REACTIONS OF α-OXIMINOKETONES WITH DIAZOMETHANE

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Treatment of diazoalkanes with aliphatic α-oximinoketones results in the formation of either O-ethers or their mixtures with nitrones [1], Z-o-quinonemonooximes — oxazoles [2, 3], or other cyclic oximinoketone–nitrone mixtures [4-8]. For example, reaction of the E-isomer of 3-oximino-2,2,5,5-tetramethylfuran-4-one [5], the Z-isomer of 2-oximino-3,3-diphenylindan-4-one [8], or various 3-isonitrosocamphor isomers [4] with diazomethane results in formation of the corresponding nitrones only; in this regard, it was also noted that either the Z-isomer was chemically inert [5], or else it underwent isomerization to the E-isomer under the influence of diazomethane [4]. We have demonstrated, however, that reaction of a mixture of the Z- and E-isomers of 3-isonitrosocamphor with diazomethane results in the formation of the O-ether as well as the nitrone [1].

In the present paper we report our results of a study of the dependence of the reaction pathway on both the configuration (Z or E) and conformation (s-cis or s-trans) of α-oximinoketones; the alkylation reactions with diazomethane were conducted in various solvents. The following materials were selected as substrates for this study; 3-isonitrosocamphor (I), acenaphthenequinonemonooxime (II), and 2-oximino-3,3-diphenylindan-1-one (III), for which both the Z- and E-isomers are known [4, 8, 9], as well as the conformationally labile derivatives E-isonitrosoacetophenone (IV) and E-isonitrosoacetanilide (V).

The E-isomers of oximes (I)-(III) and the Z-isomers of oximes (I) and (III) were all separated and isolated in their pure states. The Z-isomer of acenaphthenequinonemonooxime was prepared as a mixture with a mp of 208°C (the material described in the literature [9] as the Z-isomer (II) also exhibited a mp of 208°C, and thus is also probably a mixture of the Z- and E-isomers).

The configurations of the 3-isonitrosocamphor isomers were assigned based on literature data [10]; the E-configuration of the stable 2-oximino-3,3-diphenylindan-1-one isomer, which had previously been assigned the Z-configuration [8], was assigned based on x-ray structural analysis (XRA) of crystals prepared by us [11]. The E-configuration of the stable acenaphthenequinonemonooxime isomer has been proposed based on the similarities in the values of the νC=O and νC=N stretching frequencies in the IR spectra of oximes E-(I) through E-(III) (Table 1). The E-configurations of the oximes (I)-(III) were verified by the formation of water-insoluble complexes upon treatment with Cu^{2+} in weakly basic medium; under analogous conditions the Z-(I) oxime reacts to give a solution of the oximate salt and a $Cu(OH)_2$ precipitate.

The configuration of the oxime Z-(III) as well as the presence of some of the Z-isomer of acenaphthenequinonemonooxime with the E-isomer were established by comparison of the νC=O and νC=N stretching frequencies in the IR spectra of these compound and of the oxime Z-(I) (Table 1). The E-configurations of the oximes (IV) and (V) were established by XRA; the oxime (IV) is found in the s-trans conformation [12], whereas the oxime (V) adopts the s-cis conformation [13]

We have studied the reactions of oximes (I)-(III), in which the s-cis conformation is fixed, with diazomethane in ether solution, and have demonstrated that the E-isomers react readily over a 0.5-3 h time period to give the nitrone E-isomers (Ia)-(IIIa) exclusively (Scheme 1), whereas the Z-isomers, which contain strong intramolecular H-bonds, require 1-7 days for the analogous reactions to occur, and lead to mixtures of the corresponding nitrones (Ia) and (IIa) and Z-O-ethers (Ic) and (IIc) (Schemes 2 and 3). The formation of nitrone (Ia) in 20% yield from oxime Z-(I) (as determined by integration of the signal intensities for the MeN and MeO proton groups in the PMR spectra of the reaction mixture) may be ratio-

