Photochemistry of α-Oxo-oximes. Part 4.[1] Spectral Properties, Conformations, and Photoisomerization of α-Oxo-oximes and their Acetates

By **Peter Baas** and **Hans Cerfontain**,* Laboratory for Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

The α-oxo-oximes (1a—j) and (3a) and some of their esters have been prepared by ground state chemistry. In all cases the (*E*)-isomers were formed, except for (3a) (which was a mixture of *E* and *Z*). The (*Z*)-isomers of (1b—e) were obtained by irradiation of the corresponding (*E*)-isomers. The configurational and conformational structure of the various compounds has been assigned on the basis of n.m.r. (^{1}H and a.s.i.s.), i.r., and u.v. data. (*E*)- and (*Z*)-(3) have a fixed O=C–C=N structure. The (*E*)-isomers of the acyclic compounds exist in the O=C–C=N s-*trans* conformation which is twisted (*i.e.* non-planar) for the compounds which contain a phenyl adjacent to the carbonyl group. The (*E*)-isomers of compounds with a phenyl adjacent to the iminyl carbon have a dihedral angle of *ca.* 40° between the phenyl and the nodal plane of the iminyl group as a result of repulsion between the phenyl and the oxime oxygen. The (*Z*)-isomers of the acyclic compounds also exist in the O=C–C=N s-*trans* conformation which is non-planar due to repulsion between the oxime oxygen and the group bound to the carbonyl carbon. However, the phenyl is now fully conjugated with the iminyl group. The cyclopropyl group of (1e) has the bisected orientation relative to the carbonyl group s-*trans* for (*E*)-(1e) and s-*cis* for (*Z*)-(1e). Irradiation of the α-oxo-oximes (1b—e), (1j), and (3a), and of the acetates (2b—e), (2j), and (3b) leads to *E–Z* isomerization with formation of a photostationary state. The (*E*)-isomers of the oximes (1a), (1f—i) and of the acetates (2a, f, and h) and (4a—c) did not photoisomerize.

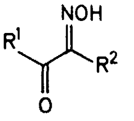
PHOTOCHEMICAL reactions and isomerizations have been observed with several systems possessing a C=C bond.[2] A major complication in the photochemically induced isomerization of imines is the rapid thermal relaxation which re-establishes the initial configurational equilibrium of the (*Z*)- and (*E*)-isomers.[3,4] Oximes in contrast to the imines possess a high configurational stability, and a number of photoisomerizations of oximes and derivatives have been reported.[2] However, only a very limited number of photochemical studies have been made on α-oxo-oximes and derivatives.[5-8] We therefore thought it of interest to study the photochemistry of these types of compounds. Recently, we reported on the photoisomerization of some α-oxo-oxime ethyl ethers.[1,9,10] In this paper we report on the photoisomerization and the conformation of the (*E*)- and (*Z*)-isomers of a number of α-oxo-oximes (1) and their acetates (2).

RESULTS

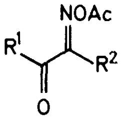
α-Oxo-oximes.—Preparation. The α-oxo-oximes (1a—i) and (3a) were prepared from the corresponding monoketones.[11,12] The α-oxo-oximes were all found to have the (*E*)-configuration {concluded from the ^{1}H n.m.r. hydroxy-absorption for [^{2}H$_6$]DMSO as solvent which ranged from δ 12.27 [for (1a)] to 12.54 [for (1e)]}, except for (3a) which was obtained as a nearly 1 : 1 mixture of *E* and *Z*.† The (*Z*)-isomers of the α-oxo-oximes (1a—e) and (3a) were obtained by irradiation of the pure (*E*)-isomers followed by subsequent column chromatographic separation on Florisil using benzene–ether (1 : 1 v/v) as eluant. (*E*)- and (*Z*)-(1j) were prepared from benzil.[13]

^{1}H *N.m.r.* The ^{1}H n.m.r. data with the assignments are collected in Table 1. The low field absorption of (1a) was assigned to the methyl at the carbonyl by comparison with the spectrum of (1f).

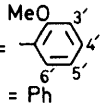
The aromatic absorptions of (*E*)-(1d) in CDCl$_3$ were assigned as follows: the multiplets centred at δ 7.38 and 7.16 are assigned to 4′- and 6′-H respectively. The remaining aromatic hydrogens give rise to a complicated multiplet in CDCl$_3$ and an almost first order pattern (a doublet at δ 6.50 for 3′-H) and a triplet at δ 6.74 for 5′-H) in C$_6$D$_6$; the a.s.i.s. is substantially less for 5′- than for 3′-H. The chemical shift of 6′-H is substantially smaller for (*Z*)- than (*E*)-(1d).

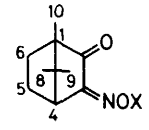


(1)

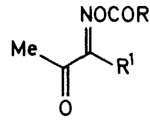


(2)

a; R^1 = R^2 = Me
b; R^1 = Ph, R^2 = Me
c; R^1 = Me, R^2 = Ph
d; R^1 = Me, R^2 = 
e; R^1 = , R^2 = Ph
f; R^1 = Et, R^2 = Me
g, R^1 = Me, R^2 = H
h; R^1 = Me, R^2 = Et
i; R^1 = Me, R^2 = CH$_2$Ph
j; R^1 = Ph, R^2 = Ph



(3)
a; X = H
b; X = Ac



(4)
a; R^1 = Me, R^2 = Et
b; R^1 = Me, R^2 = Ph
c; R^1 = CH$_2$Ph, R^2 = Et

The cyclopropyl methine hydrogen of (*E*)-(1e), 2-H, experiences a deshielding of 0.66 p.p.m. relative to that of (*Z*)-(1e) and exhibits a smaller a.s.i.s.

---

† For simplicity the (*E*)- and (*Z*)-isomers of a compound will sometimes be referred to as *E* and *Z*.

