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PHOTOCHEMISTRY OF α-OXO-OXIMES—VI[1]

IRRADIATION OF 3-ETHOXYIMINO-1,7,7-TRIMETHYLBICYCLO[2.2.1]HEPTAN-2-ONE

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Abstract—The photolysis of 3-ethoxyimino-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one **1** with λ 254 nm has been investigated in acetonitrile as solvent. Photoexcited **1** undergoes N–O bond homolysis with formation of a cyclic α-oxo-iminyl and an ethoxy radical. Cage recombination of these radicals affords the ethyl cyanocyclopentanecarboxylate **9**. The formation of the products **6–8** is explained by decarbonylation of the α-oxo-iminyl radical, followed by disproportionation and H-abstraction. The occurrence of the α-oxo-iminyl radical and (by loss of CO) the tertiary cyanocyclopentyl radical is substantiated by an ESR photoexperiment in the presence of 2-methyl-2-nitrosopropane.

The predominant photochemical process with acyclic α-oxo-oximes and their derivatives upon irradiation with λ 366 and 313 nm was found to be the (*E*)-(*Z*) isomerization.[2] Irradiation of these compounds with λ 254 nm did however also lead to photodecomposition.[1] We therefore thought it of interest to study the λ 254 nm photochemistry of the cyclic compound **1**. Irradiation of 3 - ethoxyimino - 1,7,7 - trimethyl - bicyclo[2.2.1]heptan - 2 - one **1** with λ 366 nm both in the presence and absence of triplet sensitizers in acetonitrile solution resulted only in the formation of a photostationary state (pss) mixture of the (*E*)- and (*Z*)-isomers.[2b]

RESULTS

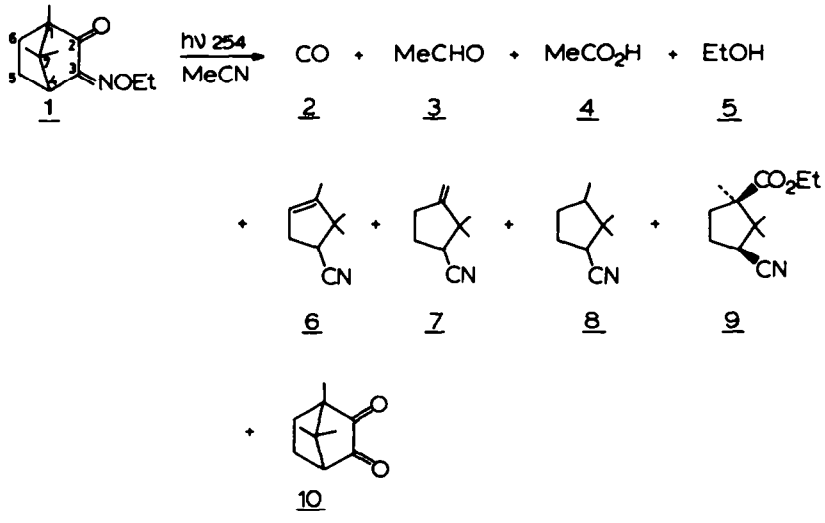
The irradiation of **1** (0.15 M) with λ 254 nm resulted in the formation of the products **2–10** (Scheme 1) and traces of methane and carbon dioxide. The products **3–5** were formed in the ratio 6:1:6, respectively.

The **6–10** ratio was found to be 10:9:21:4:1, respectively. According to ^{1}H NMR **8** consisted of the two isomers **8A** and **8B** (65:35). The assignment of the methyl absorptions in the ^{1}H NMR spectra of **8** and **9** (see Table 1) are based on (i) the difference in deshielding of the 19β-methyl group in steroids caused by the 1α- and 1β-CN respectively,[3] and (ii) the effect of an ester group in β-position on the chemical shift of a methyl group.[4]

The photolysis of 3 - acetyloxyimino - 1,7,7 - trimethylbicyclo - [2.2.1]heptan - 2 - one, i.e. the corresponding acetate of **1**, with λ 320 ± 5 nm in benzene in the presence of some 2-methyl-2-nitrosopropane (*t*-BuNO) resulted, as detected by ESR, in the formation of two radical species derived from the α-oxo-oxime ester. The signal with $a_N = 7.9$ G inferred to be due to an acyl-*t*-butylnitroxide.[5a]

The pivaloyl radical generated by H-abstraction from *t*-butylcarboxaldehyde by *t*-butoxy radicals[6] yielded in the presence of *t*-BuNO a nitroxide with $a_N = 7.8$ G; the signal with $a_N = 7.9$ is therefore assigned to the nitroxide **11** (see Scheme 2).

