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QUADRICYCLANONE KETALS AND THIOKETALS

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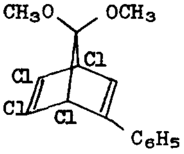
THERMAL decomposition of the highly substituted norbornadienone ketal 1 has been interpreted in terms of the hypothetical intermediate dimethoxycarbene.[1,2] Our interest in species of this ilk stimulated us to undertake a corresponding study of norbornadienone ketals and thioketals lacking substituents; such an investigation promised the advantages that side reactions traceable to the chlorines would be precluded and that vapor phase pyrolysis would be feasible.



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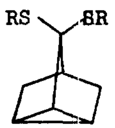
The great instability of norbornadienones ruled out the most obvious synthetic route to these compounds, but an attractive alternative was "protection" of the norbornadiene system as its quadricyclic counterpart prior to ketone and ketal formation. Accordingly, quadricyclanol, synthesized independently *via* the same sequence employed by Richey,[3] was transformed into quadricyclanone (39%)[4,5] by a modification of the Kornblum oxidation.[6] Treatment of the ketone with ethanedithiol, zinc chloride and sodium sulfate in dichloromethane at 0°[7] yielded ethylene thioketal 2a, m.p. 97-98° (79%). A similar procedure using methyl mercaptan gave the dimethyl thioketal 2b, m.p. 37.5-38.5° (53%). Ethylene ketal



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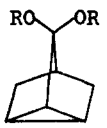

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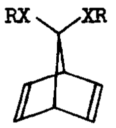
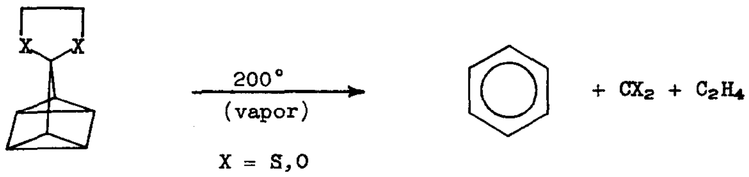


4 $X = S$
5 $X = O$

a, $R,R = CH_2CH_2$; b, $R = CH_3$

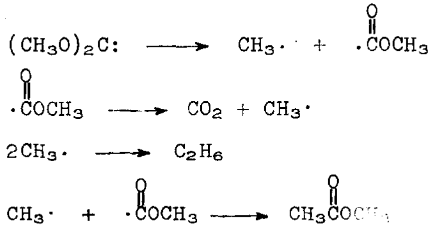
3a, m.p. 98-99° (32%) resulted from the reaction of quadricyclanone with ethylene glycol, triethyl orthoformate and *p*-toluenesulfonic acid in dichloromethane at 45-50°.[8] Prepared from the ketone, trimethyl orthoformate and *p*-toluenesulfonic acid in methanol/dichloromethane under reflux, dimethyl ketal 3b was isolated in crude form, allowed to ring-open to its bicyclic valence tautomer 5b and purified by vapor chromatography (48% overall).[8,9] The structures of the four quadricyclic ketals were established by spectral data and by elemental analysis, performed on the valence tautomer in the case of 3b.[10,11]

Pyrolysis at 200° of 2a and b either as neat liquids or in solution gave chiefly polymeric products, and the same was true of 2b in the vapor phase. Benzene and carbon disulfide were each obtained in 75% yield, however, when 2a was decomposed as a vapor ($\leq$20 mm.) at 200°. Ethylene ketal 3a fragmented in parallel fashion, but more cleanly, under these conditions: $>$95% yields each of benzene, carbon dioxide and ethylene were obtained.[12] It is noteworthy that these disintegration reactions, in which six π bonds are formed at the expense of six σ bonds, require rehybridization of all eleven atoms comprising the molecular framework. Presumably the initial step in each case is valence tautomerization to the diene ketal; the timing of subsequent bond-breaking and -forming processes will be discussed elsewhere.



Benzene is produced in good yield whether the dimethyl ketal 5b is pyrolyzed as a neat liquid, in dilute solution or in the vapor phase, but the products derived from the ketal bridge are highly dependent upon the choice of reaction conditions.[13] Dimethyl oxalate (35-45%) is generated in the neat liquid at 200-250°, but essentially none is found at 150°. Trimethyl orthoformate is a major product when **5b** is decomposed in dilute solution in inert solvents at 150°. In the vapor phase ($\leq$20 mm.) at 200° methyl acetate, ethane and carbon dioxide are formed, each in roughly 25% yield.[14]

In analogy to the investigations of ketal **1**,[1,2] we tentatively attribute to dimethoxycarbene the array of compounds derived from the ketal bridge of **5b**. Methyl acetate, carbon dioxide and ethane are very likely the ultimate products of a stepwise radical fragmentation of the carbene,[15] a process not recognized in the earlier (liquid phase) work with **1**. The fact that none of the ester (or ethane) is formed when the dimethyl ketal is decomposed in an oxygen atmosphere is consistent with this suggestion;[16] nonetheless, other mechanisms, including a 1,2-methyl shift in the carbene, deserve consideration.