The *ortho*-hydrogens of (*Z*)-(1c—e) are at lower field than the other aromatic hydrogens, this is in contrast to the corresponding (*E*)-isomers. The a.s.i.s. of the *ortho*-hydrogens is smaller for *Z* than *E*. The assignment of the low field absorptions of (1j) to the *ortho*-hydrogens of the benzoyl group is based on the generally accepted idea that the anisotropic effect is much larger for the carbonyl than the iminyl function. The assignment of the absorptions of (3a) is in agreement with that of an earlier investigation in which the deshielding of the 4-H of *E* was tentatively attributed to the anisotropy of the hydroxy group.[17] The assignment of the six methyl signals of the mixture of (*E*)- and (*Z*)-(3a) in C_6D_6 is mainly based on the generally accepted idea that benzene gives complexation preferentially at the carbonyl group.[18]

TABLE 1

^{1}H N.m.r. and a.s.i.s. [a] data of (*E*)- and (*Z*)-α-oxo-oximes

Compound		Chemical shift (δ)				Δδ (p.p.m.) [b]	
		E	*Z*	*E*	*Z*	*E*	*Z*
		[$^2H_6$]DMSO		CDCl$_3$			
(1a)	OH	12.27 [c]		9.78 [d]		0.71 [e]	
	$CH_3C=O$	2.31 [c]		2.35 [d]		0.20 [e]	
	$CH_3C=N$	1.82 [c]		1.94 [d]		0.14 [e]	
(1b)	OH	12.38 [c]	10.88	8.94 [f]		0.85	
	o-H	7.98—7.71	8.0—7.7	7.95—7.80 [f]	8.0—7.8 [f]	−0.02	0.04 [e]
	(*m* + *p*)-H	7.66—7.33 [c]	7.7—7.3	7.59—7.30 [f]	7.6—7.3 [f]	0.3	0.3 [e]
	$CH_3C=N$	2.07 [c]	2.06	2.14 [f]	2.08 [f]	0.14	0.41 [e]
(1c)	OH	12.50 [f]	11.83 [f]				
	o-H	7.53—7.17	7.58—7.36	~7.5 —7.23 [f]	7.58—7.42 [f]	0.2	0.00
	(*m* + *p*)-H				~7.5—7.23 [f]	0.3	0.3
	$CH_3C=O$	2.47	2.47	2.47 [f]	2.44 [f]	0.25	0.38
(1d)	OH	12.27	11.74	8.91		1.39	
	6′-H			7.22—7.10	7.57—7.45	0.12	−0.02
	5′-H			7.10—6.90	7.08—6.86	0.25	0.23
	4′-H			7.48—7.27	7.50—7.27	0.36	0.36
	3′-H			7.03—6.88	6.94—6.81	0.45	0.49
	CH_3O	3.67	3.61	3.75	3.72	0.53	0.59
	$CH_3C=O$	2.40	2.36	2.50	2.46	0.21	0.13
(1e)	OH	12.54	11.70	8.54			
	o-H	7.49—7.18		7.50—7.2	7.64—7.50	0.1	0.01
	(*m* + *p*)-H				7.51—7.28	0.3	0.3
	2-H [g]	3.14—2.84		3.04—2.77	2.38—2.11	0.11	0.35
	3- + 5-H [g]	1.09—0.93		1.30—1.10	1.44—0.86	0.10	0.2
	4- + 6-H [g]			1.10—0.88		0.43	0.4
(1j)	OH	12.46 [c,h]	11.76 [h]				
	o-H(PhCO)	7.99—7.85	7.91—7.79	8.06—7.90	8.02—7.90	*i*	*i*
	H(arom)	7.72—7.29	7.72—7.29	7.68—7.29	7.64—7.25	*i*	*i*
(3a)	OH	11.88					
	4-H	3.06 [j]		3.27 [j]	2.72 [j]	0.13 [e]	0.29 [e]
	5- + 6-H	2.10—1.22		2.27—1.50	2.27—1.50	0.5 [e]	0.5 [e]
	8-H_3	0.87		1.02 [j]	1.02 [j]	0.38 [e]	0.42 [e]
	9-H_3	0.83		1.02 [j]	1.02 [j]	0.46 [e]	0.53 [e]
	10-H_3	0.69		0.89 [j]	0.93 [j]	0.01 [e]	0.16 [e]

[a] The spectra of the solutes in C_6D_6 were recorded at 60°. [b] $\Delta\delta = \delta_{CDCl_3} - \delta_{C_6D_6}$. [c] Ref. 14. [d] Sadtler no. 9882. [e] The spectrum of the solute in C_6D_6 was recorded at room temperature. [f] Ref. 6. [g] For the numbering see Figure. [h] Ref. 15. [i] The solubility of the oximes in C_6D_6 was too small to obtain a ^{1}H n.m.r. spectrum. [j] Refs. 16 and 17.

I.r.—The i.r. data of the α-oxo-oximes have been deposited as Supplementary Publication No. SUP 22391 (5 pp.).* The i.r. frequencies of (1a) were assigned by Kimura and Kuroda:[19,20] *e.g.* the bands at 1 318 and 986 cm^{-1} are due to the central C–C stretching and the N–O stretching vibrations respectively. Palm and Werbin tentatively assigned the ν_{N-O} stretch of (*E*)- and (*Z*)-(1j) at 927 and 951 cm^{-1}.[21]

The carbonyl stretching vibration frequency decreases strongly on conjugation with *e.g.* phenyl (Δν *ca.* 22 cm^{-1}) and cyclopropyl (Δν *ca.* 17 cm^{-1}). The $\nu_{C=N}$ stretch is in most cases hidden under the broad carbonyl band, and only visible but very weak with aliphatic α-oxo-oximes. The carbonyl stretching frequencies of (*E*)- and (*Z*)-(1b) are about the same, *viz.* 1 664 and 1 666 cm^{-1} respectively. With α-oxo-oximes in which a phenyl is located on the imino group $\nu_{C=O}$ is *ca.* 25 cm^{-1} greater for *Z* than *E*. The lower $\nu_{C=O}$ for (*Z*)- as compared with (*E*)-(3a) was explained in terms of intramolecular hydrogen bonding,[22] which does not occur with the other α-oxo-oximes studied.

