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CYCLOADDITIONS OF 1,2,5,6-TETRAMETHYL-3,4-DIMETHYLENE-TRICYCLO$[3.1.0.0^{2,6}]$HEXANE

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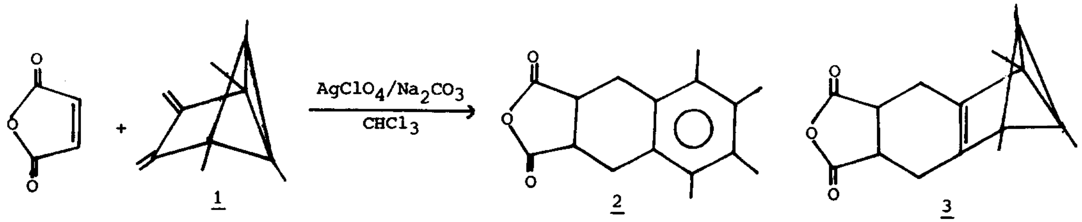
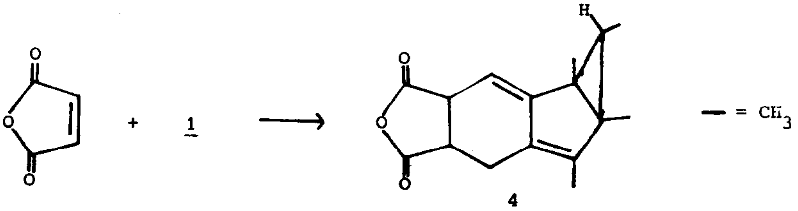
Recently[1] we reported that 1,2,5,6-tetramethyl-3,4-dimethylene-tricyclo$[3.1.0.0^{2,6}]$hexane, 1, reacts with maleic anhydride in the presence of silver perchlorate and sodium carbonate to give the aromatic valence isomer 2 of the normal Diels-Alder adduct 3. In a preliminary observation it was also noted that 1 reacts thermally with maleic anhydride in the absence of additives but the reaction product was neither 2 nor 3. We have now succeeded in elucidating the structure of this product which we report here. Moreover, the reactions of 1 towards other dienophiles, either under normal thermal conditions or under the influence of silver perchlorate and sodium carbonate, with respect to the formation of aromatic compounds of type 2 has been investigated.



When 1 (2.10^{-3} mol) was treated with maleic anhydride (2.10^{-3} mol) in chloroform or dichloromethylene solution (20 ml) at room temperature for 2 hours the homofulvene derivative 4 was formed as the main product[2] (yield > 80%).

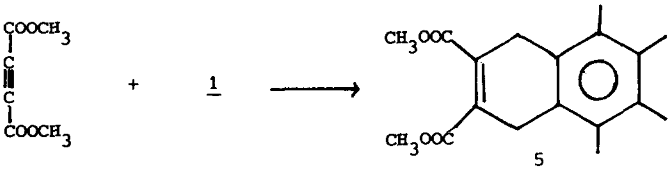


Following the reaction in the NMR cavity (T = 40°) did not give any indication for the formation of an intermediate product.[3]

Structural assignment of 4 rests on the following data: satisfactory elemental analysis, mass spectrum (parent peak at 258), IR ($\nu_{C=O}$ = 1840, 1770 cm^{-1}) U.V.[4] (λ_{max} = 264 nm ε = 12500), CMR ($CDCl_3$) shifts in ppm downfield to TMS: 7.3 (q, J_H = 121 Hz), 9.5 (q, J_H = 128 Hz), 9.9 (q, J_H = 128 Hz), 12.9 (q, J_H = 125 Hz), 19.0 (t, J_H = 130 Hz), 29.4 (s), 38.1 (s), 38.3 (d, J_H = 164 Hz), 39.8 (d, J_H = 140 Hz), 42.6 (d, J_H = 142 Hz), 102.2 (d, J_H = 166 Hz), 121.2 (s), 150.7 (s), 156.2 (s), 171.7 (s), 173.2 (s) and PMR[5], (coupling constants < 0.5 Hz are not reported) ($CDCl_3$) shifts in ppm downfield to TMS, 5.09 (1 H, d.d., J = 3.2 Hz, J = 0.6 Hz), 3.70 (1 H, d.d., J = 8.2 Hz, J = 3.2 Hz), 3.45 (1 H, d.d.d.d., J = 8.2 Hz, J = 6.7 Hz, J = 2Hz, J = 0.6 Hz).,2.94 (1 H, d.d., J = 16.5 Hz, J = 2 Hz), 2.21 (1 H, d.d.q., J = 16.5 Hz, J = 6.7 Hz, J = 2Hz), 1.76 (1 CH_3, d, J = 2 Hz), 1.04 (1 CH_3, s), 1.01 (1 CH_3, s), 0.92 (1 CH_3 distorted d., J = 6.5 Hz) and 0.6 (1 H distorted q, J = 6.5 Hz).

