Photochemistry of α-Oxo-oximes. Part 7.[1] Photolysis of Some α-Oxo-oxime Esters

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The photochemistry of six α-oxo-oxime esters has been investigated in benzene as solvent. The photoformation of the various products has been explained in terms of initial N–O cleavage, followed by β-scission of the resulting α-oxo-iminyl and acyloxyl radicals to yield a carbonitrile and an acyl radical, and carbon dioxide and an alkyl radical, respectively. The presence of the acyl and alkyl radicals has been demonstrated by e.s.r. by the spin trapping technique. The structures of the secondary amides formed upon photolysis of the various α-oxo-oxime esters, *e.g.* 3-acetamidobutan-2-one (14) from 3-acetoxyiminobutan-2-one (1a), suggest the intermediacy of the *N*-acyl α-oxoimine (37), which is then further photoconverted. The formation of 4-oxopentanenitrile (19) in the photolysis of 3-acetoxyiminopentan-2-one (1b) has been explained in terms of an initial intramolecular γ-hydrogen abstraction by the excited ketone carbonyl [$^1S(n-\pi^*)$], followed by cyclobutanol formation and a subsequent thermal reaction. Pyrolysis of 3-acetoxyiminobutan-2-one (1a) at 200° leads to a rapid conversion into mainly acetonitrile (4) and acetic acid (5).

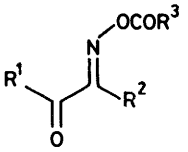
THE photolysis of oxime esters has attracted much attention.[2-8] The formation of the corresponding oxime was at first explained [2] by initial *O*-acyl bond cleavage and subsequent hydrogen abstraction; the fate of the concomitantly produced acetyl radical was, however, not discussed. Later it was shown for cyclohexanone oxime esters,[3] 2-benzoyloxyimino-1-phenylpropan-1-one,[4a] bisacetyloxyiminobutane-2,3-dione,[4b] and *O*-acyl aromatic ketoximes [6,7] that the initial process after excitation is N–O bond cleavage. Grellmann reported the photochemical formation of ketimines from aromatic ketoxime esters.[8] Also the photolysis (and pyrolysis) of bornan-2-one oxime was reported to produce the iminyl radical by initial N–O bond cleavage.[9]

The nature of the reactive excited state of aromatic oxime esters was examined by Yoshida *et al.*[7c] It appeared that the photodecomposition of *O*-acyl aromatic ketoximes originates from an excited triplet state with predominant π–π* character and that the energy of this triplet state is close to that of the parent ketone.[7c]

The photolysis of α-oxo-oxime esters has, in contrast to that of simple oxime esters, hardly been investigated. Delzenne *et al.*, who were primarily interested in the use of these compounds as radical initiators for polymerization, proposed a mechanism and tentatively discussed the possible fate of the radicals in the photolysis of 2-benzoyloxyimino-1-phenylpropan-1-one.[4a]

The photoreactions of the α-oxo-oximes and their derivatives can be divided into isomerization and decomposition. Previously, we reported on the photoisomerization of α-oxo-oximes,[10] their acetates,[10] and ethyl ethers.[11] The photodecomposition of α-oxo-oxime ethers upon irradiation with λ 313 and 366 nm is slow relative to photoisomerization; [11] with λ 254 nm the photodecomposition is fast relative to the photoisomerization.[1,12]

In this paper the photodecomposition of five α-oxo-oxime esters, *viz.* 3-acetoxyiminobutan-2-one (1a), 3-acetoxyiminopentan-2-one (1b), 3-propionyloxyiminobutan-2-one (1d), 2-acetoxyiminopentan-3-one (1e), and



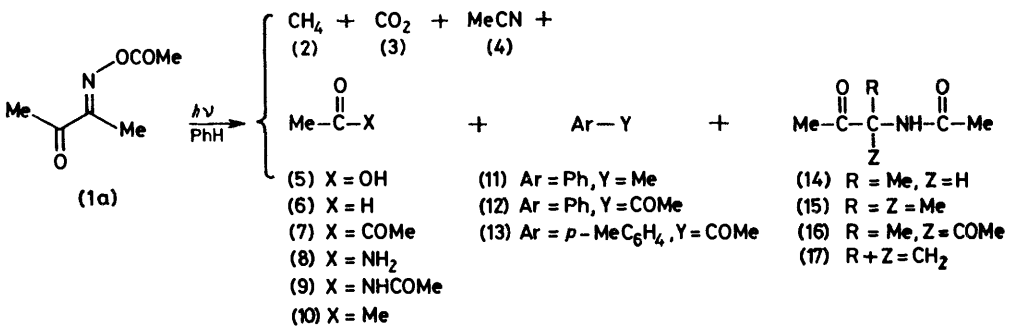
(1)

a; $R^1 = R^2 = R^3 = Me$
b; $R^1 = R^3 = Me$; $R^2 = Et$
c; $R^1 = CD_3$; $R^2 = Et$; $R^3 = Me$
d; $R^1 = R^2 = Me$; $R^3 = Et$
e; $R^1 = Et$; $R^2 = R^3 = Me$
f; $R^1 = Ph$; $R^2 = R^3 = Me$

2-acetoxyimino-1-phenylpropan-1-one (1f) are reported. In order to obtain insight into the mechanism the photolyses have also been performed in the presence of 2-methyl-2-nitrosopropane as a spin trapping reagent.

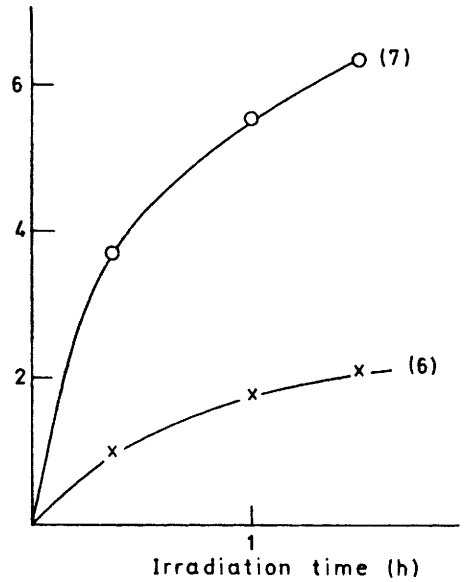
RESULTS

Irradiation of (1a).—Irradiation of (1a) (0.1—0.3M) in benzene with λ 313 or 366 nm results in the formation of products (2)—(17). G.l.c. analysis further revealed the



presence of a variety of minor products which were not identified. Products (2)—(7) and 11 are primary, as was concluded from the dependence of the product yield on the irradiation time. Typical plots are shown in the Figure. The yield of CO_2 was found to be 97%.

Irradiation of (1b).—Irradiation of (1b) with λ 366 nm in benzene as solvent results in the formation of the products listed in Table 1. The major products were found to be (2), (3), (5), (8), (18), and (21)—(23).