U.v. The u.v. absorption data are collected in Table 2. For the (*E*)-isomers of non-conjugated α-oxo-oximes there is an allowed band (ε *ca.* 10 000) at *ca.* 220 nm and a forbidden one (ε *ca.* 20) near 320 nm, which accordingly and on the basis of the observed wavelength shift on going from a non-polar to a hydroxylic solvent are assigned to a π–π* and *n*–π* transition respectively. The data for the α-oxo-oximes are very similar to those of a typical s-*trans*-(*E*)-αβ-unsaturated ketone, such as 3-methylpent-3-en-2-one

---

* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1977, Index issue.

for which the data for ethanol as solvent are $\lambda_{max.}$ 230 (ε 11 200) and 310 nm (42).[23]

TABLE 2

U.v. data of α-oxo-oximes [a]

Compound	Solvent [b]	π–π*		*n*–π*	
		E	*Z*	*E*	*Z*
(1a)	A	219 (10 100)		323 (20)	
	B	229 (10 200) [c]			
	C	280 (14 600) [c]		370sh (60)	
(1b)	B	248 (9 500) [c,d]	248 (13 800) [d]	330sh (150)	330sh (90)
	C	295 (18 000) [c,d]	245 (16 600) [d]	410sh (100)	
(1c)	B	211 (11 000)			
		244sh (5 400)	250 (10 800)		
	C	239 (6 600) [c]	227 (8 500) [c]	400 (82)	
		291 (14 000)			
(1d)	B	220 (15 900)			
		270sh (2 700)			
	C	284 (17 000)		390 (77)	
(1e)	A	253 [e]		310sh [e]	
	B	222 (16 900)			
		255sh (5 400)			
	C	290 (14 900)		394 (86)	
(1j)	A			340sh [e]	
	B	249 (14 200) [c]	251 (26 000) [c]	340sh (110)	
	C	247 (10 900) [c]	252 (17 500) [c]	420sh (90)	
		310 (9 700) [c]	281 (14 800) [c]		
(3a)	A	228 (8 500)	264 (2 300) [d]	346 (30)	380 (76) [d]
	B	242 (5 700)		383 (54)	

[a] $\lambda_{max.}$/nm ($\varepsilon_{max.}$ l mol^{-1} cm^{-1}); sh = shoulder. [b] A = cyclohexane, B = ethanol, C = ethanol containing *ca.* 1% NaOH. [c] Ref. 14. [d] The data were obtained from the u.v. spectrum of an *E–Z* mixture of known composition, as determined by ^{1}H n.m.r. [e] Saturated solution.

The π–π* absorption maximum of the (*E*)-α-oxo-oximes in basic solution is shifted to the red by 50—70 nm as compared with the neutral solution. With the (*Z*)-isomers in contrast such a shift is not observed. This behaviour of the (*E*)- and (*Z*)- isomers is in agreement with earlier reports on compounds containing an α-oxo-oxime function.[14, 24]

α-Oxo-oxime Acetates.—The α-oxo-oxime acetates (2a—f, h, and j) were prepared by stirring the corresponding oxime in acetic anhydride in the presence of a catalytic amount of concentrated hydrochloric acid. Compound (3b) was obtained from (3a) using acetyl chloride and triethylamine. With (2a, f, and h) the (*E*)-isomer was obtained exclusively. In the other cases a mixture of *E* and *Z* was formed with the former dominating, except for (2e) which has the (*Z*)-configuration. The *E* : *Z* ratio of (2j) upon synthesis was found to be 4.3, whereas it was only 0.25 after 60 days at room temperature. With (2c) the pure isomers were obtained by fractional crystallization from benzene. The ^{1}H n.m.r. and u.v. data of the α-oxo-oxime acetates are given in Tables 3 and 4; the i.r. data have been deposited as SUP 22391. The spectral data were assigned from the spectra of the irradiated mixtures, except for (2a and c).

^{1}H *N.m.r.* The assignments were made similarly as for the corresponding α-oxo-oximes (see before). The behaviour of (2b) differs from that of (1b) in that (i) the increase in the shielding of the iminyl methyl group on going from *E* to *Z* is much larger with (2b) (0.28 p.p.m.) than with (1b) (0.06 p.p.m.), and (ii) the difference in the a.s.i.s. for the iminyl methyl between *E* and *Z* is opposite in sign for (1b) and (2b). Also for (3a) the a.s.i.s. of 4-H is smaller for *E* than *Z*, whereas for (3b) they are the same with a value which is equal to that of (*Z*)-(3a).

I.r. The α-oxo-oxime acetates show two strong carbonyl stretching frequencies, one at *ca.* 1 780 cm^{-1} due to the ester group and the other at 1 750—1 670 cm^{-1} due to the ketone function, its position being dependent on conjugation and strain factors. The 1 780 cm^{-1} band is commonly observed with vinyl esters.[25a] The ester band of a related cyclic 2-oxo-1,3-dioxime diacetate was reported to be at 1 790 cm^{-1}.[26] $\nu_{C=N}$ is more intense for the α-oxo-oxime acetates than the parent oximes. The same increase is observed with biacetyl monoxime upon *O*-deuteriation and *O*-methylation.[19, 20] $\nu_{C=N}$ for the (*E*)-isomers is much more intense than that of the (*Z*)-isomers which is often hardly visible. Similar variations are observed on comparing the α-oxo-oximes with the ether derivatives.[27a] The C–O stretching vibrations of the oxime acetates (1 180—1 200 cm^{-1}) are at lower frequencies than those of aliphatic acetates which are at 1 245 cm^{-1}.[25b] The effect of intramolecular hydrogen bonding on $\nu_{C=O}$ is clearly evident on comparing (3a) with (3b). For (3b) in which there is no intramolecular hydrogen bonding the difference between *E* and *Z* is 20 cm^{-1} (neat liquid), whereas for (3a), in which intramolecular hydrogen bonding is possible, it is 34 ($CHCl_3$) and 48 cm^{-1} (CCl_4).[22]