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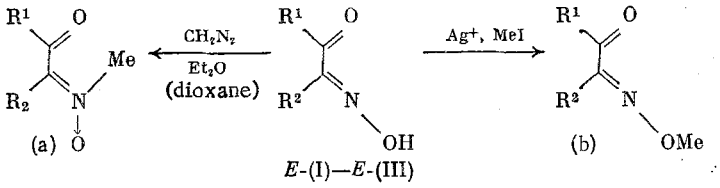
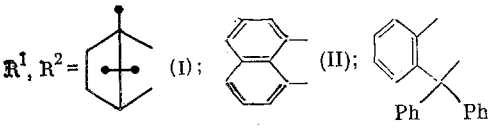
nalized in terms of initial isomerization of the oxime to the E-isomer; this was verified by the observation that over the course of a week an ethereal solution of the Z-(I) oxime undergoes isomerization and generates up to 15% of the E-(I) oxime (based on integration of the signal intensities of the 4-proton in the PMR spectra). The exclusive formation of the nitrone (IIIa) (Scheme 4) may also be explained in terms of preliminary Z–E isomerization, since the IR spectrum (KBr pellet) of a Z-(III) sample obtained after standing for 1 day in ether solution exhibited the C=O and C=N absorption peaks of both isomers in almost equal intensities.



(1)



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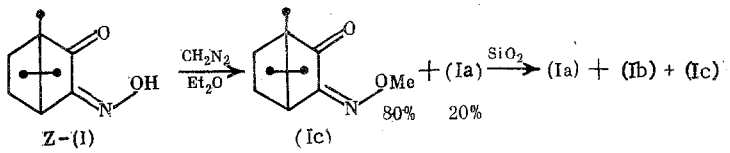

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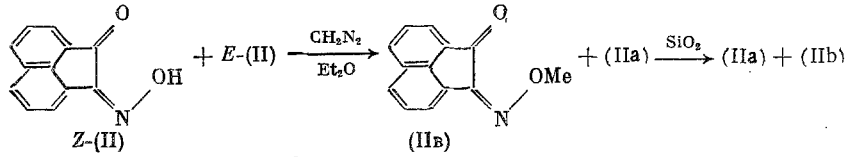

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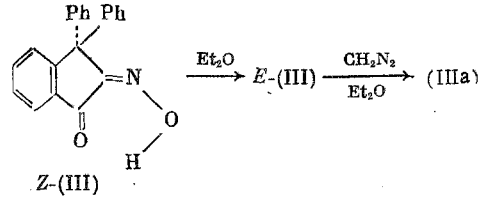
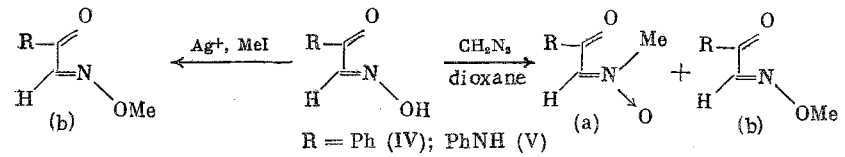


(4)

The Z-O-ether (Ic) was isolated by chromatography of a mixture of (Ia) and (Ic) (Scheme 2) in $CHCl_3$. This compound exhibits parallel Z–E isomerization which is apparently catalyzed by silica gel, since the Z-O-ether (Ic) does not undergo any noticeable thermal isomerization to the E-isomer even upon heating in diphenyl ether (5 h at 150°C). The degree of Z–E isomerization increases significantly as the duration of the chromatographic process is increased, particularly using benzene as the eluent; under these conditions the Z-O-ether (Ic) cannot be isolated. Attempted chromatographic separation of the mixture of (IIa) and (IIc) (Scheme 3) resulted in complete isomerization of (IIc) to (IIb); the formation of the Z-O-ether (IIc) was established on the basis of TLC and PMR analysis of the reaction mixture.

