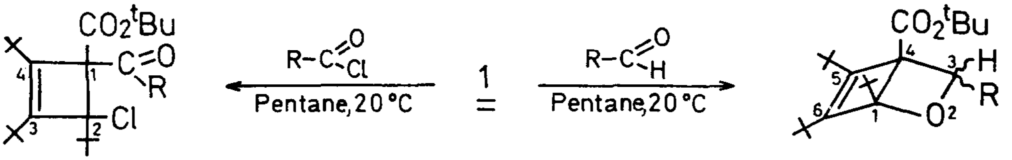
1 2 3

E = $CO_2{}^tBu$

We now show for the first time that aldehydes and activated ketones are suitable cycloaddition partners for the antiaromatic compound 1 even in the absence of light.

Carboxylic acid chlorides such as acetyl or benzoyl chloride do not react with 1 through cycloaddition at the CO group, instead 1,4-addition[4] occurs to give 4a or 4b[5]. Evidence that the di-t-butyl substituted double bond is retained is given by the only small difference in the chemical shifts of the carbon atoms C-3 and C-4. The presence of the original CO group from the acid chloride in the product is also demonstrated by the ^{13}C N.M.R.spectra (4a: $\delta = 152.7$, 153.6 (C-3/C-4), 205.22 (acetyl-CO); 4b: $\delta = 152.0$, 153.10 (C-3/C-4), 199.28 (benzoyl-CO).

In contrast to carboxylic acid chlorides, aldehydes such as trichloroacetaldehyde, acetaldehyde itself, or benzaldehyde undergo a rapid, exothermic [4+2]-cycloaddition[4] with 1[2] to give the 2-oxabicyclo[2.2.0]hexenes 5a-c which are purified by distillation (see Table 1). The ^{13}C N.M.R. spectra show - as in the preceeding case - the presence of the intact di-t-butyl substituted olefinic double bond (see the resonances for C-5 and C-6 in Table 1), thus defining the centres for the cycloaddition in the cyclobutadiene. The determination of the orientation of the carbonyl compound as shown in 5 results mainly from a direct comparison of the ^{13}C N.M.R. data of 3, the configuration of which has been unequivocally established[1], with those of the cycloadducts (see Table 1).



4a: R = CH_3 (86%)
b: R = C_6H_5 (82%)

5a: R = CCl_3 (80%)
b: R = CH_3 (90%)
c: R = C_6H_5 (80%)

Table 1. Boiling Point and ^{13}C-N.M.R. Data for the 2-Oxabicyclo[2.2.0]hexenes 5a-c and 8d

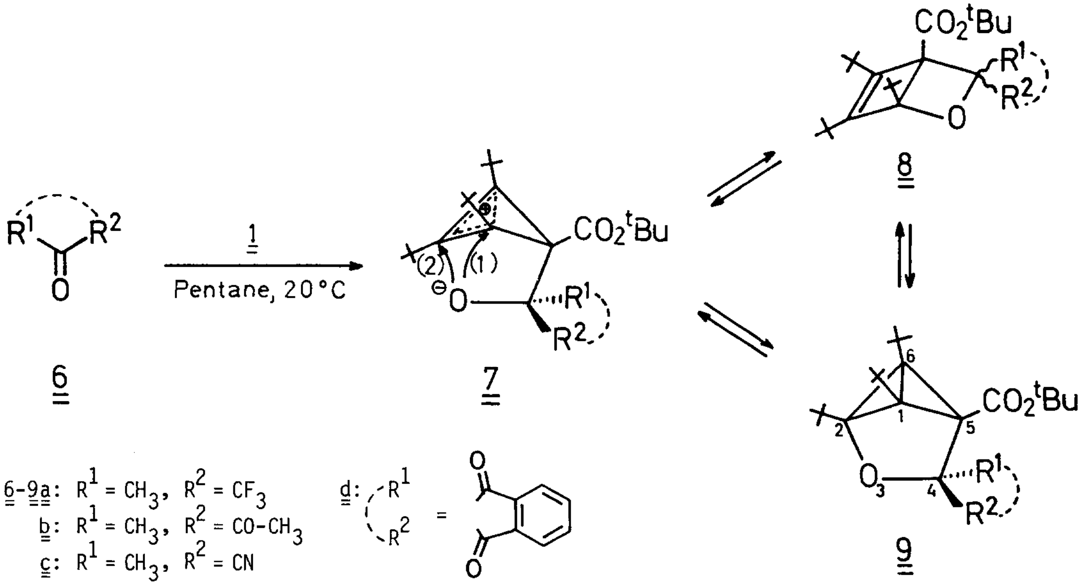
Bicyclic System	b.p. a) [°C/Torr]	^{13}C-NMR($CDCl_3$, δ in ppm, J in Hz, TMS) C-1	C-3		C-4	C-5/C-6
5a	$168/1.5\cdot10^{-5}$ b)	94.47	84.57	(d, $^1J_{^{13}C,H}$ = 162.76	61.19	149.47, 154.55
5b	$170/4\cdot10^{-6}$	95.97	73.72	(d, $^1J_{^{13}C,H}$ = 155.69	59.17	150.18, 155.22
5c	$220/4\cdot10^{-6}$	96.26	77.36	(d, $^1J_{^{13}C,H}$ = 155.34	62.61	150.54, 155.00
8d	119.5 c)	99.19	84.65	——	71.17	152.12, 157.94

a) Kugelrohr distillation, the oven temperature is given.- b) Colourless crystals with m.p. 104°C after recrystallisation from petroleum ether at -30°C.- c) m.p. of the bicyclic product.

