Tetrahedron. Vol. 33, pp. 65 to 67. Pergamon Press 1977. Printed in Great Britain

PHOTOLYSIS OF α-DIAZOCYCLODODECANONE

A. STOJILJKOVIĆ* and R. TASOVAC
Department of Chemistry, Faculty of Science, Belgrade University, and Institute for Chemistry, Technology and Metallurgy, Belgrade, Yugoslavia

(*Received in the UK* 30 *September* 1975; *Accepted for publication* 8 *June* 1976)

Abstract—The direct photolysis of α-diazocyclododecanone in methanol yields the methyl ester of cycloundecane carboxylic acid, *cis*-2-cyclododecenone, *trans*-2-cyclododecenone and *cis*-3-cyclododecenone, the last being formed by subsequent photoisomerisation of *cis*-2-cyclododecenone. During sensitized photolysis in methanol the yield of the ester was reduced to about 1%, and the three unsaturated ketones were the main reaction products.

In cyclohexene, acetone enol acetate, ether or petroleum ether as solvents, either in the presence or in the absence of the sensitizer, the three unsaturated ketones were the only products isolated. These data show that Wolff rearrangement is suppressed under photosensitization conditions, and that the intermediate cyclic 12-membered α-ketocarbene undergoes intramolecular rather than intermolecular photoreactions, probably related to its flexible conformation.

Photoreactions of open chain and bicyclic α-diazoketones have been extensively studied.[1] However, little attention has been given tò the photochemical behaviour of monocyclic α-diazoketones, especially those of medium ring size. Upon irradiation, 9 to 11 membered α-diazoketones were reported to undergo Wolff rearrangement affording the corresponding ring-contracted cycloalkane carboxylic acids in fair yields.[2] First attempts to correlate the photochemical behaviour with ring size were made by Regitz and Rütter;[3] they studied the photolysis of cyclic α-diazoketones from 5- to 12-membered rings in aqueous tetrahydrofuran, and found that the only reaction products were the corresponding ring-contracted acids, except for α-diazocyclododecanone where, in addition to ring-contracted acid, the presence of other reaction products were detected; among these photoproducts they succeeded in identifying only the *trans*-2-cyclododecenone.

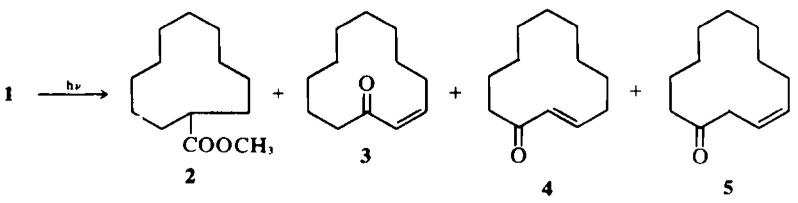
As an extension of our studies on the photochemical behaviour of 12-membered cyclic ketone derivatives,[4] we have investigated the photolysis of α-diazocyclododecanone (**1**) in polar and non-polar solvents, in the presence and in the absence of a sensitizer, in order to correlate the behaviour of this diazoketone with other cyclic and acyclic α-diazoketones.

α-Diazocyclododecanone was prepared in a yield of about 30% by the action of chloramine on α-oximinocyclododecanone (obtained by oximation of cyclododecanone). As a by-product of this reaction we isolated ω-cyanoundecanoic acid, formed by a competitive reaction, i.e. second-order Beckmann rearrangement.

Photolysis of α-diazocyclododecanone in methanol afforded a mixture of products from which we isolated by preparative GLC four photoproducts; on the basis of elemental analysis and their IR, UV, NMR and mass spectral properties they were identified as the methyl ester of cycloundecane carboxylic acid (**2**) (36%), *cis*-2-cyclododecenone (**3**) (17%), *trans*-2-cyclododecenone (**4**) (25%) and *cis*-3-cyclododecenone (**5**) (9%), relative yields being estimated from GLC peak areas. Upon hydrogenation the isomeric unsaturated ketones afforded the starting cyclododecanone in almost quantitative yield. The *cis*-2-cyclododecenone isomerized spontaneously on standing at room temperature to the *trans*-isomer. The presence of *cis*-3-cyclododecenone (**5**) is best rationalized by assuming that it is formed by photoisomerization of *cis*-2-cyclenone (**3**); according to Nozaki *et al.*[5] isomerization of **3** proceeds via a 6-membered cyclic transition state affording the *trans,cis*-dienol which is further transformed to *cis*-3-cyclodecenone (**5**). The isomerization is feasible only with *cis*-2-cyclodecenone on account of its *O-inside* conformation. On the other hand, the formation of the *trans,trans*-dienol, which would lead to *trans*-3-cyclododecenone, is less probable on conformational grounds; and, indeed this product has not been obtained in our reactions.

The products obtained in the direct photolysis of **1** in methanol demonstrate that the intermediate ketocarbene, generated by the loss of nitrogen, undergoes two competing processes, one involving Wolff rearrangement resulting in the ring-contracted acid derivative (**2**), and the other involving a 1,2-hydrogen shift leading to αβ-unsaturated ketones (**3** and **4**). This behaviour is similar to that of analogous acyclic compounds;[1] however, factors governing these two competing processes are, so far, not completely understood.