Diazomethane-based alkylation of the conformationally labile oximes (IV) and (V) in dioxane solution leads to identical ratios of O- and N-methylation products, regardless of the conformational preference of the oxime (IV) or (V) in the crystalline state (Table 2). This may be explained in terms of the similarities in the effective conformations of the substrates under the reaction conditions; proof is offered in the IR spectra of the solutions of the oximes (IV) and (V) in CCl_4, which show absorption peaks of free NOH groups only, and thus rule out the possibility of intermolecular H-bonds [12, 13], which are present in the crystalline state and which are responsible for the defined conformational preferences of the molecules.



R = Ph (IV); PhNH (V)

(5)

TABLE 1. IR Spectral Parameters of Oximes

Compound	ν, cm⁻¹ (KBr pellets)			Compound	ν, cm⁻¹ (KBr pellets)		
	O—H	C=O	C=N		O—H	C=O	C=N
E-(I)	3440	1730	1640	*Z*-(II)	3150	1715	1625
	3300,	1755 [a]	1660 [a]	*E*-(III)	3200	1725	1642
	3575 [a]			*Z*-(III)	3300	1710	1625
Z-(I)	3340	1700	1625	*E*-(IV)	3290 [b]	1677	1580
E-(II)	3260	1730	1650	*E*-(V)	3250 [b]	1670	–

a) Microlayer. Solution in CCl_4.
b) In CCl_4 solution νOH appears at 3575 cm^{-1}.

TABLE 2. Nitrone:O-Ether Ratio upon Methylation of Oximes Using Diazomethane in Various Solvents

Compound	Et_2O	Me_2CO : Et_2O, 5 : 1 (mole)	MeOH : Et_2O, 5 : 1 (mole)
E-(I)	100 : 0	100 : 0 [a]	85 : 15
E-(II)	100 : 0 [b]	100 : 0	90 : 10
E-(III)	100 : 0	100 : 0	90 : 10
E-(IV)	75 : 25 [b]	30 : 70	47 : 53
E-(V)	75 : 25 [b]	20 : 80	57 : 43

a) In MeCN:Et_2O, 5:1—92:8.
b) In C_4H_5O:Et_2O, 5:1.

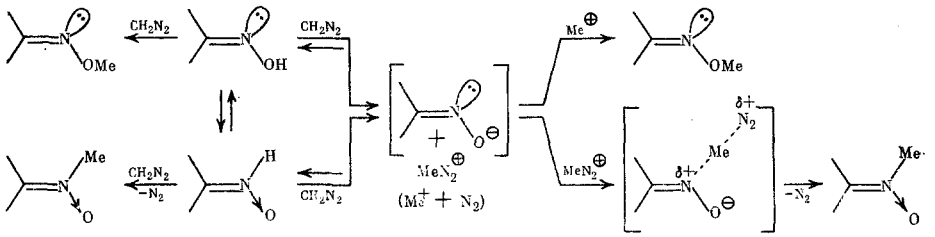
The direction of diazomethane-induced alkylation of α-oximinoketones in nonpolar solvents is thus determined by the structure of the substrate; the presence of a rigidly defined s-cis carbonyl group leads to O-alkylation in the case of Z-oximes and to N-alkylation in the case of E-oximes. The presence of a conformationally labile carbonyl group in E-oximes, on the other hand, leads to simultaneous O- and N-alkylation. The earlier results concerning the exclusive formation of nitrones in the reactions of cyclic α-oximinoketones with diazomethane may be explained in terms of the greater thermodynamic stability of the E-isomer substrates [4-8].

The alkylation reactions of solutions of the oximes E-(I) to E-(III) in acetone using diazomethane are stereospecific; when more polar solvents (MeCN) or, in particular, more protic solvents (MeOH) are used, alkylation yields small amounts of the E-O-ethers in addition to nitrones. It should also be noted that the choice of solvent has a similar significant effect on the regioselectivity of the methylation of the oximes (IV) and (V) (see Table 2).

