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SYNTHESIS OF A BICYCLOBUTANE-BRIDGED α-DIKETONE

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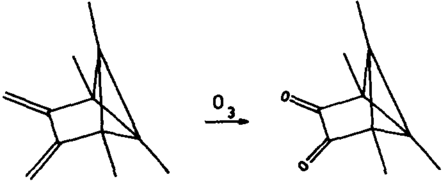
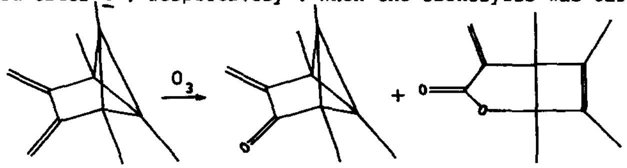
The ozonolysis of the easily available 1,2,5,6-tetramethyl-3,4-dimethylenetricyclo-[3.1.0.0^{2,6}]hexane 1[1] was examined as a possible route to the diketone 2. This compound is of interest as a potential starting material in a number of reactions such as possible Wittig-reactions leading to substituted dienes[2], which themselves could be precursors of hexacoordinated pyramidal dications[3]. We herewith report the preliminary results of our investigation.



1 2

Ozonolyses of diene 1 were performed in different solvents including n-pentane, propionaldehyde and chloroform, both at -70°C and at room temperature. No substantial differences in products formed were observed and it was decided therefore to conduct further experiments in chloroform solution at room temperature.

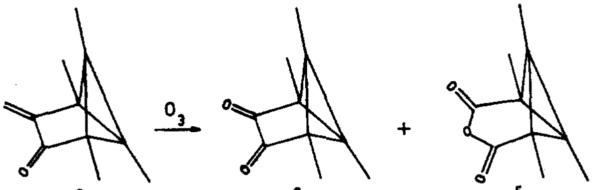
Ozone was added at a rate of 1.5 grams per hour[4] to a stirred solution of 0.80 grams (5 mmoles) of 1 in 10 ml $CHCl_3$ until no PMR-signals due to olefinic protons of the diene could be observed anymore. Two products were formed in a 1:4 ratio identified as the α,β-unsaturated ketone 3[5] and the rearranged ester 4[5], respectively[6]. When the ozonolysis was carried out in the presence



1 3 4

of 1.0 gram of Na_2CO_3 (effective stirring) or 1.0 ml of pyridine[7], the product ratio changed to 1:1 or 4:1, respectively. Further addition of pyridine did not change this ratio.

A similar ozonolysis of ketone 3 (0.81 grams, 5 mmoles) in 10 ml of $CHCl_3$ containing 1.0 ml of pyridine was performed until the signals due to the olefinic protons of 3 had disappeared from the PMR-spectrum. Two products were isolated and identified in the reaction mixture, the α-diketone 2[5] and the anhydride 5[5], which were formed in a 9:2 ratio, respectively.



3 2 5

Since the ozonolysis of diene 1 to yield α-diketone 2 can be carried out also as a one-step procedure, it is clear that this reaction provides an attractive method for the synthesis of a bicyclobutane-bridged α-diketone. Mechanisms and detailed experimental procedures will be discussed in a full paper. The chemistry of the synthesized compounds is being actively investigated.

Footnotes and references:

1. H. Hogeveen and P.W. Kwant, J. Org. Chem., 39, 2624 (1974); ibid., 39, 2626 (1974).
2. H. Hogeveen, W.F.J. Huurdeman and E.P. Schudde, Tetrahedron Lett., 4211 (1974).
3. H. Hogeveen and P.W. Kwant, ibid., 1665 (1973).
4. Oxygen flow of 20 litres per hour through the Fischer OZ III "Ozon-Generator"!
5. Structure assignment of the synthesized compounds is based on the following data: PMR ($CDCl_3$: shifts in ppm downfield to internal TMS), CMR ($CDCl_3$: shifts in ppm downfield to TMS in a proton noise decoupled spectrum), IR (nujol mull), mass spectrum and satisfactory elemental analysis.
   Unsaturated ketone 3: PMR 1.16 (s, 3H), 1.27 (s, 3H), 1.51 (s, 6H), 4.94 (s, 1H), 5.67 (s, 1H); CMR 3.3 (2C), 4.4 (1C), 7.2 (1C), 30.9 (2C), 41.3 (1C), 50.9 (1C), 106.1 (1C), 149.3 (1C), 210.3 (1C); IR 1650 ($>$c=c$<$) and 1720 cm^{-1} ($>$c=o); M^+ peak at m/e 162.
   Ester 4: PMR 1.22 (s, 3H), 1.38 (s, 3H), 1.55 (broad s, 6H), 5.53 (s, 1H), 6.28 (s, 1H); CMR 7.9 (1C), 8.5 (1C), 15.0 (2C), 53.4 (1C), 87.8 (1C), 120.3 (1C), 141.0 (1C), 142.1 (1C), 143.6 (1C), 170.5 (1C); IR 1630 ($>$c=c$<$), 1650 ($>$c=c$<$) and 1750 cm^{-1} ($>$c=o); M^+ peak at m/e 178.
   α-Diketone 2: PMR 1.30 (s, 6H), 1.67 (s, 6H); CMR 3.5 (2C), 4.6 (2C), 28.7 (2C), 51.6 (2C), 194.6 (2C); IR 1750 cm^{-1} ($>$c=o); M^+ peak at m/e 164.
   Anhydride 5: PMR 1.30 (s, 6H), 1.54 (s, 6H); CMR 3.7 (2C), 10.0 (2C), 31.6 (2C), 41.9 (2C), 169.6 (2C); IR 1770 and 1800 cm^{-1} ($\backslash\underset{\underset{O}{\|}}{C}\!/O\backslash\!\underset{\underset{O}{\|}}{C}/$); M^+ peak at m/e 180.
6. J.E. Leffler, Chem. Revs. 45, 399 (1949).
7. G. Slomp Jr. and J.L. Johnson, J. Am. Chem. Soc. 80, 915 (1958) and K. Griesbaum, Chem. Comm, 920 (1966).