Relative amounts of MeCHO (6) and MeCOCOMe (7) in the photolysis of (1a) in benzene with λ 366 nm

Replacement of the R^2 = Me in (1a) by R^2 = Et leads to the replacement of Me by Et in five photoproducts, *viz.* (18) and (20)—(23) The nitrile (19) has no homologue in

TABLE 1

Products of the photolysis of the α-oxo-oxime esters with λ 366 nm in benzene as solvent

Entry	Product	Substrate (1a)	(1b)	(1d)	(1e)	(1f)
1	R^3H	2	2	24	2	2
2	R^1H	*a*	*a*	2		*d*
3	CO_2	3	3	3	3	3
4	R^2CN	4	18	4	4	4
5	R^3CO_2H	5	5	25	5	5
6	R^1CO_2H	*a*	*a*	5	25	31
7	R^1CHO	6	6	6		32
8	R^1COCOR^1	7	7	7		35
9	R^1COCOR^2	*a*		*a*		36
10	R^1COR^3	10	10	27	27	12
11	R^1CONH_2	8	8	8	26	33
12	R^3CONH_2	*a*	*a*	26	8	8
13	R^3Ph	11	11	28	11	11
14	R^1Ph	*a*	*a*	11		
15	R^1COPh	12	12	12		
16	p-$R^3C_6H_4COR^1$	13	13	29		
17	$R^1COCH(R^2)NHCOR^1$	14	20		*b*	
18	$R^1COC(R^2)(R^3)NHCOR^1$	15	21	21	*b*	
19	$R^1COC(R^2)(COR^1)NHCOR^1$	16	22	16	30	
20	$R^1COC[=(R^2 - H)]NHCOR^1$	17	23	17	*c*	
21	Other	9	19	10		34

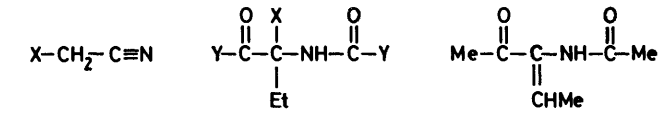
[a] This product is the same as one entry earlier. [b] Only one of these two possible products is formed. [c] Present in the photolysate according to i.r. [d] The product is identical with the solvent.

TABLE 2

Mass spectrum (g.c.–m.s.; 70 eV) of (19) and (20), and their deuteriated analogues (19a) and (20a)

Compound	*m/e*	Relative intensity	Assigned ion composition
(19)	97	35	$M^{+\cdot}$
	82	30	$(M - CH_3)^+$
	55	15	$(M - CH_2{=}C{=}O)^{+\cdot}$
	54	100	$(M - CH_3C{=}O)^+$
(19a)	100	15	$M^{+\cdot}$
	82	10	$(M - CD_3)^+$
	54	30	$(M - CD_2C{=}O)^+$
	46	100	$(M - C_3H_4N)^+$
(20)	101	5	$(M - CH_2{=}C{=}O)^{+\cdot}$
	100	45	$(M - H - CH_2{=}C{=}O)^+$ / $(M - CH_3C{=}O)^+$
	72	10	$(101 - C_2H_5)^+$
	59	5	$(101 - CH_2{=}C{=}O)^{+\cdot}$
	58	100	$(100 - CH_2{=}C{=}O)^+$ / $(101 - CH_3C{=}O)^+$
(20a)	105	5	$(M - CD_2{=}C{=}O)^{+\cdot}$
	104	10	$(M - H - CD_2{=}C{=}O)^+$
	103	55	$(M - CD_3C{=}O)^+$
	76	5	$(105 - C_2H_5)^+$
	60	15	$(104 - CD_2{=}C{=}O)^+$
	59	100	$(103 - CD_2{=}C{=}O)^+$ / $(105 - CD_3C{=}O)^+$
	46	40	$(M - C_5H_7D_3NO)^+$

the photolysis of (1a). In order to determine the origin of the acetyl groups in *e.g.* the products (19)—(23) the photolysis of the deuteriated compound (1c) with λ 366 nm was investigated. The products were identified by g.l.c.–mass spectrometric (g.c.–m.s.) analysis. The spectra of some deuteriated and corresponding non-deuteriated products are given in Table 2. On the basis of the fragmentation

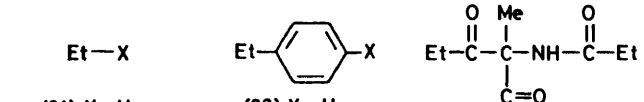


(18) X = Me
(19) X = CH_2COMe
(19a) X = CH_2COCD_3
(20) X = H, Y = Me
(20a) X = H, Y = CD_3
(21) X = Me, Y = Me
(22) X = COMe, Y = Me
(23)

pattern and the relative intensities of the various mass peaks the deuteriated products were assigned to be (19a) and (20a).

Irradiation of (1d).—Irradiation of (1d) (0.35M) in benzene with λ 366 nm results in the formation of the products listed in Table 1. The major products are (3)—(5), (12), (21), (24), and (25).

By changing the ester group from acetate [as in (1a)] to propionate seven products were formed with ethyl instead of methyl, *viz.* (21) and (24)—(29). Product (21) is also



(24) X = H
(25) X = CO_2H
(26) X = $CONH_2$
(27) X = COMe
(28) X = H
(29) X = COMe
(30)

formed upon photolysing (1b). The formation of methane (2), acetic acid (5), and a trace of toluene (11) established that in the photolysis of (1a) the methyl group of (2), (5), and (11) partly originates from R^1. Further, the formation

TABLE 3

Product yield (%) for the photolysis of (1f) in various solvents [a]

Product	Benzene	Propan-2-ol	MeCN
MeCN (4)	88	51	*b*
$MeCO_2H$ (5)	<1	31	12
$MeCONH_2$ (8)	1	4	1
PhH	*b*	5	1
PhMe (11)	16		
PhCOMe (12)	7	2	7
$PhCO_2H$ (31)	9	18	3
PhCHO (32)	2	4	2
$PhCONH_2$ (33)	4 [c]	6	4
PhCOCOPh (35)	1	3	3
PhCOCOMe (36)	1	3	1

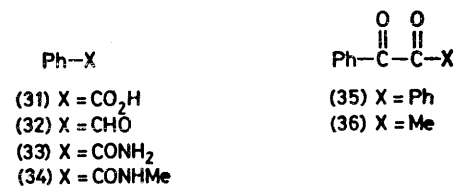
[a] Products were analysed by g.l.c. from 0.10M solutions (1 ml) irradiated with λ 313 nm for 16 h using 1,4-dichlorobenzene as internal standard, except for (4), (11), and benzene which were determined after 17 h of irradiation with λ 366 nm of 0.21M solutions (2 ml). [b] The product is identical with the solvent. [c] Sum of products (33) and (34).

of (26) from (1d) indicates that part of the methyl of acetamide (8) formed in the photolysis of (1a) comes from R^3.

Irradiation of (1e).—Irradiation of (1e) with λ 366 nm in benzene yields the photoproducts listed in Table 1. An interesting one is (30), as a comparison of this product with the tri-acetyl analogue (16) [formed in the photolysis of (1a)] reveals the origin of the acyl groups in (30) and (16).

Irradiation of (1f).—Irradiation of (1f) with λ 366 nm in benzene results in the formation of the products listed in Table 1.