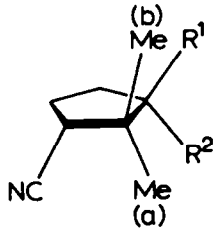
The signal with $a_N = 14.1$ G was attributed to the



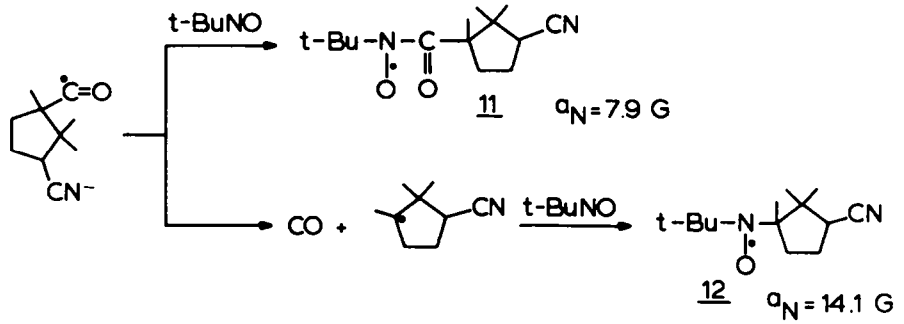
1 2 3 4 5 6 7 8 9 10

Scheme 1.

Table 1. ^{1}H NMR data of 8 and 9



	δ_{Me}		
	a	b	R^1 or R^2
8A R^1 = Me; R^2 = H	1.08	0.90	0.89
8B R^1 = H; R^2 = Me	1.16	0.90	0.87
9 R^1 = Me; R^2 = CO_2Et	1.23	1.05	1.17



Scheme 2.

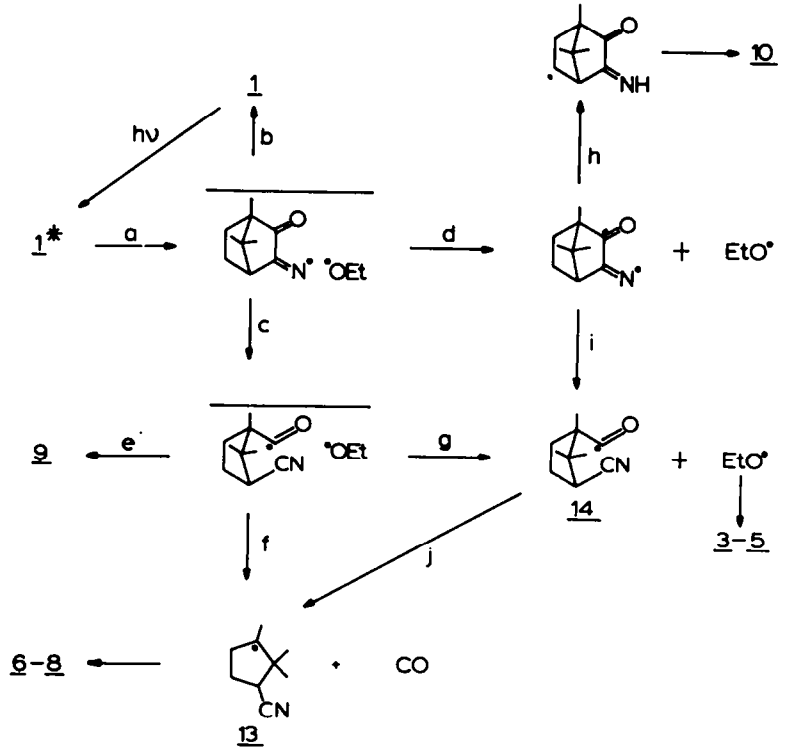
nitroxide 12 on the basis of (i) its a_N value which is typical for an alkyl-*t*-butylnitroxide[5b] and (ii) the absence of β-hydrogen splitting.†

†Di-*t*-butylnitroxide which was also detected in this experiment gives a signal with a_N = 15.1 G.

‡It seems unlikely that the corresponding free radicals formed via steps g and i combine to give 9, as the decarbonylation of the acyl radical (j) and the disproportionation and H-abstraction of the ethoxy radical will be much more favoured.

DISCUSSION

The products formed in the photolysis of 1 with λ 254 nm can be explained in terms of initial N–O bond homolysis with formation of an α-oxo-iminyl and an ethoxy radical [step (a) of Scheme 3]. Such an N–O bond homolysis also occurs in the photolysis of oxime esters[7] and α-oxo-oxime esters.[8] The resulting cage radical pair may combine to reform 1 (b), produce via β-scission of the C(2)–C(3) bond a new cage radical pair (c), or diffuse apart (d). The cage radical pair via (c) yields the ester 9(e),‡ or the tertiary radical 13 via (f) or (g), (j). The



Scheme 3.

