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# β-OXA-γ,δ-ENONES, II1). REARRANGEMENT AND INTRAMOLECULAR CYCLOADDITION OF 1-CYCLOPENTENYLOXY-2-PROPANONE.

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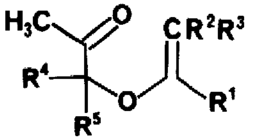
Abstract: The title compound 1 undergoes an intramolecular photocycloaddition reaction to yield the bis-oxetane 2 and a formal 1,3-shift to yield the 1,4-diketone 3. This work reveals a novel aspect of the photochemistry of β-oxa-γ,δ-enones.

## Introduction:

Although γ,δ-enones have been well investigated, there are only a few examples of reports concerning the photochemistry of β-oxa-γ,δ-enones A.3) We recently found an efficient synthesis of molecules of the general structure A.1) Some ground state reactions of A have already been described elsewhere.1,4) In this communication we wish to report the photochemistry of one representative of these bichromophoric molecules, 1-cyclopentenyloxy-2-propanone 1.5)



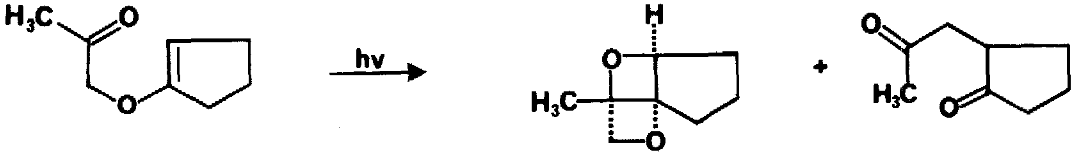
A

## Photochemical products and their structures:

Irradiation of 1 (14 g in 200 ml dioxane, 0.5 M) under $N_2$-atmosphere through Pyrex using a 125 watt high pressure mercury lamp (Philips HPK 125) for 50 hours results in 75% loss of 1.6) Upon distillation of the reaction mixture 9.1 g of a mixture were obtained which contained unreacted 1 (25%) and two products 2 (15%) and 3 (60%). Compounds 2 and 3 were separated by further distillation under reduced pressure using a Vigreux-column - 2: b.p. 70-75°C/15 torr; 3: b.p. 108°C/15 torr. Small amounts of acetone 4 and cyclopentanone 5 were also detected by vpc-analysis.6)

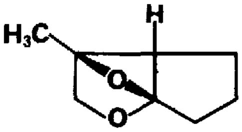
The structural assignment of the minor product 2 as 1-methyl-2,8-dioxatricyclo[5.2.0.$0^{3.7}$]·

nonane is based on the following data: $^1$H-NMR (60 MHz,CDCl$_3$) δ = 1.44 (s, 3H),1.65-2.00(m, 6H), 4.60 and 5.14 (AB,J=7Hz, 2H), 5.32 (m,1H); MS (70ev) m/e = 140 (2.2%,M$^+$), 139 (2.0, M-1$^+$), 125 (1.0, M-CH$_3^+$), 100 (3.2, M-CH$_2$O$^+$), 97 (10.8, M-C$_2$H$_3$O$^+$), 95 (20.4), 84 (19.6), 83 (39.9), 82 (17.3), 69 (35.5), 67 (32.2), 55 (23.9), 43 (76.6), 41 (100), 39 (25.9), 29(10.4), 27(13.7).[7]



1 2 3

Particularly pertinent is the lack of any IR absorption in the C=O or C=C region. The alternative intramolecular cycloaddition product 6, resulting from a "crossed" [2+2] cycloaddition would be expected to show methine NMR absorption in the δ≈3 ppm region.[8] However, the observed chemical shift (δ = 5.32 ppm) is compatible with that reported for a bisoxetane structure similar to 2.[3] Moreover, a cycloaddition product of the structure 6 would correspond to 2-alkoxyoxetanes C and consequently would show the reactivity of ketals.[9] On the contrary 2 is unreactive upon heating in alcoholic or aqueous solution.[9] Analogous to results dealing with the photochemistry of acyclic β-oxa-γ,δ-enones as reported by Dalton [3] we suggest a stereochemistry for the bisoxetane as shown in the formula 2.[10]



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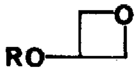


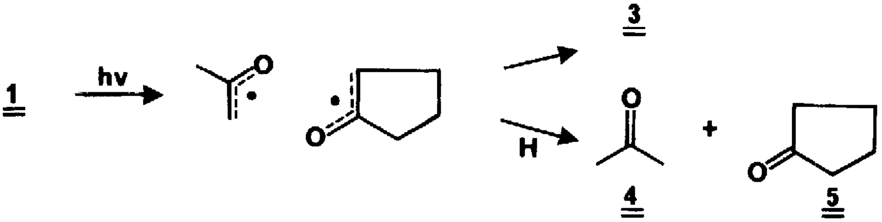
B

C

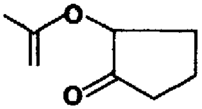
3 was identified as 2-acetonylcyclopentanone by comparison with an authentic sample:[11,12] IR (neat) $\tilde{\nu}$ = 1715 and 1738 cm$^{-1}$ (C=O); $^1$H-NMR (60 MHz,CDCl$_3$) δ = 2.18(s,3H), 1.4-3.3(m,9H); MS (70ev) m/e = 140 (11.5%,M$^+$), 125 (1.2,M-CH$_3^+$), 98 (12.6,C$_6$H$_{10}$O$^+$), 97 (27.7, C$_6$H$_9$O$^+$), 83 (32.8, C$_5$H$_7$O$^+$), 69 (15.5), 58 (5.2), 55 (11.2), 43 (100), 41 (31.8), 39 (11.6).