When the photolysis of **1** was conducted in methanol in the presence of benzophenone as sensitizer, the Wolff rearrangement product (**2**) was obtained in a yield of only



1%, while the total yield of isomeric unsaturated ketones amounted to 78%. The fact that by introducing benzophenone which is a triplet sensitizer the yield of **2** was drastically altered shows that the Wolff rearrangement involves the singlet state of the excited species, and that it is prevented by photosensitization.

Photolysis of **1** in cyclohexene or acetone enol acetate, either in the presence or in the absence of sensitizer, gave neither Wolff rearrangement product, nor expected addition products, but only isomeric unsaturated ketones.[6] Similarly, photolysis of **1** in ether or petroleum ether as solvents yielded a mixture of isomeric unsaturated ketones (see Table 1).

Table 1. Photochemical decomposition of α-diazocyclododecanone

Solvent	**2**	**3** (Yields in %)	**4**	**5**
Direct photolysis				
Methanol	36	17	25	9
Cyclohexene	—	26	47	10
Acetone enol acetate	—	22	30	8
Ether	—	25	43	13
Petroleum ether	—	16	46	21
Sensitized photolysis				
Methanol	1	21	42	14
Cyclohexene	—	16	40	16

The above results can be summarized by stating that 1,2-hydrogen shift is favoured in the photolysis of α-diazocyclododecanone in comparison with photochemical behaviour of diazoketones of medium-sized rings. It is known that 1,2-hydrogen shift to carbene centre gives rise to a mixture of *cis*- and *trans*-olefins;[7] in the case of the twelve-membered cyclic α-ketocarbene also a mixture of isomers was obtained in which the more stable *trans*-2-isomer was found predominated over the *cis*-2-cyclenone.

In terms of the foregoing it might be concluded that the 12-membered α-ketocarbene undergoes intramolecular rather than intermolecular photoreactions, 1,2-hydrogen shift being favoured; this may be attributed to the nonrigidity of its conformation.

EXPERIMENTAL

M.ps are uncorrected. IR spectra were recorded on a Perkin-Elmer 337 instrument, as films or in CCl_4 solns. UV spectra were taken on a Perkin-Elmer 137 spectrophotometer, in CH_3OH solns. NMR spectra were recorded on a Varian A-60 instrument using TMS as internal standard. Mass spectra were obtained on a Varian MAT CH5 spectrophotometer. GLC was performed with a Perkin-Elmer 116E instrument, and on a Varian Aerograph 1200; columns packed with silicone gum SE-30 were used, and hydrogen was the carrier gas. Column chromatography was carried out on silica-gel (Merck) and TLC; chromatoplates were developed with a mixture of cyclohexane and AcOEt (3:2), spots being detected with I_2 vapour. Irradiations were performed using a high-pressure Hanau Q-1 lamp.

Anti-α-Oximinocyclododecanone. Into an ice-cooled (10°) soln of cyclododecanone (10 g; 0.05 mole) in ether (50 ml) containing conc. HCl (2 ml) was passed a stream of nitrogen for 10–15 min. Gaseous methyl nitrite was then introduced into the above soln, the temp being kept between 5 and 10°C. Methyl nitrite was generated by adding dropwise a sulphuric acid soln (6.5 ml of conc. H_2SO_4 in 11.8 ml of H_2O) into a mixture of sodium nitrite (17.2 g), methanol (8 ml) and water (15.2 ml). After standing for several h at room temp. the crystalline product (10.3 g; 88%) was filtered off, washed with petroleum ether and recrystallized from cyclohexane; m.p. 74–75°C; IR (KBr): 3260 (OH), 1660 (C=O), 1620 (C=N) cm^{-1}; IR (dil CCl_4): 3580 (OH), 1690 (C=O), 1620 (C=N) cm^{-1}; UV: $\lambda_{max}^{CH_3OH} = 233$ nm; NMR (CCl_4): δ 9.37 (1 H), δ 2.7 (4 H, multiplet), δ 1.6 (4 H, multiplet); in 0.1 NaOH $\lambda_{max}^{CH_3OH} = 284$ nm indicated the *anti*-configuration. (Found: C, 67.96; H, 10.5; N, 6.73. Calc. for $C_{12}H_{21}O_2N$ (M = 211): C, 68.21; H, 10.02; N, 6.63%).