U.v. The *n*–π* band of the α-oxo-oxime acetates containing a PhC=N group is obscured by the π–π* band, indicating conjugation between the phenyl and the iminyl groups (Table 4). The α-oxo-oxime acetates show the same difference in ε for the (*E*)- and (*Z*)-isomers as the α-oxo-oximes (Table 2).

Irradiations.—Irradiation of the α-oxo-oximes (1b—e and j) and (3a) and the α-oxo-oxime acetates (2b—e and j) and (3b) led to *E–Z* isomerization with eventual formation of a photostationary state (PSS), the ratio of which depends on the structure of the α-oxo-oxime function (Table 5). The same PSS ratio is obtained on starting with *E* and *Z* [*cf.* Table 5, (1j)]. Irradiation of (1b) in the presence of phenanthrene as sensitizer led to the same PSS ratio, as observed for the direct irradiation.

The (*E*)-isomers of the α-oxo-oximes (1a and f—i) did not photoisomerize. None of the α-oxo-oximes studied did photodecompose to any significant extent under the reported conditions. The (*E*)-isomers of the α-oxo-oxime esters (2a, f, and h) and (4a—c) did not photoisomerize. All the α-oxo-oxime acetates and the other esters studied photodecomposed readily. With (2b) and (3b) the rate of the photodecomposition is of the same order of magnitude as the rate of the *E–Z* photoisomerization.

DISCUSSION

Configurations and Conformations of α-Oxo-oximes and their Acetates.—There is ample evidence that for the (*E*)-

TABLE 3

^{1}H N.m.r. data and a.s.i.s. of α-oxo-oxime acetates

Compound		Chemical shift [δ ($CDCl_3$)]		Δδ (p.p.m.)[a]	
		E	*Z*	*E*	*Z*
(2a)	$CH_3C=O$	2.48		0.26	
	CH_3CO_2	2.28		0.50[b]	
	$CH_3C=N$	2.08		0.26[b]	
(2b)	*o*-H	8.21—7.97	7.99—7.75	−0.11	0.09
	(*m* + *p*)-H	7.65—7.24	7.65—7.24	0.3	0.3
	CH_3CO_2	2.27[c]	1.85[c]	0.56	0.55
	$CH_3C=N$	2.23[c]	1.95[c]	0.31	0.18
(2c)	*o*-H	7.46—7.17[d]	7.83—7.56	0.2	0.10
	(*m* + *p*)-H		7.65—7.26		0.4
	$CH_3C=O$	2.56[d]	2.40	0.20	0.39
	CH_3CO_2	2.06[d]	2.13	0.46	0.45
(2d)	6′-H	7.24—7.11	7.87—7.74	0.15	−0.02
	5′-H	7.11—6.89		0.24	
	4′-H	7.53—7.32		0.34	
	3′-H	7.02—6.89		0.44	
	CH_3O	3.76	3.74	0.53	0.62
	$CH_3C=O$	2.63	2.55	0.19	0.26
	CH_3CO_2	2.14	2.24	0.54	0.56
(2e)	*o*-H		7.78—7.63		0.02
	(*m* + *p*)-H		7.54—7.30		0.4
	2-H[e]		2.35—2.06		0.60
	CH_3CO_2		2.20		0.59
	3- + 5-H[e]		1.49—1.29		0.28
	4- + 6-H[e]		1.27—1.05		0.68
(1j)	*o*-H(PhCO)	8.18—8.06	8.01—7.88	−0.02	0.07
	o-H	7.68—7.57	7.79—7.66	0.12	0.03
	(*m* + *p*)-H(PhCO)	7.60—7.35	7.60—7.35	0.4	0.4
	(*m* + *p*)-H				
	CH_3CO_2	2.18	1.96	0.47	0.50
(3b)	4-H	3.25	2.85	0.27	0.27
	CH_3CO_2	2.23	2.15	0.31	0.31
	5- + 6-H	2.18—1.48	−1.48	0.4	0.4
	8-H_3	1.00	1.03	0.38	0.37
	9-H_3	1.00	1.03	0.42	0.48
	10-H_3	0.88	0.90	0.03	0.10

[a] $\Delta\delta = \delta_{CDCl_3} - \delta_{C_6DC_6}$. [b] Assignments for C_6D_6 as solvent may be reversed. [c] Assignments are not definite; argument in favour of the given assignment for CH_3CO_2 is the a.s.i.s. of 0.55 and 0.56 p.p.m. which lies in the range observed for most of the other acetates. [d] Ref. 6. [e] For numbering see Figure.

α-oxo-oximes and their derivatives the s-*trans* conformation both around the (O=)C–C(=N) and the N–O bond gives the most stable structure[28-30] (Figure). From dipole moment measurements it was concluded that (1a) has the s-*trans E* structure,[28] and that (1b and c) have a non-planar transoid structure analogous to that of the corresponding acyclic diketones.[31] From gas-phase electron diffraction it followed that (1g) has the s-*trans E* structure.[29] An *X*-ray analysis of the *p*-bromobenzoate of (1j) confirmed the s-*trans-E*, N–O s-*trans*

TABLE 4

U.v. data of α-oxo-oxime acetates[a]

Compound	Solvent[b]	π–π*	*n*–π*
(*E*)–(2a)	A	215 (12 600)	326 (20)
	B	215 (11 600)	316 (22)
(*E*)–(2b)	B	259 (9 000)	335sh (96)
(*E*)–(2c)	B	260 (2 700)	
(*Z*)–(2c)	B	255 (11 300)	
(*E*)–(2d)	B	210 (17 200)	
		244 (4 200)	
		298 (2 100)	
(*Z*)–(2e)	A	255 (11 800)	

[a] $\lambda_{max.}$/nm ($\varepsilon_{max.}$/l mol^{-1} cm^{-1}). [b] A = cyclohexane, B = ethanol.