Discussion of the reaction mechanism:

Our results show that the main photochemical reaction of 1 is a formal 1,3-shift of the acetonyl group leading to the formation of 3. In order to get information about excited states and possible intermediates we investigated the photolysis of 1 (0.1 M in dioxane, Pyrex-filter) in presence of different quenchers: (1) 1,3-pentadiene (0.1-1 M) does not influence the intramolecular cycloaddition to 2 but quenches the formation of 3, 4 and 5 up to ca. 60%. (2) Tri-n-butyltinhydride as a free radical scavenger[13-15] (0.04-0.19 M) also shows no effect on the formation of 2 but quenches 3 up to ca. 50%. Simultaneously the formation of 4 and 5 is doubled in the presence of the organic tin hydride. These results may be interpreted that the intramolecular oxetane formation is an unquenchable singlet reaction, whereas 3 is formed at least partly via the triplet. Although organic tin hydrides in some cases quench triplet ketones efficiently [16] our experiments indicate the possibility that some 3 is formed via a free-radical recombination: if tri-n-butyltinhydride only quenched the triplet of 1, we should not observe an increased formation of the free radical products 4 and 5, which are very likely generated from the triplet of 1 as shown in the pentadiene quenching experiment. Polar intermediates may be excluded, because there is no significant dependence of the product formation on solvent polarity.[17] This proposed mechanism should be considered tentative.



This result is in contrast with that of Dalton who did not observe an analogous 1,3-shift in the photolysis of 3,5-dimethyl-4-oxa-5-hexen-2-one, but an intramolecular cycloaddition to yield a bisoxetane and a rearrangement to yield a formal photo-Cope product.[3] The same author reported that the inefficiency in product formation is a result of inefficient formation of a 1,4-biradical, similar to D.[3] If an intermediate such as D is involved in the reaction 1 → 2, based on Dalton's results the photo-Cope product 7 is expected to be formed. However, under our conditions and even at short irradiation times we were not able to detect a photoproduct of the structure 7.[6]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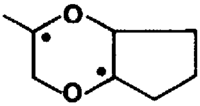
D

Preliminary investigation of 1-cyclohexenyloxy-2-propanone yielded similar results. Although the generality of these photoreactions remains to be determined, our results reveal a novel aspect of β-oxa-γ,δ-enone photochemistry, namely the formal 1,3-shift to yield 1,4-diketones. Studies dealing with homologous and hetero-substituted enones A and the mechanisms of these photoreactions are in progress to further quantify the present picture.

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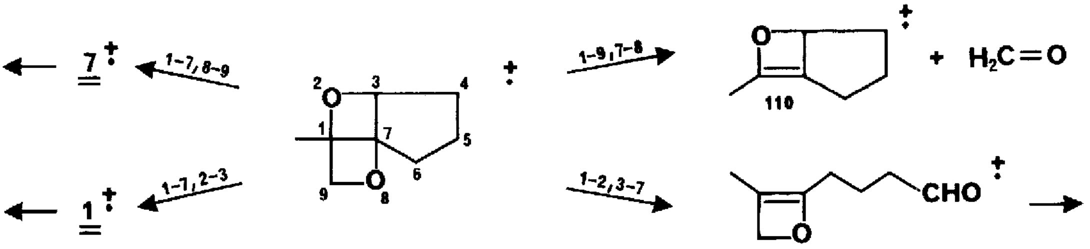
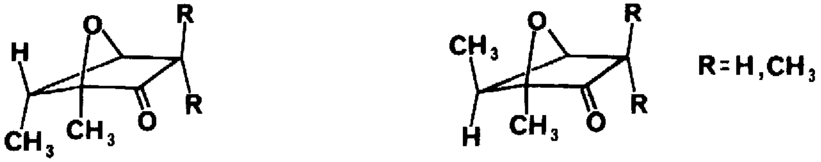
1) Part one: J. Mattay, W. Thünker, and H.-D. Scharf, Chem. Ber. in press.
2) Present address: Department of Chemistry, Columbia University, New York, NY 10027.
3) J.C. Dalton and S.J. Tremont, Tetrahedron Lett. 1973, 4025; J. Am. Chem. Soc. 97, 6916 (1975).
4) W. Thünker, J. Mattay, and H.-D. Scharf, Chem. Ber. in press.
5) 1: b.p. 72°C/10 torr; $n_D^{23}$ 1.4650; IR (neat) $\tilde{\nu}$ = 1724 (C=O), 1647 $cm^{-1}$ (C=C); $^1H$-NMR (60 MHz, $CDCl_3$) δ = 1.60-1.90 (m, $CH_2$, 2H), 2.00-2.55 (m, $CH_2$, 4H), 2.18 (s, $CH_3$, 3H), 4.28 (s, $OCH_2$, 2H), 4.39 ppm (m, =CH, 1H); MS (70 ev) m/e = 140 (44.0%, $M^+$), 139 (4.4, $M-1^+$), 125 (1.2, $M-CH_3^{\dot{+}}$), 122 (3.8, $M-H_2O^+$), 97 (12.2, $M-CH_3CO^+$), 84 (20.8, $[CH_2]_4CO^+$), 83 (59.5, $C_5H_7O^+$), 69 (19.2), 67 (47.1), 65 (19.1), 58 (9.7, $CH_3COCH_3^{\dot{+}}$), 57 (14.6, $C_3H_5O^+$), 56 (2.7, $C_3H_4O^+$), 55 (29.5, $C_4H_7^{\dot{+}}$), 43 (81.0, $CH_3CO^+$), 41 (100, $CHCO^+$), 39 (28.2, $C_3H_3^{\dot{+}}$), 29 (19.2, $CHO^+$); 27(19.3); calcd for $C_8H_{12}O_2$: C 68.54%, H 8.63%, found: C 68.67%, H 8.78%.
6) Product analyses were carried out by vpc using a 3m X 3mm glass column containing 10% UCC or 10% Carbowax both on Gaschrom Q (80-100 M).
7) The products in the mass spectrum can be interpreted by assuming a fragmentation of the