The different effects of solvent nature on the methylation of cyclic and conformationally labile oximes may be attributed to changes in the effective conformations of oximes (IV) and (V) induced by changes in the solvent. It has proved difficult to study the conformations of these oximes because of the nontransparency of the solvents under consideration in the region of the carbonyl group stretching frequencies and also because of the infeasibility of measuring the shifts induced by aromatic solvents (SIAR effect) on the protons of the HC=N groups; this latter problem arises from the insolubility of the oximes in CCl_4 ($CDCl_3$) and C_6D_6 ($C_6H_5CD_3$). It is our feeling, however, that the conformations of the oximes (IV) and (V) in various solvents may be estimated based on conformational studies of their close structural analogs, namely the O-ethers (IVb) and (Vb). The IR spectra of these latter compounds contain two carbonyl group absorption peaks (Table 3); in each case, the lower frequency band, corresponding to the s-trans carbonyl group, predominates (in O-ethers of α-oximinoketones the frequency order is $\nu_{s\text{-}trans}C{=}O < \nu_{s\text{-}cis}C{=}O$ [1]). The predominance of the s-trans conformation in the O-ethers (IVb) and (Vb) has also been confirmed by the very large SIAR effect of the MeON group (0.43 and 0.53 ppm, respectively); the SIAR effects for s-cis and s-trans conformers of α-oximinoketone O-ethers are in the range 0.18-0.30 and 0.46 ppm, respectively

[1]. The equivalence of the equilibrium mixtures of the O-ether conformers (IVb) and (Vb) reflects the similarities in the effective conformations of the oximes (IV) and (V) and thus similar solvent-induced conformational changes may be assumed to occur in these materials.

Two mechanisms have been proposed for the reactions of diazomethane with tautomeric or potentially tautomeric systems. By analogy with the results obtained for the alkylation of carboxylic acid amides with diazomethane [14, 15], the O- versus N-alkylation product ratio should be determined by the differing electron densities and nucleophilicities of the reactive sites in the intermediate ambident anions (Scheme 6); in this regard, O-alkylation, which occurs via an S_N1 mechanism, should be favored by higher electron density on the O atom, whereas N-alkylation, which proceeds via an S_N2 mechanism, should be favored by greater nucleophilicity of the N atom [16]. By analogy with [15], methylation takes place on the site of proton localization, and thus the O- versus N-methylation product ratio should depend on the tautomeric equilibrium constant and on the kinetic acidity of the tautomers (see Scheme 6).



The observed decreased yields of nitrones in polar solvents may be ascribed in full to the well-known fact that a bimolecular reaction occurs at a slower rate than a unimolecular reaction as the solvent polarity is increased [17], i.e., these results are consistent with the mechanism outlined in [14]. If the diazomethane alkylation is carried out under identical temperature and concentration conditions, and in the same solvent systems, then the ratio of intrinsic alkylating agents, namely, Me^+ and MeN_2^+, should be identical and should not affect the direction of the reaction course. Under these conditions the ratio of nucleophilicity and electron density of the reactive sites, the O and N atoms, in particular, should also be nearly identical for the anions generated from both the Z- and E-isomers of the same oximes, and should vary in the same manner for the anions derived from the E-isomeric oximes (I)-(V) as the solvent nature is varied. Based on these considerations and the mechanism proposed in [14], it is impossible to explain the stereospecificity of the methylation reactions of the oximes (I)-(III) or to account for the inverse regioselectivity noted for the reactions of the conformationally labile and cyclic α-oximinoketones upon replacement of acetone (or acetonitrile) with methanol as the solvent and the dependence of the direction of methylation on the conformation of the oxime. The above-noted facts, however, are consistent with a mechanism proposed elsewhere [15], in which it is assumed that the oximes exist in the tautomeric NH-nitrone forms [1, 18], which are characterized by a greater kinetic acidity and are stabilized by intramolecular H-bond formation with the s-cis-carbonyl group. The observed stereospecificity and regioselectivity of the diazomethane-induced methylation reactions are therefore associated with the predominance in solution of oxime forms containing s-cis-carbonyl groups of nitrones in the case of E-isomeric oximes and parent oxime forms in the case of the Z-isomeric oximes or E-isomers incorporating the s-trans conformations of the carbonyl groups; the solvent effects can then be rationalized in terms of changes in the tautomeric equilibrium constants and accompanying changes in the conformations of the oximes (IV) and (V). The observed results can also be explained in terms of the "field effects" of the polar oximino- and carbonyl groups [14], which lead to electrostatic attraction between the electrophilic reagent, namely Me^+ or MeN_2^+, and the center of the ambident anion, the O atom in the case of the Z-(I) and Z-(II) oximes, the N atom in the case of the E-(I) to E-(III) oximes, and either the N atom or O atom in the case of the conformationally labile oximes (IV) and (V), depending on the conformation of the carbonyl group. At the present time it is difficult to distinguish between the straightforward methylation mechanism and the polar field effects mechanism.