By comparison with the PMR spectra of homofulvene derivatives of known stereochemistry[6], it appears that the hydrogen atom on the cyclopropyl ring is probably in the endo position. Attempts to assign additional stereochemical details of 4 have thus far been unsuccessful.[7]

In contrast with maleic anhydride, acetylenedicarboxylic dimethylester (10^{-3} mol) reacts with 1 (10^{-3} mol) in chloroform solution (0.3 ml) at room temperature to form 5 as the main product. The reaction is very slow: after 7 days compound 5 was formed only in 50% yield and 40% of the starting diene 1 was unchanged.



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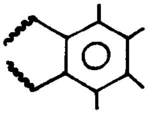
Structural assignment of 5 (m.p. 153.5-154.5) rests on the following data: correct elemental analysis, mass spectrum (parent peak 302) IR ($\nu_{C=O}$ = 1732, 1712 cm^{-1}) and PMR ($CDCl_3$) shifts in ppm downfield to TMS: 3.96 (6 H, s), 3.65 (4 H, s), 2.24 (6H, s), 2.20 (6H, s).

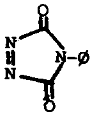
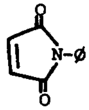
The remarkable difference in the behaviour of these two dienophiles towards the title compound prompted us to study the reactions of a variety of dienophiles towards 1 under thermal and silver perchlorate/sodium carbonate[8] conditions. Preliminary results with respect to formation of aromatic compounds of type 2 are reported in the Table.

Table

Formation of aromatic products of type 2 in the reaction

dienophile + 1 →



dienophile	Under the influence of $AgClO_4/Na_2CO_3$[a]		thermally[b]	reaction conditions[a]
	yield[c]	m.p.	yield[c]	
	>97%	261.6-262.2	<3%	20°, 2h, c = 10^{-1}mol/l $CHCl_3$
	95%	182.2-182.6	<3%	20°, 2h, c = 10^{-1}mol/l $CHCl_3$
	90%	180.0-181.2	12%	20°, 23h, c = 10^{-1}mol/l CH_2Cl_2
$H_3CO_2CC{\equiv}CCO_2CH_3$	50%	153.5-154.5	8%	20°, 17h, c = 4.10^{-1}mol/l CH_2Cl_2
$H_2C{=}CHCN$[a,d]	65%[a,e]	152.8-153.8	<3%	20°, 16h, c = 10^{-1}mol/l $H_2C{=}CHCN$
			50%	80°, 50h, c = 10^{-1}mol/l $H_2C{=}CHCN$
$H_2C{=}CHCOOCH_3$[a,d]	95%[a,e]	91.3-91.6	<3%	20°, 3h, c = 10^{-1}mol/l $H_2C{=}CHCOOCH_3$
			40%	80°, 40h, c = 10^{-1}mol/l $H_2C{=}CHCOOCH_3$
$H_3CO_2CH{=}CHCO_2CH_3$ (trans)	12%	177 -178.3	6%	20°, 48h, c = 1 mol/l $CHCl_3$
	84%		70%	61°, 24h, c = 1 mol/l $CHCl_3$
$C_6H_5COCH{=}CHCOC_6H_5$ (trans)	51%	205-207	36%	20°, 24h, c = 1 mol/l $CHCl_3$
	77%		70%	61°, 3h, c = 1 mol/l $CHCl_3$
$C_6H_5SO_2CH{=}CHSO_2C_6H_5$ (trans)	18%	242.5-243.3	12%	20°, 23h, c = 1 mol/l $CHCl_3$
	87%		80%	61°, 24h, c = 1 mol/l $CHCl_3$

a) see note 9 for additional information.
b) other, not yet identified products are formed in some cases.
c) Yields were determined by PMR analysis, all new compounds gave satisfactory elemental and spectral analysis.

Mechanistic implications of these results will be discussed in a full paper.

References and notes

1) H. Hogeveen and W.F.J. Huurdeman, Tetrahedron Lett. 1255 (1974).

2) The homofulvene derivative 4 is not very stable at room temperature, decomposition leads to unidentified products, probably polymers.

Compare M. Rey, K.P. Huber and A.S. Dreiding, Tetrahedron Lett. 3583 (1968).

3) This does not, of course, rigorously exclude the occurrence of a minute quantity of an intermediate Diels-Alder product of type 3, from which, possibly by a [1.5] homosigmatropic shift, 4 could conceivably be formed.

4) Compare ref. 2 and H. Hogeveen and H.C. Volger, Chem. Commun. 1133 (1967).

5) Decoupling and INDOR experiments confirmed the structure; detailed information about the PMR spectra of 4 will be given in a full paper. The authors wish to thank Dr. J.H. Wieringa for running the NMR spectra and for helpful discussions.

6) H. Hogeveen and P.W. Kwant, J. Org. Chem. 39, 000 (1974) and references cited therein.

7) Addition of various amounts of $Eu(DPM)_3$ shift reagent to a solution ($CDCl_3$) of 4 did not cause linear shifts, possibly due to decomposition of 4.

8) For a discussion on the use of sodium carbonate see ref. 1).

9) Equimolar amounts of diene and dienophile were used except in the cases where the dienophile was used as solvent. In the reactions under the influence of silver perchlorate/sodium carbonate 1.3 equivalents of sodium carbonate and 0.13 equivalents of silver perchlorate were used unless stated otherwise.

d) The dienophile was used as solvent.

e) o.5. equivalent of silver perchlorate and no sodium carbonate was used.