α-oxo-iminyl radical formed by step (d) may abstract hydrogen to yield eventually the diketone **10**, or lead via β-scission (i) and decarbonylation (j) also to the radical **13**.

The decarbonylation of the acyl radical **14** [(f) and (j)] will be very much faster than that of, e. g. the acetyl radical, the rate of decarbonylation of the pivaloyl and acetyl radical in the liquid phase at 40° being 5.2×10^4 and *ca.* $1\ s^{-1}$ respectively.[9] The ESR experiment with the corresponding acetate of **1** corroborates the facile decarbonylation of the acyl radical **14**.

The cyanocyclopentyl radical **13** either disproportionates or abstracts hydrogen. The ratio of **6** to **7** is 1.07. It would be 0.67 if it was determined only by statistical factors. 1-Methylcyclopentene is 3.9 kcal mol^{-1} more stable than methylenecyclopentane;[10] this would infer a ratio of **6** to **7** of more than 700. The formation of the olefins **6** and **7** is apparently determined rather by kinetic than by thermodynamical control. A similar observation was made with the *s*-butyl radical in pentane solution which yields the more stable 2-butene and the less stable 1-butene in a ratio of 0.8 (the statistical ratio is 0.67).[11] The dimerization product of **13** was not detected. This is comparable with the behaviour of, e.g. the *t*-butyl radicals, which in pentane solution have a ratio of disproportionation to combination of 7.2.[11]

The ester **9** is obtained in only one isomeric form, whereas two isomers of compound **8** are formed. This is not surprising as in the formation of **9** the C(1)–C(2) and C(3)–C(4) bonds are not broken, which infers that the cyano and carbethoxy groups remain in the *cis* position. However, by decarbonylation the C(1)–C(2) bond is broken and the planarity of the resulting radical center at C(1) leads to the formation of two isomers of **8**.

The formation of **10** proceeding via steps (a), (d), (h) and subsequent hydrolysis (see Scheme 3) is analogous to the formation of 1-phenyl-1,2-propanedione on photolyzing 2-acetyloxyimino-1-phenylpropan-1-one.[12]

From the relative product formation it follows that the step (d), (h) is less important than the cage combination (e), or the decarbonylation (f).

The formation of the products **3–5** and methane may be explained by reactions of the ethoxy radical. These reactions will be discussed in detail for the photolysis of 3-ethoxyiminobutan-2-one.[1]

EXPERIMENTAL

Materials

The synthesis of 3 - ethoxyimino - 1,7,7 - trimethylbicyclo - [2.2.1]heptan - 2 - one (**1**) has been described.[2] The solvents were purified by distillation and dried before use.

Irradiations and analysis

The photochemical and analytical techniques were described before.[12]

Carbon monoxide (**2**) was identified on comparison of its GSC (3 m, 1/8 in, Carbosieve B, 120–140 mesh) retention time with that of an authentic sample. *Methanal* (**3**), *acetic acid* (**4**) and *ethanol* (**5**) were identified on a 2 m, 1/4 in, Porapak Q + S, 60–80 mesh, copper column. *Acetic acid* (**4**) was also identified by comparison of its IR data with the Sadtler Spectra Collection ones.

4,5,5 - Trimethyl - 3 - cyclopentene - 1 - carbonitrile (**6**). IR ($CHCl_3$): 2970 (s), 2220 (w, CN), 1650 (vw, C=C), 1360 (m), 895 (m). ^1H NMR ($CDCl_3$): 5.21 (m, 1H, C=CH), 2.87–2.68 (m, 1H, CH–CN), 2.64–2.44 (m, 2H, CH_2), 1.62 (d, 3H, J = 2 Hz, CH_3C=), 1.15 [s, 6H, $(CH_3)_2C$].†

2,2 - Dimethyl - 3 - methylenecyclopentane - 1 - carbonitrile (**7**). IR ($CHCl_3$): 2980 (s), 2230 (w, CN), 1660 (w, C=C), 1465 (m), 1365 (w), 890 (s). ^1H NMR ($CDCl_3$): 4.87 (q, 2H, J = 2 Hz, CH_2=C), 2.71–2.36 (m, 3H, CH_2–C=+CH–CN), 2.28–1.86 (m, 2H, CH_2–CH), 1.22 (s, 3H, CH_3C), 1.20 (s, 3H, CH_3C).†