The structures of the diazomethane-induced oxime alkylation products were verified by independent syntheses [for the oxime O-ethers (Ib)-(Vb), see Schemes 1 and 5], and by the

TABLE 3. Properties of Nitrones and Oxime O-Ethers

Compound	Yield, %[a]		bp, °C (p, mm Hg)	ν, cm^{-1} (KBr pellets)		δ, ppm, from HMDS (5 mole % solutions in CCl_4)[b]		Found/Calculated, %		
	A	B		C=O	C=N	CH_3	=CH	C	H	N
(Ia)	100	–	107 (3) [c] (cf. [1])	1707 [d]	1578	3,93 (0,24)	3,13 (0,00) [e]	–	–	–
(Ib)	–	87	107–108 (cf. [1])	1725	1625	3,89 (0,18)	3,01 (0,10) [e]	–	–	–
(Ic)	29	–	84–85	1730	1610	3,82 (0,12)	2,49 (0,17) [e]	67,90/67,67	8,72/8,78	7,15/7,17
(IIa)	100	–	167 (cf. [3])	1690	1555	4,35 (0,33)	4,40 [f]	–	–	–
(IIb)	10	79	152	1720	1610	4,32 (0,30)	4,30 [f]	74,08/73,92	4,22/4,30	6,52/6,67
(IIIa)	100	–	178 (cf. [8])	1685	1550	4,22 (0,35)	–	–	–	–
(IIIb)	–	58	196	1710	1605	3,80 (0,30)	–	80,49/80,71	5,17/5,24	4,15/4,28
(IVa)	55	–	92	1677, 1660	1548	4,20 (0,35)	8,20	66,38/66,25	8,38/8,58	5,69/5,56
(IVb)	15	67	– [g]	1650, 1640 [d]	1620	4,10 (0,53)	7,67	66,46/66.25	8,44/8,58	5,86/5,56
(Va)	62	–	98	1670	1550	3,85 (1,25)	7,20	60,54/60,66	5,79/5,65	15,42/15,72
(Vb)	22	57	88	1685, 1670	–	4,00 (0,43)	7,27	60,77/60,66	5,82/5,65	15,48/15,72

a) Alkylation: A, with diazomethane; B, with methyl iodide.
b) The values of the SIAR effects, $\Delta\delta^{C_6H_6}_{CCl_4} = \delta_{CCl_4} - \delta_{C_6H_6}$.
c) n_D^{20} 1.5302.
d) Microlayer.
e) 4-H.
f) δMe$(CD_3)_2CO$.
g) n_D^{20} 1.5488.

IR and PMR spectral data (Table 3). The configuration assignments for compounds (Ia, b, and c) were made based on the magnitude of the chemical shifts of the bridgehead protons in the PMR spectra of the isomeric oximinocamphor derivatives [10] (see Table 3). The E-configuration of nitrone (Ia) had been assigned in an earlier work as well [19]. The identities of the nitrones obtained from the Z- and E-isomeric oximes (Schemes 1-4) were confirmed by IR spectral analysis and by the absence of a melting point depression for mixed probes; the E-configuration of the nitrones (IIa)-(Va) was assumed based on the retention of configuration upon alkylation of unsymmetrically substituted oximes [1] and oxime E-(I) with diazomethane as well as based on the greater thermodynamic stability of nitrone (Ia) in comparison with the isomeric Z-nitrone [19].