By replacement of R^1 = Me in (1a) by R^1 = Ph six new products are found, *viz.* (31)—(36).* The yields of some



photoproducts are listed in Table 3. The material balance for the methyls of the MeC=N and $MeCO_2$ fragments is *ca.* 75%. The material balance for the phenyl of the PhC=O fragment is only *ca.* 35%. This might be due at least in part to the presence of a variety of other products as is evident from a number of unaccounted peaks of low intensity in the g.l.c. diagram.

E.s.r. Experiments.—Upon irradiation of (1a, b, d, and f) in benzene at λ 320 ± 5 nm in the presence of some 2-methyl-2-nitrosopropane (Bu^tNO) in the cavity of the e.s.r. spectrometer two radical species derived from the oxime esters were observed (see Table 4).† For (1a, b, and d) the strong signals with the small a_N were assigned to acetyl-t-butyl nitroxide,[13] in accordance with the nitroxide with a_N 7.72 G generated from ethanal, di-t-butyl peroxalate [14] and Bu^tNO. The weak signals with the large a_N were identical for (1a, b, and f). In view of the large a_N this signal may be either an alkoxyalkyl nitroxide or an iminoxyl radical. The most plausible possibility, *i.e.* the 3-iminoxybutan-2-one radical, has a larger a_N and other a_H values [15] than observed for the present radical. This radical is therefore tentatively assigned to be t-butylmethoxy nitroxide for (1a, b, and f), and t-butylethoxy nitroxide for (1d). Its formation may be conceived by the addition of an alkoxyl radical, resulting from reaction of an alkyl radical with oxygen, to the nitroso group of Bu^tNO.‡

Pyrolysis.—Substrate (1a) completely decomposed at 200° with the formation of (4), (5), (8), (10), ethane-1,1-diol diacetate, methyl acetate, and acetic anhydride, of which (4), (5), and acetic anhydride are by far the major products. All the irradiations of the α-oxo-oxime esters (1) were therefore performed until complete substrate conversion.

TABLE 4

Hyperfine splitting constants [a] of the radical species derived from the α-oxo-oxime esters

Substrate	a_N	a_H	Intensity
(1a)	7.75		Strong
	29.8	1.5 (3 H)	Weak
(1b)	7.72		Strong
	ca. 30	1.5 (3 H)	Weak
(1d)	7.75		Strong
	29.2	1.1 (2 H)	Weak
(1f)	7.94		Strong
	29.8	1.5 (3 H)	Weak

[a] In Gauss at room temperature in benzene solution.

DISCUSSION

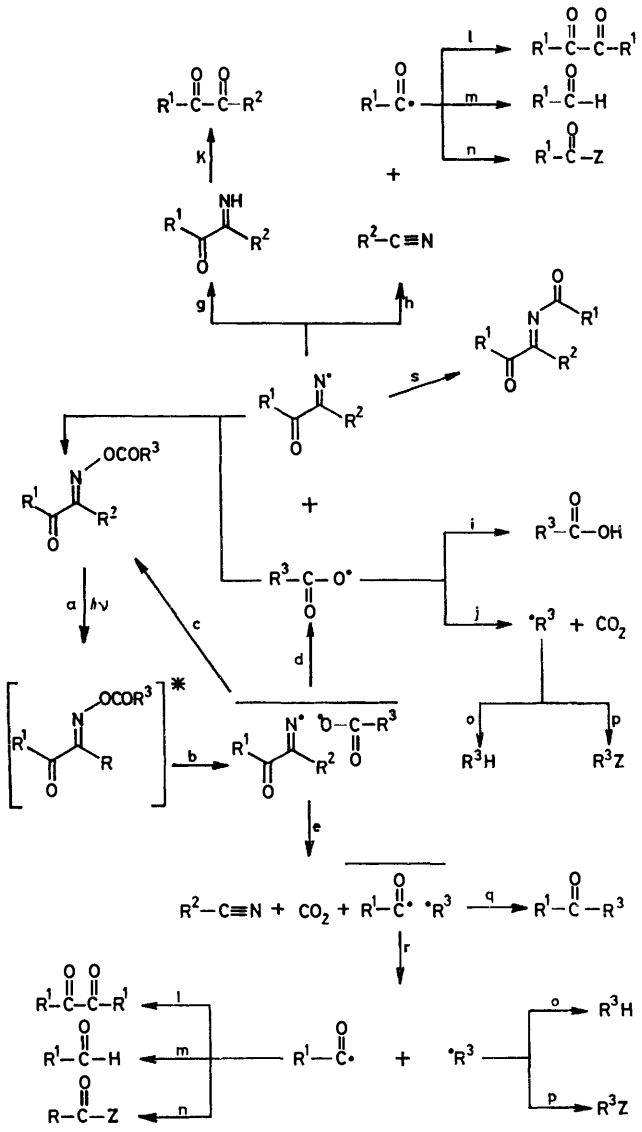
The formation of the photoproducts of (1) listed in the entries 1—10 of Table 1 may be explained in terms of the mechanism outlined in Scheme 1. After excitation (a) of (1) bond cleavage may occur in two ways. N–O Bond cleavage (b) produces an iminyl and acyloxyl radical, whereas O–acyl bond cleavage will yield an iminoxyl and acyl radical. With oxime esters the preference for N–O over O–acyl bond cleavage is well documented.[3,4,6-8] Supporting evidence for this type of bond cleavage with the α-oxo-oxime esters is the quantitative production of CO_2 (3) which results from decarboxylation of the acyloxyl radical, and the absence of 3-iminoxybutan-2-one radical which would certainly have been detected by e.s.r. in the photolysis of (1a). The solvent cage radical pair produced by reaction (b) may react in three different ways. They may (i) escape from the solvent cage (d), (ii) yield *via* β-scission (e) the solvent cage radical pair $\overline{R^1\dot{C}O\ \dot{R}^3}$, and (iii) recombine with the formation of (1) (c). The cage radical pair formed by route c can recombine to yield R^1COR^3 (q), and escape from the solvent cage (r). The free acyl radical formed by r can (i) recombine with another acyl radical to give diketone (l), (ii) abstract hydrogen from a suitable H-donor to give an aldehyde (m), and (iii) exhibit reactions leading to acyl-containing products (n). The alkyl radical formed by step r can either abstract hydrogen from a suitable hydrogen donor to yield an alkane (o) or produce alkyl-containing products (p). The free radicals formed by step d can recombine to (1) (f), or yield *via*

* Photolysis of (1f) in propan-2-ol or acetonitrile as solvent yields in addition to (31)—(36) some benzene.

† Two other radical species derived from Bu^tNO were observed, *viz.* di-t-butyl nitroxide with a_N 15.3 G and t-butoxy-t-butyl nitroxide with a_N 27.2 G (weak signal).

‡ The presence of t-butylmethoxy, t-butylethoxy, and especially of t-butyl-t-butoxy nitroxide illustrates the presence of oxygen of the air in the reaction mixture, despite the precaution taken to remove it by bubbling nitrogen through the solution for 10 min. However, alkyl radicals are good scavengers for removing even traces of molecular oxygen.

β-scission acyl and alkyl radicals (h and j) which will react as discussed before (l—p). The free α-oxoiminyl radical may also recombine with an acyl radical to give the proposed intermediate (37) (s, see below).



SCHEME 1

The formation of acyl-t-butyl nitroxide in the e.s.r. experiments illustrates the existence of free acyl radicals formed by step h and/or r.

