REACTION OF ACTIVATED OXIMES WITH DIAZOALKANES

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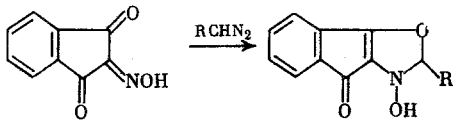
Four paths have been reported for the reactions of oximes with diazoalkanes: N-alkylation of hydroxyiminocamphor by diazomethane with the formation of a nitrone [1]; O-alkylation of benzaldehyde oxime (which only reacts in the Z form) [1] and hexafluoroacetone oxime [2]; 1,4-cycloaddition to o-quinone monooximes (sometimes with subsequent dehydration) and to 2-hydroxyimino-1,3-indanedione (Scheme 1) [3]



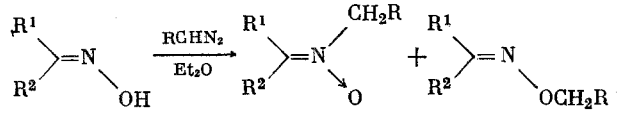
(R = H, Me) (1)

addition of methylene at the C=N bond [4]

$$(MeSO_2)_2C{=}NOH \xrightarrow{CH_2N_2} \underset{(35\%)}{(MeSO_2)_2CCH_2NOH} + \underset{(41\%)}{(MeSO_2)_2C{=}NOMe} \quad (2)$$

We have shown that for hydroxyiminomalonic esters only O- and predominantly N-alkylation are realized in this reaction [5]. In the present work we give detailed data on the reaction of activated oximes with diazoalkanes.

Acetone oxime does not change when treated with an excess of an ether solution of diazomethane at 20°C for 2 months. Activated oximes react with an equivalent of diazoalkane at 0-20°C according to Schemes (3)-(9) (Table 1):



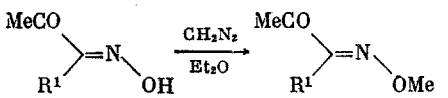
(3)

(a) (b)

$R^1{=}R^2{=}CO_2Me$, R=H(Ia, b); R = Me(IIa, b); R = H, $R^1 = R^2 = CO_2Et$(IIIa, b);
$R^1{=}CO_2Et$, $R^2{=}CN$ (IVa,b); $R^1{=}R^2{=}CN$ (Vb)

$$(MeO_2C)_2C{=}NOH \xrightarrow[Et_2O]{Ph_2CN_2} (MeO_2C)_2C{=}NOCHPh_2 \quad (4)$$

(VI)

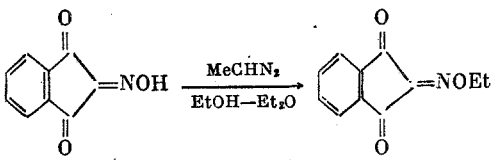


(5)

R^1=Me (VII), CO_2Et (VIII), COMe (IX)

$$(PhCO)_2C{=}NOH \xrightarrow[Et_2O]{CH_2N_2} (PhCO)_2C{=}NOMe \quad (6)$$

(X)



(7)

(XI)

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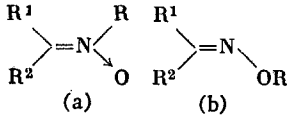
TABLE 1. Nitrones (a) and Oxime O-Ethers (b)



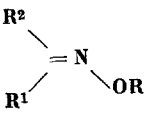
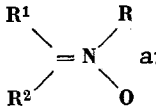
(a) (b)

Compound	Yield, %[a]			bp, °C (p, mm Hg)	n_D^{20}	IR spectrum, ν, cm^{-1} (mol. layer)			Found/calculated, %		
	A	B	C			C=N	C=O	N→O	C	H	N
(Ia)	66,6	–	–	112–113(4) mp 76–77	–	1559[b]	1730	1239	41,11 / 41,15	5,25 / 5,17	7,84 / 7,99
(Ib)	6,7	3,7	–	88–89(4)	1,4485	1600	1740 1720		41,23 / 41,15	5,18 / 5,17	7,71 / 7,99
(IIa)	42,0	–	–	111–113(3) mp 51–52	–	1555[b]	1738	1234	44,39 / 44,44	5,71 / 5,86	7,38 / 7,40
(IIb)	11,0	30,5	–	83–84(3)	1,4454	1600	1740 1720		44,36 / 44,44	5,98 / 5,86	7,55 / 7,40
(IIIa)	56,0	–	28	115–116(3)	1,4730	1553	1730	1230	47,29 / 47,29	6,49 / 6,45	6,82 / 6,89
(IIIb)	11,3	33,0	20	105–107(5)	1,4432	1600	1735 1710		47,26 / 47,29	6,35 / 6,45	6,89 / 6,89
(IVa)	22,5	–	–	97–98 (0,5)	1,4973	1510	1725	1140	46,11 / 46,15	5,27 / 5,16	17,83 / 17,93
(IVb)	46,3	–	–	61–62(1)[c]	1,4508	1552	1729		–	–	–
(Vb)	16,1	–	–	55(20)	1,4458	1523	–		44,19 / 44,04	2,92 / 2,77	38,50 / 38,53
(VI)	33,3	–	–	mp 96	–	1608[b]	1742 1713		66,10 / 66,05	5,37 / 5,23	4,24 / 4,28
(VII)	43,2	–	40,2	126–127[c]	1,4358	1690	1690		–	–	–
(VIII)	50,0	–	56,7	74,5–75,5(4)	1,4429	1596	1740 1690		48,71 / 48,55	6,52 / 6,40	8,08 / 8,09
(IX)	56,0	–	–	54–55(1,5)	1,4459	1591	1721 1682		50,33 / 50,35	6,54 / 6,34	9,93 / 9,79

