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ANOMALOUS OZONE DEGRADATION OF A CONJUGATED DIENE SYSTEM: OZONOLYSIS OF 2,7-DICHLORO-3,4,5,6-TETRAMETHYL-2,4-OCTADIENE

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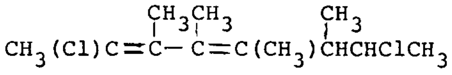
Recently we have reinvestigated the reaction of anhydrous hydrogen chloride with 2-butyne in the liquid phase (1). One of the previously unknown products of this reaction was the acyclic trimeric compound 2,7-dichloro-3,4,5,6-tetramethyl-2,4-octadiene (1), which was formed in selectivities of up to 22 %. For structure proof, 1 was submitted to ozone degradation in the presence of methanol. A priori this was anticipated to afford equal amounts of the fragments 2, 3 and 4. The result of the ozonolysis was, however, significantly different.


$CH_3(Cl)C{=}C(CH_3){-}C(CH_3){=}C(CH_3)CH(CH_3)CHClCH_3$

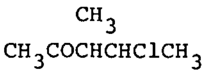
1

$CH_3COCOCH_3$

2

CH_3COOCH_3

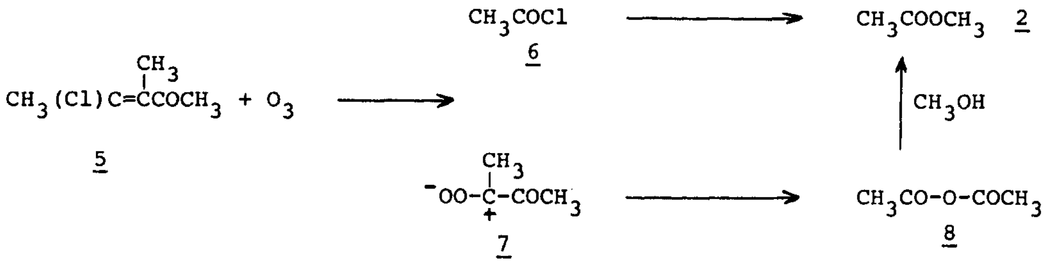
3


$CH_3COCH(CH_3)CHClCH_3$

4

Ozonolysis of 1 was carried out in deuteriated chloroform at - 50 °C in the presence of five molar equivalents of methanol, and the reaction was monitored by pmr-spectroscopy. When the substrate 1 had disappeared, introduction of ozone was terminated and the reaction mixture was allowed to warm up to room temperature. Subsequent analysis by pmr-spectroscopy showed that the fragments 2 and 4 were formed in a ratio of 3:1, respectively, whereas fragment 3 could not be detected.

Obviously, ozonolysis has resulted in the cleavage of both the double bonds and the single bond of the conjugated diene system of 1. This anomalous fragmentation can be rationalized by the following sequence of reactions: In the first step, ozone attacks preferentially the more reactive, non-chlorinated double bond of 1 so as to produce the fragments 4 and 5 (2). Subsequently, the less reactive, chlorinated double bond in 5 is attacked by ozone. This occurs selectively (3) in such a manner, that acetyl chloride (6) and the zwitterion 7 are formed. The latter, then, is not trapped by methanol to form a methoxy hydroperoxide, but undergoes fast rearrangement (4) to afford acetic anhydride (8). In the final steps, 6 and 8 are solvolyzed by methanol to form methyl acetate (2).



Fragment 4 was independently synthesized by the reaction of acetyl chloride with Z-2-butene in the presence of aluminium trichloride at 10 °C. Its pmr-spectrum showed doublets at δ=1.13 (7 cps, 3H) and δ=1.50 (6.5 cps, 3H), a singlet at δ= 2.22 (3H) and multiplets centered at δ= 2.87 (1H) and at δ=4.25 (1H). Double irradiation at δ= 1.13 and at δ = 1.50 resulted in doublet signals for the methine protons at δ = 2.87 and δ = 4.25, respectively with a coupling constant of 8 cps. Addition of anhydrous hydrogen chloride to E-3-methyl-3-pentene-2-one in pentane at - 78 °C produced the other diastereomer of 4 (5). Its pmr-spectrum showed doublets at δ = 1.26 (7 cps, 3H) and at δ = 1.50 (6.5 cps, 3H), a singlet at δ = 2.22 (3H) and multiplets centered at δ = 2.72 (1H) and δ = 4.57 (1H). The coupling constant for the methine protons was found to be 6.5 cps by double irradiation. By analogy with other examples (6), the isomer with the larger coupling constant,i.e. fragment 4, is assigned the structure of a racemic mixture of 3(S),4(S)- and of 3(R),4(R) -3-methyl-4-chloropentanone.

References

1. H. Schneider, Dissertation, Universität Karlsruhe (T.H.), 1977
2. For other examples see: R. Criegee and H. Huber, Angew. Chem. 81, 749 (1969); J. E. Franz, W.S. Knowles and C.J. Osuch, J.Org.Chem. 30, 4328 (1965); R. Criegee, C. Schweickhardt and H. Knoche, Chem.Ber. 103, 960 (1970).
3. Previous example: K. Griesbaum and H. Keul, Angew. Chem. 87, 748 (1975); Angew. Chem. Internat. Edit. (English) 14, 716 (1975)
4. Rearrangements of this type have been reported before: E. Bernatek, F. Christenssen and T. Ledaal, Acta Chem.Scand. 21, 822 (1967); E. Logemann, G. Schill and H. Fritz, Chem.Ber. 110, 3228 (1977)
5. Reported previously without assignment of stereochemistry: H. Hart and R.H. Schlosberg, J.Am.Chem.Soc. 90, 5189 (1968).
6. A. Bothner-By and C. Naar-Colin, J. Am. Chem. Soc. 84, 743 (1962).

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