The trapping of alkoxyl radicals by Bu^tNO, as is evident from the formation of alkoxy-t-butyl nitroxide, reveals the presence of free alkyl radicals which are probably formed by decarboxylation of acyloxyl radicals (steps e and/or h). The formation of the symmetrical and asymmetrical diketones (entries 8 and 9) proceeds *via* recombination of acyl radicals (l), and hydrogen abstraction by the α-oxoiminyl radical and subsequent hydrolysis (g and k), respectively,[16] as suggested before for the formation of bornane-2,3-dione in the photolysis of 3-ethoxyiminobornan-2-one.[1]

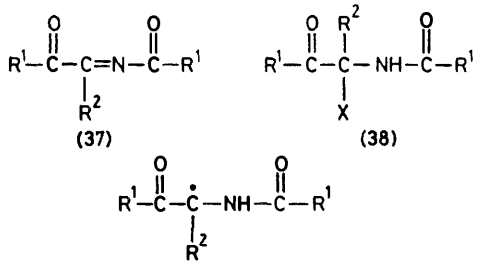
Butan-2-one (27) is formed upon photolysis of both (1d and e), and acetophenone (12) in that of (1f) (entry 10). In view of the preferred N–O bond cleavage, it is then most probable that these products result from combination of the free radicals $R^1\dot{C}{=}O$ and $\dot{R}^3$. The cage radical combination (sequence b, e, q, Scheme 1) will be at most of minor importance, since the formation of (12) is minimal for propan-2-ol as solvent (see Table 3).

The products in the entries (2) and (14) of Table 1 are formed in trace amounts only, and apparently the decarbonylation of $R^1\dot{C}{=}O$ is an unimportant process. In fact, no CO was found above the photolysate.

The origin of the products in entry 6 of Table 1 is uncertain. Oxidation by dissolved air might be a possible route to these products (indicated by step n) as oxygen was not always completely excluded from the reaction mixtures.

The photolysis of (1a) in the presence of dodecane-1-thiol allowed a more quantitative mechanistic picture.[16] It appeared that in the absence of the thiol *ca.* 43% of the initially formed radical pairs escape from the solvent cage. These free radicals recombine for *ca.* 37% to regenerate (1a); they further yield *via* β-scission acetyl and methyl radicals. The major process for the acetyl radical is the formation of butane-2,3-dione (7). The solvent cage radical pairs eventually lead to free acetyl and methyl radicals. In the presence of the thiol the radicals which escape from the solvent cage yield acetic acid (5) and butane-2,3-dione (7). The solvent cage radical pairs eventually yield methane (2), carbon dioxide (3), and ethanal (6).

Formation of $R^1COC(R^2)(X)NHCOR^1$.—The secondary amides (14)—(17), (20)—(23), and (30) have the common skeleton (38). It is very likely therefore that they all originate from the same precursor (37). The structures of (20a) and (30) give a very strong indication that the acyl groups of these amides originate from the ketone part of the α-oxo-oxime esters. The amide (21) is a product in the photolysis of both (1b and d). Further, in the photolysis of (1b) (20)—(22), *i.e.* the homologues of (14)—(16), and (23), *i.e.* the homologue of (17), are obtained. The formation of these amides is thus explained in terms of the photoconversion of the inter-



(37) (38)

(39)

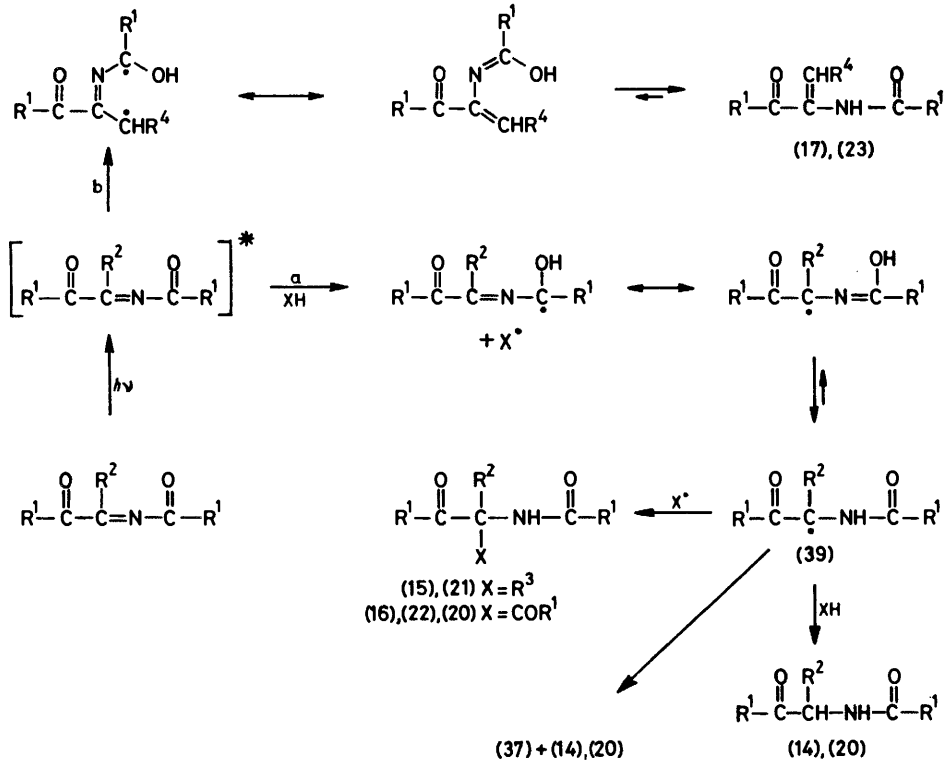
mediate (37), as depicted in Scheme 2. This intermediate (37) may be formed by combination of the α-oxoiminyl and acyl radicals (s, Scheme 1).[12] *N*-Acetyl-α-oxoimines are to our knowledge not described in the

literature. However, the photochemistry of *N*-acylimines was studied by the groups of Hirai [17] and Padwa.[18] In proton-donating solvents like propan-2-ol the *N*-acylimines are photoreduced, whereas in olefinic solvents containing allylic protons addition products are formed. Padwa concluded that the hydrogen abstraction occurred rather by the carbonyl oxygen than by the iminyl nitrogen.[18] On this basis it is proposed for the present system (*cf.* Scheme 2) that the hydrogen abstraction of excited (37) occurs by the oxygen atom of the *N*-acyl group (step a). The eventually resulting relatively stable (*cf.* ref. 19) radical (39) can (i) disproportionate, (ii) abstract hydrogen, and (iii) recombine with alkyl or acyl radicals. The photolysis of (1a) in the presence of dodecane-1-thiol clearly indicated [16] that the better the proton-donating ability of the solvent system, the higher is the yield of (14) and the lower that of (15), as proton abstraction by (39) and by alkyl radicals [with formation of (14) and an alkane, respectively] then predominates over the recombination of (39) with the alkyl radical R^3 with formation of (15).