molecular ion into oxetenes and aldehydes as well as 1 and 7 which undergo further cleavage: N.C. Yang, M. Nussim, and D.R. Coulson, Tetrahedron Lett. 1965, 1525; Y. Bahurel, G. Descotes, and F. Pautet, C.R. Acad. Sci., Ser. C, Paris 270, 1528 (1970); Bull. Soc. Chim. France 1971, 2222.



e.g. 1-9 = bond cleavage between atom 1 and 9.

8) In model compounds methine proton absorption occurs in the region of $\delta \approx 3$ ppm: R. Bishop and N.K. Hamer, J. Chem. Soc. (C), 1970, 1197.



9) 3- and 2-alkoxyoxetanes of the structure B or C, respectively, have been found to show selective reactions, S. Schroeter, J. Org. Chem. 34, 1188 (1969): 2-alkoxyoxetanes react readily with alcohols upon heating to give acetals of substituted β-hydroxy-propionaldehydes, ring opening occurs exothermally upon mixing with water at room temperature. 3-alkoxyoxetanes are stable under these conditions. Even after heating in alcoholic or aqueous solution at the boiling temperature 2 remains unchanged.

10) The geometric constraints of the cyclopentene ring make other stereochemistries highly unlikely. This can easily be demonstrated by molecular models.

11) H. Paul, Chem. Ber. 93, 2395 (1960).

12) R.M. Jacobson, R.A. Raths, and J.H. McDonald III, J. Org. Chem. 42, 2545 (1977) reported the following data for 3: b.p. 108-111°C/0.02 torr; ${}^1$H-NMR ($CCl_4$) $\delta$=2.07 (s,3H), 0.8-3.1 (m,9H); IR (neat) 1738 (C=O), 1719cm$^{-1}$ (C=O); MS (70ev) m/e = 140 ($M^+$) (14), 97(38), 83(40), 43(100). However, our measured data (b.p. 108°C/15 torr and $n_D^{21}$ 1.4628) are nearly identical with those which are reported by H. Paul and I. Wendel, Chem. Ber. 90, 1342 (1957) (see also ref. 11) and M.A. Volodina, V.G. Mishina, A.P. Terent'ev, and G.V. Kiryushkina, J. Gen. Chem. USSR 32, 1899 (1962). In addition the authentic sample of 3 was synthesized using two different methods: (1) according to Paul's prescription 11), (2) a precursor was synthesized analogous to a method reported by A.M. Islam and R.A. Raphael, J. Chem. Soc. 1952, 4086. Both methods yielded same results.

13) H.G. Kuivila, Acc. Chem. Res. 1, 299 (1968).

14) D.J. Carlsson and K.U. Ingold, J. Am. Chem. Soc. 90, 7047 (1968).

15) Experiments to use alkyl thiols as radical traps 16) failed because thiols react with 1. 1) Tri-n-butyltin hydride shows no measureable reaction with 1 at room temperature.

16) R.G. Zepp and P.J. Wagner, J. Chem. Soc. Chem. Comm. 1972, 167; J. Am. Chem. Soc. 94, 287 (1972).

17) The formation of polar intermediates - e.g., generated by electron transfer from the initial radical pair - should yield a strong dependence on the solvent polarity. On the contrary there is no significant change in the relative quantum yields of product formation using either cyclohexane, benzene, dioxane, or acetonitrile as solvent.

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