For 5a-c the configuration at C-3 is not certain but it is probable from general steric considerations that the larger group is orientied away from the two bulky groups on the 1,4-bridge. In support of this is the fact that, in 5c, the signal for the protons of the t-butyl group at C-5 in the ^{1}H N.M.R. spectrum is shifted to higher field, presumable due to a ring current effect of the phenyl nucleus [^{1}H-N.M.R. ($CDCl_3$): $\delta = 0.70$ as compared to 1.06 - 1.53 for the other C-t-butyl groups in 5a-c]. The bicyclic compounds do not undergo isomerisation to the 3-oxatricyclo[3.1.0.0^{2,6}]hexanes in acetonitrile/chloroform in the presence of traces of conc. hydrochlorid acid, as we found for the first time for compound 3[1].

In contrast to aldehydes, acceptor-substituted ketones such as 1,1,1-trifluoroacetone (6a), biacetyl (6b), or acetyl cyanide (6c) do not react with 1 to give the bicyclic products 8a-c; instead, the tricyclic compounds 9a-c are formed. This process can be formally interpreted as a cis,trans [2+2+2]-cycloaddition[6]. Trioxoindane (6d) also reacts with 1 in a rapid, exothermic process to give the bicyclic product 8d, which in $CDCl_3$ solution, is in equilibrium with 9d (ratio 8d : 9d = 43 : 57, 20°C).

The I.R. and ^{1}H N.M.R.spectra are in accord with the tricyclic structure for 9a-d. The ^{13}C N.M.R. spectra again provide conclusive evidence for the structure. In the case of 9a and c, no ketone CO groups are detected, they are, of course present in the spectra of the diketone and triketone adducts 9b and d ($\delta = 211.92$ or 201.32, respectively). The carbon atoms C-1, C-6, and C-5 give resonances in the region $\delta = 45.00$ to 56.69, in relation to these, the resonances for C-2 and C-4 are shifted to lower field as a result of the oxygen bridge (see Table 2). Furthermore, all of the above-mentioned resonances are in good correlation with those of t-butyl 1,2,6-tri-t-butyl-4,4-diphenyl-3-oxatricyclo[3.1.0.0^{2,6}]hexane-5-carboxylate (9, $R^1 = R^2 = C_6H_5$), the structure of which has been unequivocally established [1].



6-9a: $R^1 = CH_3$, $R^2 = CF_3$
b: $R^1 = CH_3$, $R^2 = CO\text{-}CH_3$
c: $R^1 = CH_3$, $R^2 = CN$
d: R^1, R^2 =

Table 2. Melting Point and ^{13}C-N.M.R. Data for the 3-Oxatricyclo[3.1.0.0^{2,6}]hexanes

Tricyclic System	m.p. [°C]	^{13}C-NMR($CDCl_3$, δ in ppm, TMS) C-1/C-6	C-2	C-4	C-5
9a	Öl	47.01, 47.42	87.20	81.74	53.09
9b	95.8	45.00, 45.93	87.13	81.27	54.26
9c	71.0	45.97, 48.22	88.26	70.43	56.07
9d	a)	jeweils 48.24	93.46	82.94	56.69

a) Only obtained as a mixture with 8d.

Finally, 9d possesses a mirror plane, as can be seen from the identical chemical shifts for C-1 and C-6 (see Table 2), the t-butyl groups bonded to these carbon atoms ($\delta = 33.14$ for the primary carbon atom), and the appearance of only three aromatic carbon atoms ($\delta = 123.23$, 135.79, and 142.48).

We attribute a key role in the reactions described here to the homocyclopropenylium betains [7] of the type 7. These are formed by nucleophilic attack of the cyclobutadiene carbon atom bearing the ester group with the carbonyl carbon atom of the reaction partner.

Both the formation of the initially mentioned cyclobutenes 4 through a chloride shift (7, R^1 or $R^2 = Cl$) and the ring closures according to (1) or (2) to give the bicyclic systems 5 and 8 and the tricyclic system 9 proceed from the intermediate 7. Also, the formation of the equilibrium mixture of 8d and 9d starting from 8d is assumed to proceed through the homoaromatic betain 7d.

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[4] In the present case it is, in principle, not possible to distinguish between 1,4- or 1,2-addition of between the later discussed [4+2]- or [2+2]-cycloaddition.

[5] For analogous reactions of 1,2,3-tris t-butylcyclobutadiene see: G. Maier and W. Sauer, Angew.Chem. 87, 675 (1975); Angew. Chem., Int. Ed. Engl. 14, 648 (1975).

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