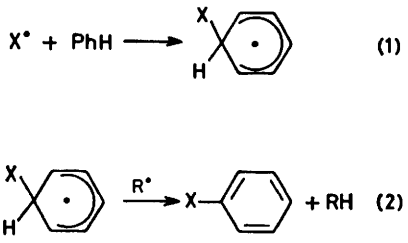
The formation of the amides (17) and (23) may be explained by photoenolization of the intermediate (37). The intermolecular counterpart of this type of photoenolization was observed with *N*-acylimines.[18] The amide (23) is formed in much larger amounts than (17), probably because of a better stabilization of the 1,4-biradical intermediate. Disproportionation of radical (39; $R^1 = R^2 = Me$) produces (37) and (14), or (17) and (14).* The latter process is less likely than the former in view of the lower energy content of the products.

The Formation of ArX.—The products listed in entries 13—16 of Table 1 are formed exclusively in benzene as solvent. The formation of the alkylbenzenes PhR^1 and PhR^3 (entries 14 and 13) is easily explained by the reaction steps (1) and (2) with $X = R^2$ and R^1, in which the intermediate cyclohexadienyl radical acts as hydrogen donor for other radicals. The formation of acetophenone (entry 15) can also be interpreted in terms of the steps (1) and (2), now with X = COMe. The absence of acetophenone (12) as a product in the photolysis of (1a) in a mixture of dodecane-1-thiol and benzene [16] supports this interpretation. Further, Ogata *et al.* reported the formation of acetophenone upon irradiation of 1-phenylpropan-2-one in benzene.[20]

At first thought *p*-$R^3C_6H_4COR^1$ (entry 16) may be formed by (3) or (4). The photolysis of (1a) in toluene produces *p*-methylacetophenone (13) and 1-phenyl-

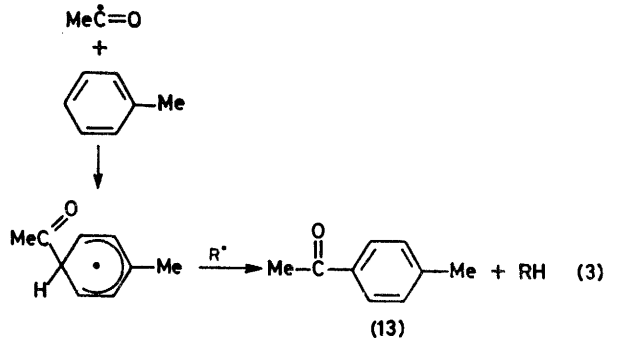


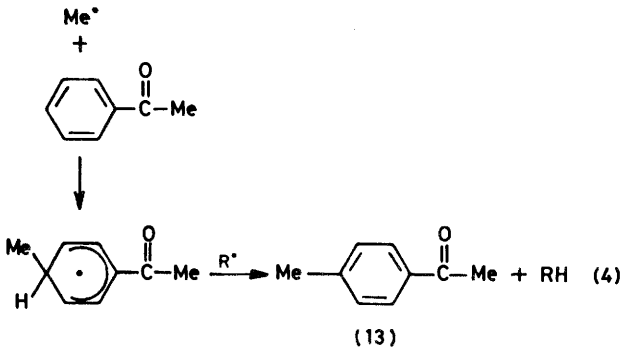
SCHEME 2



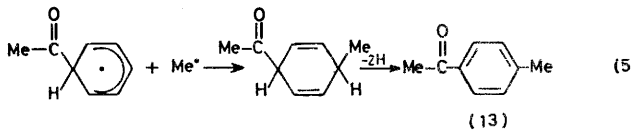
* Likewise radical (39; $R^1 = Me$, $R^2 = Et$) produces (37) and (20), or (23) and (20).

propan-2-one in a ratio of 0.24 : 1. The latter ketone is not formed in the photolysis of (1a) in benzene. Thus the formation of (13) upon irradiation of (1a) in benzene as solvent by reaction of the toluene produced, as shown in (3), is highly unlikely.





The yield of (13) upon irradiation of (1a) in benzene in the presence and absence of 1 mol. equiv. of acetophenone is the same. Also, the photolysis of 3-acetoxyiminopentan-2-one (1d) in propan-2-ol in the presence of 1 mol. equiv. of acetophenone did not yield any (13). These two observations render the formation of (13) by (4) highly unlikely. The observation that exclusively the *para*-substituted product is formed is also inconceivable with (4), since substitution of acetophenone with methyl radical (generated from diacetyl peroxide) yield 26% *o*-, 14% *m*-, and 60% *p*-methylacetophenone.[21] Another route to (13) may be by the steps (1; X = COMe) and (5). The intermediate cyclohexadienyl

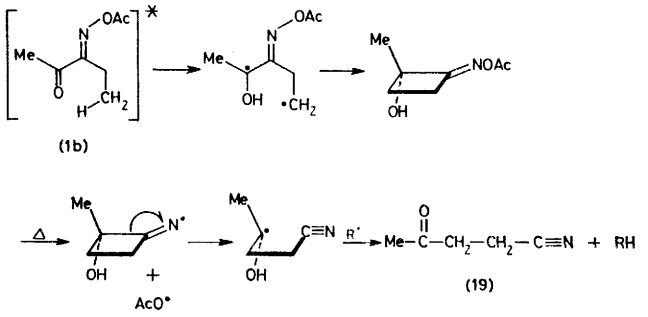


(5)

radical formed by (1) will recombine with a methyl radical. The resulting cyclohexa-2,5-diene will then rapidly lose hydrogen to give the aromatic compound (13). The acetyl and methyl radical very likely originate from the cage radical pair formed by step e (*cf.* Scheme 1).*

The Formation of Nitrile (19).—The formation of the nitriles (19) (entry 21 of Table 1) and (19a) (Table 2) by photolysis of (1b and c) respectively can be rationalized in terms of Scheme 3. After excitation intramolecular γ-hydrogen abstraction occurs from $^1S(n-\pi^*)$,[11a] leading *via* a 1,4-biradical to the cyclobutanol derivative. The N–O bond in oxime esters is weak and thus thermally labile. Homolytic cleavage of this bond in the cyclobutanol derivative, followed by β-scission, generates a ketyl radical. This radical is a good hydrogen donor, and in the presence of *e.g.* methyl radicals yields the nitrile (19).† Supporting evidence for the mechanism shown in Scheme 3 is the cyclobutanol formation upon irradiation of α-oxo-oxime ethers containing γ-hydrogens, as the N–O bond of oxime ethers, in contrast to that of oxime esters, is thermally not labile.[11c]

The Formation of Amides.—The formation of products (8), (9), (33), and (34) (entries 11 and 21) indicates the presence of acylaminyl radicals in the system which yield the amides by hydrogen abstraction and radical combination.[12] The intermediacy of the acetylaminyl radical in the photolysis of 3-ethoxyiminobutan-2-one was discussed in more detail previously.[12] The origin of the amides in entry (12) is uncertain.