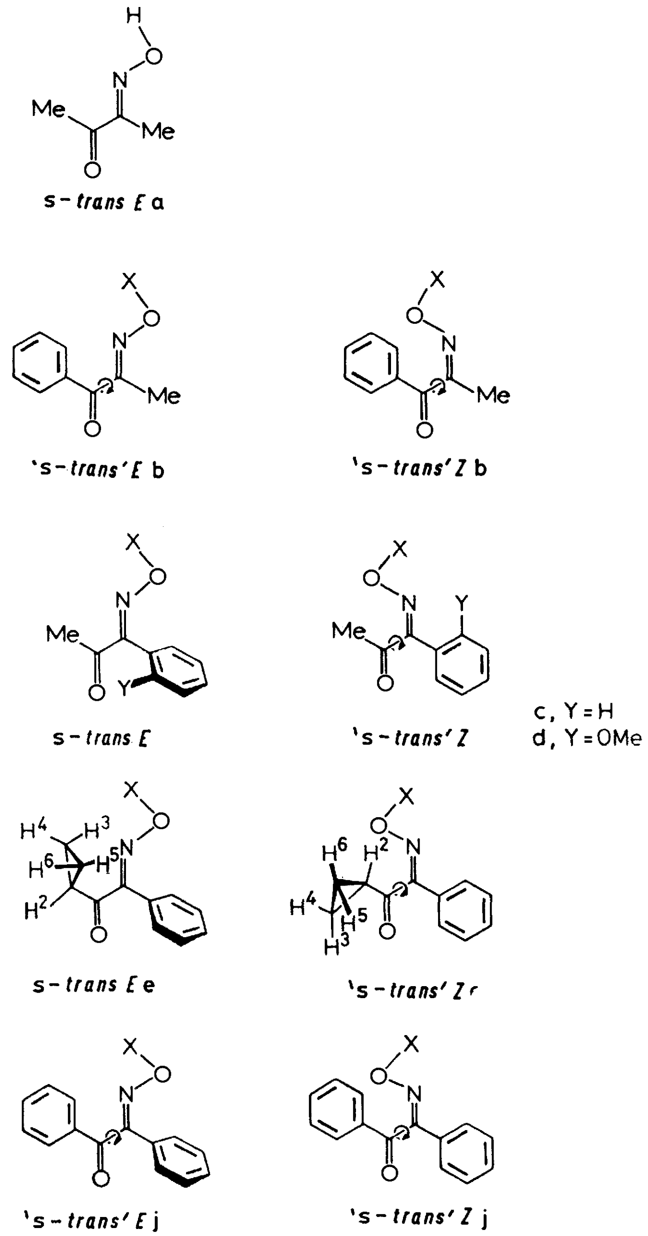
TABLE 5

Photostationary state ratios for the isomerization of the α-oxo-oximes and some of their acetates with λ 366 nm

Compound	Solvent	([*E*] : [*Z*])$_{PSS}$
(*E*)–(1b)	CH_3CN	1.8
(*E*)–(1b)[a]	CH_3CN	2.3
(*E*)–(1b)[a,b]	CH_3CN	2.4
(*E*)–(1c)	CH_3CN	1.2
(*E*)–(1d)	CH_3CN	1.1
(*E*)–(1d)	[$^2H_6$]DMSO	1.0
(*E*)–(1e)	CH_3CN	1.0
(*E*)–(1j)	CH_3CN	0.43
(*Z*)–(1j)	[$^2H_6$]DMSO	0.47
(*E*)– + (*Z*)–(3a) (1 : 1)	C_6D_6	1.5
(*E*)–(2b)	C_6D_6	0.30
(*E*)–(2c)	C_6D_6	0.41
(*E*)–(2d)	C_6D_6	0.32
(*E*)–(2e)	C_6D_6	0.43
(*E*)– + (*Z*)–(3b) (4 : 3)	C_6D_6	2.4

[a] Wavelength of irradiation 254 nm. [b] In the presence of phenanthrene as sensitizer which absorbed >95% of the incident radiation.

conformation.[32] The observed solvent effects on the ^1H n.m.r. data of several oximes were interpreted in terms of an s-*trans* conformation around the N–O bond.[30] Finally, it was proposed, based on a comparison of the observed and calculated dipole moment, that 2-acetylpyridine has exclusively the s-*trans* conformation.[33] It is therefore concluded that (1a) is a model compound for the s-*trans* (O=)C–C(=N),s-*trans* N–O conformation (Figure).



Conformations of the acyclic α-oxo-amines (1; X = H) and the acetates (2; X = Ac)

The ^1H n.m.r. chemical shift of the OH hydrogen of oximes in [$^2H_6$]DMSO is solute concentration independent as a result of solute-solvent intermolecular hydrogen bonding[15] and this characteristic for a particular class of oximes, *e.g.* the OH hydrogen of (1j) is more deshielded when it is closer (*i.e.* with *E*) to the adjacent iminyl phenyl group.[15] The OH absorption of the (*E*)-α-oxo-oximes, except for that of (3a), is in the range of δ 12.54—12.27 and those of the photoisomers in the range of 11.83—10.88 p.p.m. (see Table 1). It is concluded therefore that these photoisomers possess the (*Z*)-configuration.*

Compounds (3a *and* b). These compounds exist in a fixed s-*cis* structure. At room temperature (*Z*)-(3a) isomerizes thermally to the more stable (*E*)-isomer both in solution and in the solid state.[22] The bicyclic structure allows only a variation of *ca.* 10° in the dihedral angle between O=C(2) and N=C(3).