α-Diazocyclododecanone (**1**). To a stirred soln of *anti-α*-oximinocyclododecanone (3.1 g; 0.014 mole) in 10% NaOH (100 ml), cooled to 0°C, was added 15N ammonium hydroxide (12.5 ml), followed by dropwise addition of freshly prepared sodium hypochlorite (150 ml; 5.25%) soln; during the addition the temp. was not allowed to rise above 5°C. When the addition was over, the mixture was stirred at 0°C for 1 h and then, at room temp. for 5 h. Water (100 ml) was then added and the mixture was extracted with petroleum ether; the dried extract gave first a viscous yellow oil (0.9 g; 29%) which crystallized upon cooling to −10°C yielding yellow crystals, m.p. 42–44°C. IR (film): 2065 ($C=N_2$), 1640 (C=O), 1600 (C=N); UV: $\lambda_{max}^{CH_3OH} = 252$ and 294 nm; (Found: C, 69.00; H, 9.76; N, 13.21. Calc. for $C_{12}H_{20}ON_2$ (M = 208): C, 69.11; H, 9.68; N, 13.46%).

ω-Cyanoundecanoic acid. The alkaline soln left after the extraction of **1** with petroleum ether was acidified with HCl; the precipitate was filtered off and recrystallized from cyclohexane affording white crystals (0.5 g; 16.12%), m.p. 56–57°C[8] IR(KBr) 3195 (OH), 2260 (C≡N), 1722 (C=O) cm^{-1}; (Found: C, 68.03; H, 10.00; N, 6.76. Calc. for $C_{12}H_{21}O_2N$ (M = 211): C, 68.21; H, 10.02; N, 6.63%).

Photolytic decomposition of α-diazocyclododecanone (**1**). Irradiations were performed with a mercury Q-1 Hanau Lamp, in a quartz immersion cell fitted with a water jacket. The solutions were 0.4% (g/ml), 230 ml being contained by the apparatus. Solutions were degassed with nitrogen before irradiation. The changes during photolysis were followed by TLC and the irradiations were carried until the evolution of nitrogen ceased. All experiments were carried out under the same experimental conditions.

A soln of **1** (1 g; 0.0048 mole) in anhydrous methanol (230 ml) was irradiated for 4 h, at 18°C, with constant stirring. After the decomposition ceased and the yellow colour of the soln disappeared, the solvent was removed in vacuo and the residual mixture of photoproducts was in the first instance separated by column chromatography, and then by preparative GLC; four photoproducts were identified:

Methyl ester of cycloundecane carboxylic acid (**2**). IR(film): 1735 (C=O), 1160 (C–O) cm^{-1}; NMR (CCl_4): δ 3.5 (3H, s); (Found: C, 73.23; H, 11.10. Calc. for $C_{13}H_{24}O_2$ (M = 212): C, 73.53; H, 11.39%). M^+ 212, *m/e* 180(M − 32), 152(M − 60).

cis-2-Cyclododecenone (**3**). IR(film): 1700 (C=O), 1630 (C=C), 748 $(\underset{|}{C}=\underset{|}{C})$ cm^{-1}; NMR (CCl_4): δ 5.3 and 6.2; (Found: C, 79.75; H, 11.30. Calc. for $C_{12}H_{20}O$: C, 79.94; H, 11.18%).

trans-2-Cyclododecenone (**4**). IR(film): 1700 and 1685 (C=O), 990 $(\underset{|}{C}=\overset{|}{C})$ cm^{-1}; NMR (CCl_4): δ 6.12 (1 H, doublet), δ 6.6 (1H, multiplet); (Found: C, 79.81; H, 11.03. Calc. for $C_{12}H_{20}O$: C, 79.94; H, 11.18%).

cis-3-Cyclododecenone (**5**). IR(CCl_4): 3020 (H–C=), 1710 (C=O) cm^{-1}; NMR (CCl_4): δ 5.5 (2 H, multiplet), δ 2.81 and δ 3.1 (2 H, quartet), δ 2.35 (4 H, multiplet); (Found: C, 79.90; H, 11.28. Calc. for $C_{12}H_{20}O$: C, 79.94; H, 11.18%).

Photoproducts obtained from **1** in other solvents were analyzed by GLC and identified by comparison of their retention times with authentic samples; relative yields were estimated from appropriate peak area.

REFERENCES

[1] W. Kirmse, *Carbene Chemistry*, Academic Press, New York (1964); B. Eistert, M. Regitz, G. Heck and H. Schwall, In *Houben-Weyl*: *Methoden der Organischen Chemie*, Stuttgart (1968), Bd. 10/4; A. Schönberg, *Preparative Organic Photo-*

chemistry, Springer Verlag, Berlin (1968); H. Meier and K. P. Zeller, *Angew. Chem.* **87**, 52 (1975).

[2] A. T. Blomquist and F. W. Schlaefer, *J. Am. Chem. Soc.* **83**, 4547 (1961).

[3] M. Regitz and J. Rüter, *Chem. Ber.* **102**, 3877 (1969).

[4] A. Stojiljković and R. Tasovac, *Tetrahedron Letters* 1405 (1970).

[5] H. Nozaki, T. Mori and R. Noyori, *Tetrahedron* **22**, 1207 (1966).

[6] W. Ando and M. Jones, *J. Am. Chem. Soc.* **90**, 2200 (1968).

[7] Y. Yamamoto and I. Moritiani, *Tetrahedron* **26**, 1235 (1970); and references therein.

[8] J. A. Perkins and A. O. Cruz, *J. Am. Chem. Soc.* **49**, 1073 (1968).