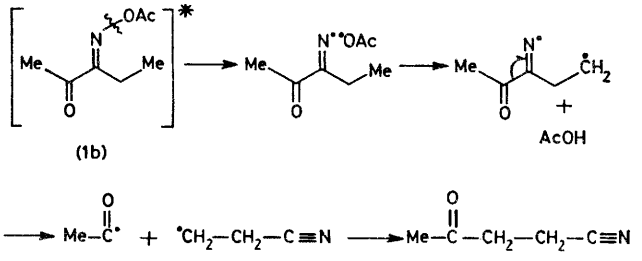


SCHEME 3

EXPERIMENTAL

Materials.—α-Oxo-oximes were prepared from commercially available ketones by treatment with methyl nitrite in acidic solutions,[23] the precursor of (1a) from butan-2-one, of (1b) from pentan-2-one, of (1d) from pentan-3-one, and of (1f) from propiophenone. The precursor of (1c) was prepared by selective deuteriation as follows.[21] A solution of (1b) (1.13 g) and Na_2CO_3 (*ca.* 3 mg) in D_2O (20 ml) was refluxed overnight, the mixture was extracted with ether, and the product was isolated and recrystallized

† The alternative route for the formation of (19) depicted in Scheme 4 cannot be rigidly excluded. It is however a less



SCHEME 4

probable one, as the nitrile homologous to (19) is not found in the photolysis of (1a).

* A similar type of mechanism was proposed by Hey *et al.* for the decomposition of arylazotriphenylmethane in benzene.[22] Also in that system the *para*-isomer was formed exclusively in a chemical yield of 30%.

from cyclohexane. According to ^1H n.m.r. deuteriation of the methyl α to the keto-group was complete.

The acetates (1a—c, e, and f) were prepared from the corresponding oximes. The synthesis of (1a) is given as example. Butan-2-one oxime (11 g, 0.11 mol) in acetic anhydride (54 ml, 1.1 mol) and concentrated HCl (10 drops) was stirred overnight at room temperature; the mixture was poured into ice-water and under continuous stirring neutralized with solid $NaCO_3$ until the evolution of gas had ceased; then the mixture was extracted with ether (3 ×), dried ($MgSO_4$), and the ether evaporated; distillation of the residue yielded (1a) (35%), b.p. 88—89.5° at 13 mmHg. Ester (1d) was synthesized from 3-hydroxyiminobutan-2-one using propionyl chloride and triethylamine in CH_2Cl_2.[3b]

3-Acetamidobutan-2-one (14),[25] 2-methyl-2-nitropropane,[26] and di-t-butyl peroxalate [14] were prepared as described. Dodecane-1-thiol was obtained commercially. Benzene was dried and used without further purification.

Irradiations.—The irradiations were performed in Rayonet photochemical reactors (RPR 208) equipped with 366 or 313 nm lamps, using Pyrex vessels. In the e.s.r. experiments a high pressure xenon arc fitted with a monochromator was used as light source for the photolyses in the cavity of the e.s.r. spectrometer (Varian E-3), and nitrogen was bubbled through the solutions prior to the irradiation for 10 min to remove (most of) the dissolved oxygen.

Analyses.—I.r. spectra (cm^{-1}) were recorded on an Unicam SP 200 or a Perkin-Elmer 125 spectrometer. ^1H N.m.r. spectra (δ) were obtained on Varian A-60D, HA-100, or XL-100 instruments, using tetramethylsilane as internal standard. Mass spectra were recorded on an A.E.I. MS-902 spectrometer with an all-glass heated inlet system; mass peaks with relative intensities below 5% are not listed in Table 2. The mass spectra of (19), (20), and (22) were obtained on a g.c.–m.s. apparatus (mass peaks below *m/e* 50 were not recorded) consisting of a Hewlett–Packard 5830A gas chromatograph coupled with a Hewlett–Packard 5982A mass spectrometer.

Photolyses were monitored by g.l.c. or g.s.c. analysis. The heavier products were isolated by means of preparative g.l.c. using 12—15% OV-225 copper columns [on Chromosorb W (AW), 60—80 mesh, 4 m × 1/4 in, 50—250°, 4° min^{-1}].

Methane (2) and carbon dioxide (3) were identified on comparison of their g.s.c. (2 m × 1/4 in, Porapak Q + S, 60—80 mesh, 60°) retention times with those of authentic samples. The amount of carbon dioxide (3) was determined by passing a stream of nitrogen through the solution which was subsequently led through a $Ba(OH)_2$ solution. The absence of carbon monoxide was established on two columns in series (1 m × 1/4 in, molecular sieve 5A + 4.5 m × 1/4 in, Porapak Q, 25°). Ethane (24) was identified on the basis of its g.l.c. (10 m × 1/4 in, 33% dimethylsulpholan–firebrick, 0°) retention time. Acetonitrile (4), acetic acid (5), ethanal (6), butane-2,3-dione (7), acetone (10), toluene (11), propiononitrile (18), propionic acid (25), butan-2-one (27), ethylbenzene (28), benzene, methyl acetate, and acetic anhydride were *inter alia* identified on the basis of their g.s.c. (2 m × 1/4 in, Porapak Q + S, 60—80 mesh, 150°, 2° min^{-1}) retention times.

Acetonitrile (4), acetic acid (5), ethanal (6), butane-2,3-dione (7), acetamide (8), *N*-acetylacetamide (9), acetophenone (12), *p*-methylacetophenone (13), propionic acid (25), propionamide (26), *p*-ethylacetophenone (29), benzoic acid (31), benzaldehyde (32), benzamide (33), *N*-methylbenzamide (34), 1,2-diphenylethane-1,2-dione (35), 1-phenylpropane-1,2-dione (36), acetic anhydride, and ethane-1,1-diol diacetate were identified by comparison of their spectral data with those in the Sadtler spectra collection. The ^1H n.m.r. spectrum of *N*-methylbenzamide (34) showed two singlets (at δ 3.05 and 3.00) for the methyl group due to restricted rotation around the amide bond (*cf.* ref. 27), while the Sadtler spectrum (13556) showed one broad signal (at δ 2.97).