Compounds (1b) *and* (2b). The spectral data for the two configurational isomers of (1b) are similar, except for the a.s.i.s. Based on dipole moment considerations Lumbroso suggested for (*E*)-(1b) a non-planar s-*trans* conformation † with a dihedral angle of 125° between O(=C) and N(=C).[28] From a study of Dreiding and Catalin molecular models it appeared that for (*E*)-(1b), in contrast to (*Z*)-(1b), there is no steric reason for a non-planar structure, provided that the carbonyl is not conjugated with the phenyl group. ^1H N.m.r. evidence on (*E*)- and (*Z*)-(1b) and (*Z*)-(2b), however, indicates that the phenyl is fully conjugated with the carbonyl group.‡ Accordingly it is proposed that the two geometric isomers both exist in a slightly distorted s-*trans* conformation in which the phenyl and carbonyl group are (almost) fully conjugated (see Figure). As to (2b) there are large differences between *E* and *Z* in both chemical shifts and a.s.i.s. (see Table 3), *viz.* a shielding of 0.22 p.p.m. for the *ortho*-hydrogens and of 0.28 and 0.42 p.p.m. for the hydrogens of the methyl at the imine carbon and of the acetate group respectively. The difference for the *ortho*-hydrogens may be explained in terms of their presence in the deshielding cone of the ester carbonyl with *E*, but just in or near the shielding cone with *Z*. From a Dreiding molecular model it appeared that the acetate hydrogens, as a result of free rotation around the (O=)C–O bond, spend some time directly above the phenyl group with *Z* but not with *E*, leading to a shielding with *Z*. The molecular model further revealed that the methyl at the imine function is closer to the ester carbonyl with *E* than *Z*.

Compounds (1c) *and* (2c). These two compounds have the following characteristics in common. (i) The *ortho*-

---

* The rotation barrier of an s-*trans*–s-*cis* isomerization is *ca.* 5 kcal mol^{-1} (as obtained from acrolein [34]), whereas the barrier for the *E–Z* isomerization is at least 23 kcal mol^{-1} (as obtained for chinoid oxime ethers [35]).

† A twisted and a distorted s-*trans* conformation will be further referred to as ' s-*trans* '.

‡ The *ortho*-hydrogens of acetophenone for which compound the dihedral angle between phenyl and carbonyl is 0°,[36] resonate at δ 7.95 ($CDCl_3$). On substitution of one *ortho*-hydrogen by methyl, the remaining *ortho*-hydrogen resonates at δ 7.64.[36] The *ortho*-hydrogens of (*E*)- and (*Z*)-(1b) and (*Z*)-(2b) absorb at δ 7.87—7.90 (see Tables 1 and 3), indicating that the phenyl is fully conjugated with the carbonyl group.

hydrogens of *Z*, in contrast to those of *E*, exhibit an isolated low-field ^{1}H n.m.r. absorption, and the a.s.i.s. of these hydrogens is smaller for *Z* than *E* (Tables 1 and 3). (ii) The molar extinction coefficient at 245—260 nm is larger for *Z* than *E* (Tables 2 and 4). (iii) The carbonyl stretching frequency is higher for *Z* than *E* [($CHCl_3$) (*Z*)-(1c) 1 690; (*E*)-(1c) 1 665; (*Z*)-(2c) 1 723; (*E*)-(2c) 1 706 cm^{-1}]. All these observations are consistent with the structures indicated in the Figure. In the (*E*)-isomer the phenyl group, as a result of steric interaction with the oxime oxygen, is forced out of conjugation with C=N.* An estimate of the dihedral angle θ between the phenyl and imine groups of the (*E*)-isomers was obtained using the formula $\cos^2\theta = \varepsilon/\varepsilon_0$,[39] in which ε and ε_0 are the u.v. molar extinction coefficients for the twisted and planar conformations respectively. The ε_0 values were taken to be equal to those of the corresponding (*Z*)-isomers in view of their planar conformation. It then followed that for (*E*)-(1c) θ = 45°, for (*E*)-(1e) 47°, and for (*E*)-(1j) 40°.

From the observations that $\nu_{C=O}$ of (*E*)-(1a) (1 671) and (*E*)-(1c) (1 665) differ by only 6 cm^{-1} and that $\nu_{C=O}$ of (*E*)-(2a) and (*E*)-(2c) are the same (both 1 706 cm^{-1}), it is concluded that the C=O and C=N groups of (*E*)-(1c) and (*E*)-(2c) are fully conjugated and thus coplanar.

In (*Z*)-(1c) the phenyl and imine groups can be coplanar. The differences between *Z* and *E* [see (i)—(iii) before] indicate that the conjugation between the C=O and C=N groups is substantially less for *Z* than *E*.†

The chemical shift of the acetate hydrogens of (2c) is at lower field for *Z* than *E*, because of shielding by the phenyl group.

Compounds (1d) *and* (2d). These compounds show the same characteristics as (1c) and (2c), *viz.* (i) the 6′-H signal is 0.37 p.p.m. more deshielded in *Z* than *E*, and has a negative a.s.i.s. for *Z*, (ii) both (*E*)-(1d) and (*E*)-(2d) have a small ε at λ 245—270 nm (Tables 2 and 4), and (iii) $\nu_{C=O}$ is higher for *Z* than *E*. The structural conclusions drawn for (1c) and (2c) therefore also apply to (1d) and (2d).