2,2,3-Trimethylcyclopentane-1-carbonitrile (**8**). IR ($CHCl_3$): 2970 (s), 2870 (m), 2220 (m, CN), 1470 (m), 1450 (m), 1390 (w), 1370 (m). MS (70 eV): 136 [6, $(M–H)^+$], 122 [26, $(M–CH_3)^+$], 120 (5), 110 [6, $(M–HCN)^{+\cdot}$], 109 [20, $(110–H)^+$], 96 [38, $(M–CH_3CN)^{+\cdot}$], 95 [41, $(110–CH_3)^+$], 84 [79, $(M–CH_2{=}CH–CN)^{+\cdot}$], 83 [22, $(84–H)^+$], 81 [32, $(96–CH_3)^+$: m^*_{obs} 68.26 and m^*_{calc} 68.34], 69 [100, $(84–CH_3)^+$], 56 [26, $(84–C_2H_4)^{+\cdot}$: m^*_{obs} 37.37 and m^*_{calc} 37.33], 55 [36, $(83–C_2H_4)^+$: m^*_{obs} 36.50 and m^*_{calc} 36.45], 41 [64, $(69–C_2H_4)^+$: m^*_{obs} 24.41 and m^*_{calc} 24.36]. According to ^1H NMR this compound existed in two isomeric forms: **8A** with 1–CN and 3–Me *trans* (65%) and **8B** with 1–CN and 3–Me *cis* (35%). ^1H NMR ($CDCl_3$) of **8A**: 2.62–2.33 (m, 1H, CH–CN), 2.11–1.68 (m, 5H, $2xCH_2$ + CH–CH_3), 1.08 (s, 3H, CH_3C, *cis* to CN), 0.90 (s, 3H, CH_3C, *trans* to CN), 0.89 (d, 3H, J = 5.7 Hz, CH_3CH, *trans* to CN). ^1H NMR ($CDCl_3$) of **8B**: 2.62–2.33 (m, 1H, CH–CN), 2.11–1.68 (m, 5H, $2xCH_2$ + CH–CH_3), 1.16 (s, 3H, CH_3C, *cis* to CN), 0.90 (s, 3H, CH_3C, *trans* to CN), 0.87 (d, 3H, J = 6.5 Hz, CH_3CH, *cis* to CN).

Ethyl 3-cyano-1,2,2-trimethylcyclopentane-1-carboxylate (**9**). IR ($CHCl_3$): 2975 (m), 2210 (vw), 1710 (s), 1460 (w), 1370 (w), 1255 (m), 1145 (m), 1095 (m). ^1H NMR ($CDCl_3$): 4.14 (q, 2H, J = 7 Hz, CH_2O), 2.92–2.66 (m, 1H, CH–CN), 2.20–1.86 (m, 4H, $2xCH_2$), 1.27 (t, 3H, J = 7 Hz, CH_3CH_2), 1.23 (s, 3H, CH_3C, *cis* to CN), 1.17 (s, 3H, CH_3CCO_2Et, *trans* to CN), 1.05 (s, 3H, CH_3C, *trans* to CN). MS (70 eV): 209 (8, $M^{+\cdot}$), 182 [9, $M–HCN)^{+\cdot}$], 181 [7, $(182–H)^+$, 164 [7, $(M–C_2H_5O)^+$], 137 [13, $(164–HCN)^+$], 136 [100, $(164–CO)^+$: m^*_{obs} 112.82 and m^*_{calc} 112.78], 135 [44, $(181–C_2H_5OH)^+$: m^*_{obs} 100.69 and m^*_{calc} 100.69], 120 [26, $(135–CH_3)^{+\cdot}$: m^*_{obs} 106.65 and m^*_{calc} 106.67], 109 [45, $(136–HCN)^+$: m^*_{obs} 87.44 and m^*_{calc} 87.36], 95 [54, $(136–CH_3CN)^+$: m^*_{obs} 66.41 and m^*_{calc} 66.31], 94 [22, $(109–CH_3)^+$], 93 [11, $(136–C_3H_7)^+$: m^*_{obs} 63.69 and m^*_{calc} 63.60].

1,7,7,-Trimethylbicyclo[2.2.1]heptan-2-dione (**10**). The IR and ^1H NMR were identical with Sadtler spectra 48091 and 20616, respectively.

†The spectroscopic data of 2,3,3 - trimethyl - 4 - cyanomethyl - 1 - cyclopentene and 2,2 - dimethyl - 3 - methylcyano - 1 - methylidenecyclopentane[13] proved helpful in elucidating the structures of **6** and **7**, respectively.

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