The following compounds were assigned directly on the basis of their spectral data: 3-acetamidobutan-2-one (14) (i.r. and ^1H n.m.r. spectra were identical with the spectra of a sample synthesized independently by the Dakin–West reaction [28]) δ ($CDCl_3$) *ca.* 6.4br (1 H, NH), 4.62 (1 H, quintet, *J* 7 Hz, CH), 2.25 (3 H, s, CH_3COC), 2.04 (3 H, s, CH_3CON), and 1.40 (3 H, d, *J* 7 Hz, CH_3CH); *m/e* (15 eV) 127 [12, $(M - 2H)^{+\cdot}$], 111 (6), 92 (6), 87 [18, $(M - CH_2{=}C{=}O)^{+\cdot}$], 86 [100, $(M - CH_3CO)^+$ or $(M - H - CH_2{=}C{=}O)^+$], 85 (24), 60 (5), 59 (9), 44 [62, $(86 - CH_2{=}C{=}O)^+$], 43 [12, $(M - C_4H_8NO)^+$], and 42 (8); i.r. spectrum identical with Sadtler spectrum 19626; 3-acetamido-3-methylbutan-2-one (15), $\nu_{max.}$ ($CHCl_3$) 3 440 (w, NH), 3 050 (m), 1 705 (s, C=O, ketone), 1 660 (s, amide I), 1 510 (s, amide II), 1 450 (m), 1 380 (m), 1 360 (m), and 1 120 (m) cm^{-1}; δ ($CDCl_3$) *ca.* 6.5br (1 H, NH), 2.18 (3 H, s, CH_3COC), 1.98 (3 H, s, CH_3CON), and 1.48 (6 H, s, CH_3C); 3-acetamido-3-methylpentane-2,4-dione (16), $\nu_{max.}$ ($CHCl_3$) 3 390 (m, NH), 2 990 (w), 1 700 (s, C=O, ketone), 1 660 (s, amide I), 1 480 (s, amide II), 1 430 (w), 1 364 (m), 1 352 (m), and 1 170 (w) cm^{-1}; δ ($CDCl_3$) *ca.* 7.3br (1 H, NH), 2.09 (6 H, s, CH_3COC), 2.05 (3 H, s, CH_3CON), and 1.68 (3 H, s, CH_3C); *m/e* (70 eV) 129 [13, $(M - CH_2{=}C{=}O)^{+\cdot}$], 128 [8, $(M - CH_3CO)^+$], 112 (5), 111 (47), 110 (5), and 87 [48, $(129 - CH_2{=}C{=}O)^{+\cdot}$; $m^*_{obs.}$ 58.70, $m^*_{calc.}$ 58.67], 86 [93, $(128 - CH_2{=}C{=}O)^+$], 70 [8, $(87 - NH_3)^{+\cdot}$; $m^*_{obs.}$ 56.38, $m^*_{calc.}$ 56.32], 69 (5), 68 (9), 60 (8), 58 (5), 55 (14), 45 [8, $(87 - CH_2{=}C{=}O)^{+\cdot}$], 44 [62, $(86 - CH_2{=}C{=}O)^+$; $m^*_{obs.}$ 22.58, $m^*_{calc.}$ 22.51], 43 [100, $(M - C_6H_{10}NO_2)^+$], 42 (30), 41 (11), and 40 (5); 3-acetamidobut-3-en-2-one (17), $\nu_{max.}$ (CCl_4) 3 400 (vw, NH), 2 950 (vw), 1 700 (m, C=O, ketone), 1 670 (s, amide I), 1 500 (s, amide II), 1 370 (m), 1 300 (w), and 1 130 (vw) cm^{-1}; δ ($CDCl_3$) *ca.* 8.0br (1 H, NH), 6.90 (1 H, s, C=CH), 5.76br (1 H, s, C=CH), 2.39 (3 H, s, CH_3COC), and 2.12 (3 H, s, CH_3CON); assignment supported by Sadtler spectra 19581 (i.r.) and 2 213 (^1H n.m.r.); 4-oxopentanenenitrile (19), $\nu_{max.}$ ($CHCl_3$) 2 250 (vw, CN), 1 715 (s, C=O), 1 660 (sh), 1 420 (m), 1 370 (m), and 1 160 (m) cm^{-1}; δ ($CDCl_3$) 2.91—2.73 (2 H, m), 2.64—2.45 (2 H, m), 2.21 (3 H, s, CH_3CO); m.s., see Table 2; 3-acetamidopentan-2-one (20), $\nu_{max.}$ ($CHCl_3$) 3 410 (w, NH), 2 970 (w), 1 706 (m, C=O, ketone), 1 658 (s, amide I), 1 494 (m, amide II), 1 370 (w), and 1 140 (w) cm^{-1}; δ ($CDCl_3$; lock C_6H_6) 4.64 (1 H, m, CH_2CH), 2.05 (3 H, s, CH_3COC), 1.98 (1 H, m, $CH_3CH_2C^*$), 1.89 (3 H, s, CH_3CON), 1.61 (1 H, m, $CH_3CH_2C^*$), 0.81 (3 H, t, *J* 7.5 Hz, CH_3CH_2), NH absorption not visible; m.s., see Table 2; 3-acetamido-3-methylpentan-2-one (21), $\nu_{max.}$ (CCl_4) 3 430 (w, NH), 3 350 (w, NH), 2 980 (w), 1 710 (s, C=O, ketone), 1 670 (s, amide I), 1 500 (s, amide II), 1 450 (m), 1 370 (m), and 1 125 (w) cm^{-1}; δ ($CDCl_3$, lock C_6H_6) *ca.* 6.5br (1 H, NH), 2.48 (1 H, septet, *J* 7.5 Hz, $CH_3CH_2C^*$), 2.12 (3 H, s, CH_3COC), 1.95 (3 H, s, CH_3CON), 1.65 (1 H, septet, *J* 7.5 Hz, $CH_3CH_2C^*$), 1.50 (3 H, s, CH_3C), and 0.68 (3 H, t, *J* 7.5 Hz, CH_3CH_2); double resonance experiment: as a result of irradiation of the triplet at δ 0.68 the two multiplets at δ 2.48 and 1.65 changed into an AB system; triple

resonance experiment: as a result of irradiation of the two multiplets at δ 2.48 and 1.65 the triplet at δ 0.68 changed into a singlet; *m/e* (70 eV) 114 [40, $(M - CH_3CO)^+$], 100 [8, $(M - CH_3 - CH_2{=}C{=}O)^+$; $m^*_{obs.}$ 70.28, $m^*_{calc.}$ 70.42], 86 [18, $(M - C_2H_5 - CH_2{=}C{=}O)^+$; $m^*_{obs.}$ *ca.* 57.8, $m^*_{calc.}$ 57.78], 73 [6, $(M - CH_2{=}C{=}O)^{+\cdot}$], 72 [100, $(114 - CH_2{=}C{=}O)^+$; $m^*_{obs.}$ 45.54, $m^*_{calc.}$ 45.47], 58 [9, $(100 - CH_2{=}C{=}O)^+$; $m^*_{obs.}$ 33.70, $m^*_{calc.}$ 33.64], 55 [15, $(83 - C_2H_4)^+$; $m^*_{obs.}$ 36.52, $m^*_{calc.}$ 36.45], and 43 [37, $(M - C_6H_{12}NO)^+$]; 3-acetamido-3-ethylpentane-2,4-dione (22), $\nu_{max.}$ ($CHCl_3$) 3 390 (m, NH), 2 980 (w), 1 700 (s, C=O, ketone), 1 660 (s, amide I), 1 480 (s, amide II), 1 335 (m), and 1 168 (m) cm^{-1}; δ ($CDCl_3$, lock C_6H_6) 2.44 (2 H, q, *J* 7.5 Hz, CH_3CH_2), 2.00 (6 H, s, CH_3COC), 1.90 (3 H, s, CH_3CON), and 0.62 (3 H, t, *J* 7.5 Hz, CH_3CH_2); NH absorption not visible; *m/e* (70 eV) 143 [10, $(M - CH_2{=}C{=}O)^{+\cdot}$], 142 [10, $(M - CH_3CO)^+$], 125 (35), 101 [55, $(143 - CH_2{=}C{=}O)^{+\cdot}$], 100 [100, $(143 - CH_3CO)^+$ or $(142 - CH_2{=}C{=}O)^+$], and 72 [5, $(114 - CH_2{=}C{=}O)^+$]; 3-acetamidopent-3-en-2-one (23), $\nu_{max.}$ ($CHCl_3$) 3 440 (w, NH), 3 040 (m), 1 690 (sh, C=O, ketone), 1 670 (s, amide I), 1 495 (s, amide II), 1 385 (m), 1 370 (m), 1 265 (s), and 810 (vw) cm^{-1}; δ ($CDCl_3$) *ca.* 7.25br (1 H, NH), 6.66 (1 H, q, *J* 7 Hz, C=CH), 2.33 (3 H, s, CH_3COC), and 2.11 (3 H, s, CH_3CON); *m/e* (70 eV) † 123 [21, $(M - H_2O)^{+\cdot}$], 100 [20, $(M - C_3H_5)^+$], 99 [56, $(M - CH_2{=}C{=}O)^{+\cdot}$; $m^*_{obs.}$ 69.43, $m^*_{calc.}$ 69.51], 98 [10, $(M - CH_3CO)^+$], 72 (21), 60 (14), 58 (36), 57 (14), 56 [92, $(99 - CH_3CO)^+$; $m^*_{obs.}$ 31.72, $m^*_{calc.}$ 31.68], 55 (12), 54 (16), 45 [15, $(72 - HCN)^+$], 44 (15), 43 [100, $(M - C_5H_8NO)^+$], 42 (14), 41 (12), and 39 (13); 4-methyl-4-propionamidoheptane-3,5-dione (30), $\nu_{max.}$ ($CHCl_3$) 3 430 (w, NH), 3 020 (w), 1 720 (sh), 1 700 (s, C=O, ketone), 1 665 (s, amide I), 1 495 (s, amide II), 1 085 (w), and 800 (w) cm^{-1}; δ (CCl_4) 7.13br (1 H, NH), 2.30 (4 H, q, *J* 7 Hz, CH_2COC), 2.22 (2 H, q, *J* 7 Hz, CH_2CON), 1.61 (3 H, s, CH_3C), 1.13 (3 H, t, *J* 7.5 Hz, CH_3CH_2CON), and 0.98 (6 H, t, *J* 7 Hz, CH_3CH_2COC); ethane-1,1-diol diacetate, *m/e* (70 eV) 103 [5, $(M - CH_3CO)^+$], 87 [23, $(M - CH_3CO_2)^+$], 44 (15), and 43 [100, $(87 - CH_3CHO)^+$; $m^*_{obs.}$ 21.27, $m^*_{calc.}$ 21.25].