Compounds (1e) *and* (2e). The two geometric isomers of (1e) show again the same three characteristics as those of and (1c and d) and (2c and d). The conformations of (*E*)- and (*Z*)-(1e) as far as the CO-CNOH-Ph moiety is concerned (see Figure) are therefore proposed to be the same as those of (*E*)- and (*Z*)-(1c). In addition two other differences invoked by the cyclopropyl group, are apparent between *E* and *Z*, *viz.* 2-H (*cf.* Figure) resonates at much lower field in (*E*)- than (*Z*)-(1e), and 3- and 5-H are somewhat deshielded in *Z* as compared with *E* (Tables 1 and 3). In view of (i) the low-field absorption and small a.s.i.s. of 2-H, (ii) the crystallographically determined structure of dicyclopropylethanedione,[42] and (iii) Hoffmann's theoretical considerations on the structure of cyclopropanecarbaldehyde,[43] the bisected conformation of the cyclopropyl group relative to the carbonyl group is proposed. For (*E*)-(1e) and (*E*)-(2e), the cyclopropyl group is suggested to be s-*trans* to the carbonyl group, as 2-H is then in the deshielding cone of the carbonyl group.

As to (*Z*)-(1e) and (*Z*)-(2e), the cyclopropylcarbonyl group is forced out of the PhC=N plane, similar to the acetyl group in (*Z*)-(1c) (see before). There would be substantial steric hindrance between the oxime oxygen and the two hydrogens 3- and 5-H, if the conformation of the cyclopropyl relative to the carbonyl were bisected and s-*trans* (as with *E*). Actually, 2-H resonates at much higher field with *Z* than *E*. Accordingly, the s-*cis* bisected conformation is much more likely than the s-*trans* one. The s-*cis* conformation is also consistent with the downfield resonance shift of 3- and 5-H of *Z* compared with *E*.

Compounds (1j) *and* (2j). Between *E* and *Z* the same spectral differences are observed, as discussed before for the geometric isomers of the couples (1b) and (2b), and (1c) and (2c). The results are therefore interpreted in terms of the structures shown in the Figure. With both isomers the carbonyl is fully conjugated with the adjacent phenyl.‡ The PhC=O group is twisted out of the C=N nodal plane, probably by 60°, the value determined crystallographically for benzil.[31a] $\nu_{C=O}$ is greater for (*Z*)- than (*E*)-(1j) [(KBr) 1 671 *vs.* 1 643 cm^{-1}], whereas they are the same for (*Z*)- and (*E*)-(1b) [($CHCl_3$) 1 666 and 1 664 cm^{-1}, respectively]. This may infer that the (O=)C–C(=N) dihedral angle is larger for (*Z*)-(1j) than (*Z*)-(1b).

By analogy with (1c—e) and (2c—e), it is proposed that the iminyl phenyl is fully conjugated with C=N in *Z*, whereas with *E* the phenyl group is forced out of the C=N nodal plane as a result of steric hindrance by the oxime oxygen. This proposition is consistent with the u.v. data of (1j) and the ^{1}H n.m.r. data of (2j).

Photoisomerization. Irradiation of the α-oxo-oximes and the α-oxo-oxime acetates listed in Table 5 lead to *E*–*Z* isomerization and formation of a PSS. The $[E] : [Z]_{PSS}$ is greater for the four acyclic oximes (1b—e) than for the corresponding acetates.

The (*E*)-isomers of the α-oxo-oximes (1a and f—i) and of the α-oxo-oxime esters (2a, f, and h) and (4a—c) do not photoisomerize. The (*Z*)-isomers of the α-oxo-oximes and α-oxo-oxime esters which do photoisomerize exhibit intramolecular steric hindrance between the oxime oxygen and the group located at the ketone function. This correlation is probably fortuitous as the corresponding ethyl ether of (1a) does photoisomerize.[9]

---

* Similar observations were made with alkylbenzaldehyde oxime *O*-methyl ethers [37] and arylmethyl-*N*-methylimines.[38]

† For αβ-unsaturated ketones $\nu_{C=O}$ of the planar s-*cis* conformation is 20 cm^{-1} higher than that of the planar s-*trans* conformation.[40] The $\nu_{C=O}$ of a non-planar s-*trans* conformation will also be at higher frequencies than that of planar s-*trans*. For example, Groves and Jones reported for 1-acetyl-2-methylcyclohexene a calculated dihedral angle of 31° and an observed $\nu_{C=O}$ of 1 688 cm^{-1}, compared with an angle of 0° and $\nu_{C=O}$ of 1 665 cm^{-1} for 1-acetylcyclohexene.[41]

‡ The absorption of the *ortho*-hydrogens of the benzoyl group of (1j) is centred at δ 7.99, *i.e.* the same value as observed for acetophenone (δ 7.95), see the note in the section on (1b) and (2b).

EXPERIMENTAL

Materials.—All α-oxo-oximes were prepared by the method of Ferris [11] starting from the appropriate ketones and *in situ* generated methyl nitrite. The required ketones were obtained commercially, except benzyl cyclopropyl ketone which was available.[44] The α-oxo-oxime acetates were synthesized using standard procedures.[27b] For all new compounds satisfactory elemental analyses were obtained.

Irradiations.—The irradiations were performed in Rayonet photochemical reactors (type RPR 208) equipped with 366 or 254 nm lamps as required. The concentration of starting material was varied in between 0.08 and 0.15M.

Spectra.—The i.r. spectra were recorded on Perkin-Elmer 125 or 177 spectrophotometers and in some cases on a Unicam SP 200 instrument and the u.v. spectra on a Cary 14 spectrophotometer. The ^{1}H n.m.r. spectra were recorded on Varian A 60-D, HA-100, or XL-100 spectrometers using tetramethylsilane as internal standard.

[8/236 *Received*, 10*th February*, 1978]

REFERENCES

[1] Part 3, P. Baas and H. Cerfontain, preceding paper.

[2] A. Padwa, *Chem. Rev.*, 1977, **77**, 37.

[3] D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Amer. Chem. Soc.*, 1966, **88**, 2775.