$$(CH_3O)_2C: \longrightarrow CH_3\cdot + \cdot\overset{O}{\overset{\|}{C}}OCH_3$$

$$\cdot\overset{O}{\overset{\|}{C}}OCH_3 \longrightarrow CO_2 + CH_3\cdot$$

$$2CH_3\cdot \longrightarrow C_2H_6$$

$$CH_3\cdot + \cdot\overset{O}{\overset{\|}{C}}OCH_3 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}OCH_3$$

Working with a capillary furnace mounted at the inlet of a mass spectrometer, Dr. F. P. Lossing has analyzed the pyrolysis fragments obtained at very low pressures from a derivative of **5b**. No direct evidence for dimethoxycarbene was obtained in this experiment, probably because it dissociates too rapidly under the gentlest conditions (350°, 1 msec.) suitable for decomposing the starting material. In harmony with our vapor phase study, Dr. Lossing detected methyl radicals, carbon dioxide and methyl acetate among the pyrolysis products.

We are currently seeking answers to some of the mechanistic questions raised by the results described above.

Acknowledgment. The authors are very grateful to Dr. F. P. Lossing of the National Research Council of Canada both for valuable discussions and for his experimental contribution. The National Science Foundation and the National Institutes of Health generously provided financial support.

REFERENCES AND FOOTNOTES

1. R. W. Hoffmann and H. Häuser, Tetra. Letters, 197 (1964), Tetrahedron, 21, 891 (1965).

2. D. M. Lemal, E. P. Gosselink and A. Ault, ibid., 579 (1964); E. P. Gosselink, Ph.D. Dissertation, University of Wisconsin, 1964.

3. H. G. Richey, Jr. and N. C. Buckley, J. Am. Chem. Soc., 85, 3058 (1963).

4. P. R. Story and S. R. Fahrenholtz subsequently reported the same oxidation in 14% yield using t-butyl hypochlorite (ibid., 86, 1270 (1964)). Yields are also very poor in our procedure if the scale is not small.

5. Analogy to the mercury-sensitized photodecarbonylation of nortricyclanone to tricyclo[2.2.0.$0^{2,6}$]hexane (36%) (D. M. Lemal and K. S. Shim, ibid., 86, 1550 (1964)) suggested that prismane should be available from quadricyclanone. Mercury-sensitized and direct photolysis of the tetracyclic ketone in the vapor phase under a variety of conditions and direct photolysis of Fluorolube and water solutions led to polymeric materials accompanied in most cases by small amounts of benzene, but no prismane.

6. N. Kornblum, W. J. Jones and G. J. Anderson, ibid., 81, 4113 (1959).

7. H. Hauptmann, ibid., 69, 562 (1947).

8. W. T. Moreland, D. P. Cameron, R. G. Berg and C. E. Maxwell, III, ibid., 84, 2966 (1962).

9. In certain runs the quadricyclanone → dimethyl ketal reaction failed to turn its usual beautiful deep blue color and the product was the diene tautomer instead of the tetracyclic one. This surprising result indicated inter alia that the norbornadienone as well as the quadricyclanone ketal could survive treatment with p-toluenesulfonic acid; in contrast, the diene tautomer of Gassman's ketal (footnote 10) is destroyed rapidly by dilute acid at -20°.

10. 2,3-Dimethylquadricyclanone dimethyl ketal has recently been synthesized *via* a route different from ours by P. G. Gassman, D H. Aue and D. S. Patton, *ibid.*, **86**, 4211 (1964). This substance is reported to tautomerize to the norbornadiene even at 0°.

11. All four ketals displayed a tendency to tautomerize in solution to their norbornadiene analogs at room temperature. A preliminary kinetic study by n.m.r. has revealed that the ring opening is not a simple unimolecular process, but a catalyzed one whose rate depends both upon the choice of ketal and upon the history and environment of the sample.

12. Similar fragmentations of highly substituted norbornadienone ethylene ketals are described in ref. 2 and in K. Mackenzie, J. Chem. Soc., 5710 (1964).

13. All pyrolysis products were identified by comparison with authentic specimens in terms of vapor chromatographic retention times and n.m.r. or mass spectra. Yields were determined from n.m.r. peak area comparisons with standard samples.

14. In contrast to the report of H. Feichtinger and H. Linden, Ger. pat. 1,105,862 (1961) (C.A. **56**, 12803 (1962)), concerning pyrolysis of a related ketal, **5b** yields no carbon monoxide and no dimethyl ether.

15. Interestingly, a different mode of fragmentation has been observed in the thermal and photochemical decomposition of N'-diethoxymethylene-*p*-toluenesulfonhydrazide sodium salt (R. J. Crawford and R. Raap, Proc. Chem. Soc., 370 (1963)).

16. Benzene, methyl formate and methanol are major products in this experiment, and lesser amounts of dimethyl carbonate (~10%) are formed.