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† Mass peaks with a relative intensity < 10% are not reported.

REFERENCES

[1] Part 6, P. Baas and H. Cerfontain, *Tetrahedron*, 1979, **35**, 1135.

[2] J.-P. Vermès and R. Beugelmans, *Tetrahedron Letters*, 1969, 2091; R. Beugelmans and J.-P. Vermès, *Bull. Soc. chim. France*, 1970, 342.

[3] (*a*) R. S. Andrews, Ph.D. Thesis, University of Alabama, 1969; (*b*) W. White, jun., *ibid.*, 1972.

[4] (*a*) G. A. Delzenne, U. Laridon, and H. Peeters, *Eur. Polymer J.*, 1970, **6**, 933; (*b*) S. I. Hong, T. Kurosaki, and M. Okawara, *J. Polymer Sci. Part* A-1, 1972, **9**, 97 (*Chem. Abs.*, 1973, **78**, 30300).

[5] M. Onda and K. Takeuchi, *Chem. and Pharm. Bull.* (*Japan*), 1973, **21**, 1287; 1975, **23**, 677.

[6] T. Okada, M. Kawanisi, and H. Nozaki, *Bull. Chem. Soc. Japan*, 1969, **42**, 2981.

[7] (*a*) H. Ohta and K. Tikumaru, *Bull. Chem. Soc. Japan*, 1975, **48**, 2393; (*b*) S. Ishikawa, H. Sakuragi, M. Yoshida, N. Inamoto, and K. Tokumaru, *Chem. Letters*, 1975, 819; (*c*) M. Yoshida, H. Sakuragi, T. Nishimura, S. Ishikawa, and K. Tokumaru, *ibid.*, p. 1125; (*d*) H. Sakuragi, S. Ishikawa, T. Nishimura, M. Yoshida, N. Inamoto, and K. Tokumaru, *Bull. Chem. Soc. Japan*, 1976, **49**, 1949.

[8] K. H. Grellmann and E. Tauer, *Tetrahedron Letters*, 1974, 3707.

[9] T. Sato and H. Obase, *Tetrahedron Letters*, 1967, 1633.

[10] P. Baas and H. Cerfontain, *J.C.S. Perkin II*, 1979, 156.

[11] P. Baas and H. Cerfontain, (*a*) *J.C.S. Perkin II*, 1979, 151; (*b*) *ibid.*, 1977, 1351; (*c*) *Tetrahedron Letters*, 1978, 1501.

[12] P. Baas and H. Cerfontain, *J.C.S. Perkin II*, 1979, 1025.

[13] A. Mackor, Ph.D. Thesis (in English), University of Amsterdam, 1968, p. 87.

[14] P. D. Bartlett, E. P. Benzing, and R. E. Pinckock, *J. Amer. Chem. Soc.*, 1960, **82**, 1762.

[15] R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, 1967, **71**, 14.

[16] P. Baas, Ph.D. Thesis (in English), University of Amsterdam, 1977, ch. 4.

[17] T. Okada, M. Kawanisi, H. Nozaki, N. Toshima, and H. Hirai, *Tetrahedron Letters*, 1969, 927; N. Toshima, S. Asao, K. Takada, and H. Hirai, *ibid.*, 1970, 5213; M. Saeki, N. Toshima, and H. Hirai, *Bull. Chem. Soc. Japan*, 1975, **48**, 476; S. Asao, N. Toshima, and H. Hirai, *ibid.*, p. 2068; N. Toshima, S. Asao, and H. Hirati, *Chem. Letters*, 1975, 451; S. Asao, N. Toshima, and H. Hirai, *Bull. Chem. Soc. Japan*, 1976, **49**, 224; N. Toshima, K. Aoki, and H. Hirai, *ibid.*, 1977, **50**, 1235.

[18] A. Padwa, W. Bergmark, and D. Pashayan, *J. Amer. Chem. Soc.*, 1969, **91**, 2653; A. Padwa and W. P. Koehn, *J. Org. Chem.*, 1975, **40**, 1896.

[19] T. H. Koch, J. A. Olesen, and J. DeNiro, *J. Amer. Chem. Soc.*, 1975, **97**, 7285.

[20] Y. Ogata, K. Takagi, and Y. Izawa, *Tetrahedron*, 1968, **24**, 1617.

[21] H. C. McBay, *J. Org. Chem.*, 1975, **40**, 1883.

[22] D. H. Hey, M. J. Perkins, and G. H. Williams, *Tetrahedron Letters*, 1963, 445.

[23] A. F. Ferris, *J. Org. Chem.*, 1959, **24**, 1726.

[24] R. L. Beach, *Tetrahedron Letters*, 1972, 1913.

[25] R. H. Wiley and O. H. Borum, *Org. Synth.*, 1953, **33**, 1.

[26] J. A. Maassen, Ph.D. Thesis (in English), University of Amsterdam, 1972, p. 36.

[27] K. Spaargaren, Ph.D. Thesis (in English), University of Amsterdam, 1970, ch. 2.

[28] Y. Iwakura, F. Toda, and H. Suzuki, *J. Org. Chem.*, 1967, **32**, 440; R. Knorr and R. Huisgen, *Chem. Ber.*, 1970, **103**, 2598.