[4] R. J. Cook and K. Mislow, *J. Amer. Chem. Soc.*, 1971, **93**, 6703.

[5] A. Mustafa, A. K. Mansour, and H. A. A. Zaher, *J. Org. Chem.*, 1960, **25**, 949.

[6] A. Stojiljković and R. Tasovac, *Tetrahedron Letters*, 1970, 1405.

[7] J. C. Danilewicz, *J. Chem. Soc.* (*C*), 1970, 1049.

[8] G. A. Delzenne, U. Laridon, and H. Peeters, *European Polymer J.*, 1970, **6**, 933.

[9] P. Baas and H. Cerfontain, *J.C.S. Perkin II*, 1977, 1351.

[10] P. Baas and H. Cerfontain, *Tetrahedron Letters*, 1978, 1501.

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

[12] L. Claisen and O. Manasse, *Annalen*, 1893, **274**, 71.

[13] A. I. Vogel, ' A Text-book of Practical Organic Chemistry ', Longman, London, 1970, p. 720.

[14] J.-P. Guetté, J. Armand, and L. Lacombe, *Compt. Rend.* (*C*), 1967, **264**, 1509; J. Armand and J.-P. Guetté, *Bull. Soc. chim. France*, 1969, 2894.

[15] G. G. Kleinspehn, J. A. Jung, and S. A. Studniarz, *J. Org. Chem.*, 1967, **32**, 460.

[16] A. A. Pavia and A. Daniel, *Compt. Rend.* (*C*), 1966, **263**, 643.

[17] A. Daniel and A. A. Pavia, *Tetrahedron Letters*, 1967, 1145.

[18] J. Ronayne and D. H. Williams, *J. Chem. Soc.* (*B*), 1967, 540.

[19] M. Kimura, Y. Kuroda, H. Takagi, and M. Kubo, *Bull. Chem. Soc. Japan*, 1960, **33**, 1086.

[20] Y. Kuroda and M. Kimura, *Bull. Chem. Soc. Japan*, 1963, **36**, 464.

[21] A. Palm and H. Werbin, *Canad. J. Chem.*, 1954, **32**, 858.

[22] P. C. Cherry, W. R. T. Cottrell, G. D. Meakins, and E. E. Richards, *J. Chem. Soc.* (*C*), 1968, 459.

[23] J. C. Timmons; B. P. Stranghan, W. F. Forbes, and R. Shilton, Proc. 4th. Internat. Meeting Mol. Spectroscopy, Bologna, 1959 (*Chem. Abs.*, 1963, **59**, 4680g.

[24] D. H. R. Barton and J. M. Beaton, *J. Amer. Chem. Soc.*, 1961, **83**, 4083; M. P. Cava and B. R. Vogt, *J. Org. Chem.*, 1965, **30**, 3775; H. E. Smith and A. A. Hicks, *ibid.*, 1971, **36**, 3659.

[25] L. J. Bellamy, ' The Infrared Spectra of Complex Molecules ', Methuen, London, 1966, (*a*) p. 182; (*b*) p. 189.

[26] M. Hirama and S. Itô, *Tetrahedron Letters*, 1975, 1071.

[27] P. Baas, Thesis, University of Amsterdam, 1977, (*a*) ch. 3; (*b*) pp. 25, 26.

[28] C. Pigenet, J. Armand, and H. Lumbroso, *Bull. Soc. chim. France*, 1970, 2124.

[29] P. Alderliesten, A. Almenningen, and T. G. Strand, *Acta Chem. Scand.*, 1975, **B29**, 811.

[30] G. J. Karabatsos and R. A. Taller, *Tetrahedron*, 1968, **24**, 3347.

[31] (*a*) C. J. Brown and R. Sadanaga, *Acta Cryst.*, 1965, **18**, 158; (*b*) C. Pigenet, J.-P. Morizur, Y. Pascal, and H. Lumbroso, *Bull. Soc. chim. France*, 1969, 361.

[32] K. A. Kerr, J. M. Robertson, and G. A. Sim, *J. Chem. Soc.* (*B*), 1967, 1305.

[33] J. Barassin, G. Queguiner, and H. Lumbroso, *Bull. Soc. chim. France*, 1967, 4707.

[34] A. Devaquet, *J. Amer. Chem. Soc.*, 1972, **94**, 5160; T. Liljefors and N. L. Allinger, *ibid.*, 1976, **98**, 2745.

[35] H. Kessler, *Angew. Chem.*, 1967, **79**, 997.

[36] G. Montaudo, P. Finocchiaro, and P. Maravigna, *J. Amer. Chem. Soc.*, 1971, **93**, 4214.

[37] G. J. Karabatsos and N. Hsi, *Tetrahedron*, 1967, **23**, 1079.

[38] J. Bjørgo, D. R. Boyd, C. G. Watson, and W. B. Jennings, *Tetrahedron Letters*, 1972, 1747; *J.S.C. Perkin II*, 1974, 757; E. P. Kyba, *Tetrahedron Letters*, 1973, 5117.

[39] H. H. Jaffé and M. Orchin, ' Theory and Applications of Ultraviolet Spectroscopy ', Wiley, New York, 1962, p. 414.

[40] W. P. Hayes and C. J. Timmons, *Spectrochim. Acta*, 1968, **A24**, 323.

[41] J. K. Groves and N. Jones, *Tetrahedron*, 1969, **25**, 223.

[42] C. N. A. Lute and C. H. Stam, *Rec. Trav. chim.*, 1976, **95**, 130.

[43] R. Hoffmann, *Tetrahedron Letters*, 1965, 3819; R. Hoffmann and R. B. Davidson, *J. Amer. Chem. Soc.*, 1971, **93**, 5699.

[44] J. Kelder, J. A. J. Greenevasen, and H. Cerfontain, *Synth. Comm.*, 1972, **2**, 125.