EXPERIMENTAL

PMR spectra were recorded on a RYa-2305 spectrometer (60 MHz), while IR spectra were obtained on a UR-20 spectrophotometer (micro or thin layer in the case of liquid samples, CCl_4 solutions or KBr pellets in the case of crystalline derivatives).

E-3-Isonitrosocamphor E-(I). This material was prepared according to a literature method [20] in 43% yield, mp 149-150°C (see [20]).

Z-3-Isonitrosocamphor Z-(I). A solution of 50 g (0.33 mole) of camphor in 200 ml of absolute ether and containing 8 g (0.35 mole) of finely divided Na was treated dropwise with stirring with 20 ml (0.33 mole) of amyl nitrite. After completion of the exothermic reaction the reaction mixture was poured into water, the unreacted camphor was extracted into ether (2 × 100 ml), and the aqueous layer was charged with CO_2 gas; the resulting crystals were removed by filtration. Yield 9 g (15%) of Z-(I), mp 115-116°C (see [10]).

E-2-Oximino-3,3-diphenylindan-1-one E-(II). This was obtained by nitrosation of 3,3-diphenylindan-1-one in basic medium according to [8] in 82% yield, mp 206-207°C (see [8]).

Z-2-Oximino-3,3-diphenylindan-1-one Z-(II). Nitrosation of 3,3-diphenylindan-1-one in acidic medium according to [8] gave this material in 72% yield, mp 215°C (from i-PrOH). Oxime Z-(II) isomerized completely to the E-isomer upon standing for 1 week in benzene solution.

E-Acenaphthenequinoneoxime E-(III). Prepared in 62% yield according to [9], mp 228°C (from dioxane) (see [9]).

E-Isonitrosoacetoiphenone (IV). Prepared in 48% yield according to [21], mp 127°C (see [21]).

E-Isonitrosoacetanilide (V). According to [22], 62% yield, mp 76°C (see [22]).

E-3-Methylnitronocampha-2,3-dione (Ia). A solution of 0.2 g (1.1 mmole) of oxime E-(I) in 37.5 ml of ether was treated with 7.5 ml of an ethereal diazomethane solution (3.5 mmole), stirred for 3 h, and the solvent was removed. Nitrone (Ia) (see Table 3) was obtained in quantitative yield (see [1]).

3,3-Diphenyl-2-methylnitronoindan-1-one (IIIa) (Table 3) was prepared in an analogous manner.

E-8-Methylnitronoacenaphthen-7-one (IIa). This material was obtained in a manner analogous to that described above for nitrone (Ia) using a solution of oxime E-(II) in dioxane (Table 3) (see [3]).

Z-3-(O-Methylisonitroso)camphor (Ic). A solution containing 1.6 g (8.9 mmole) of oxime Z-(I) in ether was treated with excess diazomethane in ether solution, maintained under these conditions for 1 week, and the solvent was removed; the residue was subjected to column chromatography (silica gel L100/160 μ, $CHCl_3$). Yield 0.5 g (29%) of the Z-O-ether (Ic) (see Table 3). Attempted crystallization of the Z-O-ether (Ic) from EtOH—H_2O (7:3) led to its partial isomerization to the E-O-ether (Ib).

Reaction of a Mixture of Z- and E-Isomeric Acenaphthenequinonemonooximes with Diazomethane. A suspension of 4.2 g (21.3 mmole) of acenapththenequinonemonooxime (prepared according to [9], mp 208°C) in 50 ml of ether was treated with 50 ml of ethereal diazomethane solution (ca. 25 mmole), stirred for 24 h, and filtered to remove the crystalline precipitate of nitrone (IIa) (2.7 g); the filtrate was evaporated. The PMR spectrum of a solution of the residue in $(CD_3)_2CO$ contained signals at 4.40 ppm [MeN of nitrone (IIa)] and 4.24 ppm [MeO, Z-O-ether (IIc)]. TLC data (Silufol UV-254; $CHCl_3$): nitrone (IIa) R_f 0.46; Z-O-ether (IIc), R_f 0.78. Column chromatography of this residue (silica gel L100/160 μ, $CHCl_3$) gave 0.45 g (10%) of the E-O-ether (IIb) (R_f 0.59) and 0.6 g of nitrone (IIa) (see Table 3).

α-Benzoyl-N-methylnitrone (IVa) and E-(O-Methylisonitroso)acetophenone (IVb). A solution of 1.5 g (10 mmole) of oxime (IV) in 30 ml of ether was treated with 60 ml of ethereal diazomethane solution (30 mmole) and maintained under these conditions for 24 h; the solvent was removed and the residue was washed with MeOH and recrystallized from benzene–hexane (1:5). Yield 0.9 g (55%) of nitrone (IVa) (see Table 3). The methanolic solution was concentrated and the residue was subjected to column chromatography (silica gel L100/160 μ, $CHCl_3$). Yield 0.25 g (15%) of O-ether (IVb) (Table 3).

α-Phenylcarbamoyl-N-methylnitrone (Va) and E-(O-Methylisonitroso)acetanilide (Vb). A solution containing 3 g (18 mmole) of oxime (V) in 45 ml of dioxane was treated with 120 ml of ethereal diazomethane (60 mmole) and maintained under these conditions for 24 h; solvents were removed and the residue was crystallized from benzene–hexane (1:5). Yield 2.0 g (62%) of nitrone (Va) (see Table 3). The mother liquor was concentrated and the residue recrystallized from hexane. Yield 0.7 g (22%) of O-ether (Vb) (Table 3).

E-3-(O-Methylisonitroso)camphor (Ib). A solution of 0.13 g (3.3 mmole) of NaOH and 0.6 g (3.3 mmole) of oxime E-(I) in 10 ml of water was treated with a solution of 0.56 g (3.3 mmole) of $AgNO_3$ in 10 ml of water; the residue was filtered, washed with acetone, and dried. The resulting silver oximate salt of E-(I) was suspended in 40 ml of ether, 2.3 g of methyl iodide was added, and the mixture was refluxed for 3 h; the residue was removed by filtration, washed with $CHCl_3$, and the combined filtrates were concentrated to yield a residue which was recrystallized from benzene–hexane (1:5). Yield 0.56 g (87%) of E-O-ether (Ib).

The O-ethers (Ib)-(Vb) were all prepared in a similar manner (see Table 3).

The N- versus O-alkylation product ratios for the reactions of α-oximinoketones with diazomethane were determined in the following manner: A solution of 1 mmole of oxime in 30 ml of ether (21 ml acetone, 12 ml methanol, 15 ml acetonitrile, or 25 ml of dioxane) was treated with 6 ml of ethereal diazomethane solution (ca. 3 mmole), stirred for 24 h, and separated from solvent. The ratio of nitrone to O-ether was determined by measuring the integrated intensities of the MeON and MeN signals in the PMR spectra.

CONCLUSIONS

1. The direction of diazomethane-induced alkylation of α-oximinoketones is determined by the structure of the substrate: The presence of a fixed s-cis-carbonyl group leads to N-alkylation in the presence of E-isomeric substrates, and to O-alkylation in the case of Z-isomers; in contrast, the presence of conformationally labile carbonyl groups leads to simultaneous N- and O-alkylation of E-isomeric substrates.

2. Increasing the polarity of the solvent does not significantly affect the direction of diazomethane-induced alkylation of cyclic α-oximinoketones, but leads to a marked increase in the yield of O-alkylation products in the case of conformationally labile α-oximinoketones.

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