TABLE 1 (continued)

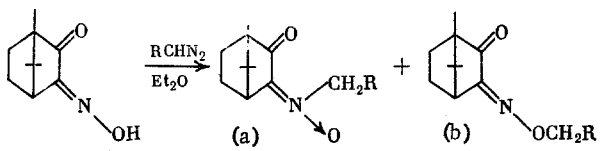
Compound	Yield % [a]			bp, °C (p, mm Hg)	n_D^{20}	IR spectrum, ν, cm^{-1} (mol. layer)			Found/calculated, %		
	A	B	C			C=N	C=O	N→O	C	H	N
(X)	64,3	–	50,0	mp 65–66	–	1590 b	1678 1642		71,28 71,36	5,68 5,61	5,23 5,20
(XI)	60,0	–	–	mp 170	–	1595 b	1725 1694		65,03 65,02	4,67 4,46	6,82 6,89
(XIIa)	33,3	–	–	107(3)	1,5302	1578	1707	1270	67,71 67,67	8,77 8,78	7,05 7,17
(XIIb)	13,8	–	–	97(3) mp 40–41	–	1610 b	1730		67,90 67,67	8,72 8,78	7,15 7,17
(XIIIa)	53,0	–	–	104–108(3)	1,5178	1565	1700	1269	68,81 68,87	9,22 9,15	6,57 6,69
(XIIIb)	8,1	–	–	100–102(3)	1,4904	1615	1736		68,77 68,87	9,13 9,15	6,70 6,69
(XIV)	–	34,2	–	86,5–87(3,5)	1,4450	1600	1745 1720		47,34 47,29	6,54 6,45	7,12 6,89
(XV)	–	56,8	29,5	104–105(4)	1,4408	1600	1739 1710		49,52 49,77	6,93 6,96	6,67 6,45
(XVI)	–	60,0	–	97–98(3)	1,4425	1600	1739 1711		51,98 51,94	7,55 7,41	6,11 6,06
(XVII)	–	11,9	–	88,5–89,5(6)	1,4402	1595	1740 1690		53,83 53,72	7,49 7,51	7,15 6,96

[a] Alkylation: A) by diazoalkanes; B) by alkyl halides; C) by dialkyl sulfates.
[b] Tablets with potassium bromide.
[c] Cf. [6].

TABLE 2. The Parameters of the PMR Spectra of the Oxime O-Ethers  and Nitrones  and the ASIS Effect ($\Delta\nu_{CCl_4}^{C_6H_6} = \nu_{CCl_4} - \nu_{C_6H_6}$) (δ, ppm from HMDS, 5 mole % solutions in carbon tetrachloride)

Compound No.	R[a]		R[1a]		R[2a]	
	Me	CH_2(CH)	Me	CH_2(CH)	Me	CH_2(CH)
(Ia)	4,20 (0,64)	–	3,82 (0,63)	–	3,82 (0,36)	–
(Ib)	4,08 (0,44)	–	3,82 (0,41)	–	3,82 (0,48)	–
(IIa)	1,42 (0,41)	4,59 (0,42)	3,85 (0,60)	–	3,85 (0,34)	–
(IIb)	1,30 (0,40)	4,31 (0,31)	3,81 (0,36)	–	3,81 (0,51)	–
(IIIa)	4,16 (0,51)	–	1,27 (0,46)	4,30 (0,44)	1,27 (0,31)	4,32 (0,16)
(IIIb)	4,07 (0,46)	–	1,29 (0,38)	4,30 (0,20)	1,31 (0,50)	4,30 (0,38)
(IVa)	4,32 (0,85)	–	1,37 (0,54)	4,36 (0,54)	–	–
(IVb)	4,30 (0,78)	–	–	–	1,35 (0,54)	4,32 (0,47)
(Vb)	4,41 (0,46)	–	–	–	–	–
(VI)	5,64 b	4,91 (–1,55)	2,87 (–0,27)	–	2,95 (–0,41)	–
(VII)	4,04 (0,40)	–	1,83 (0,05)	–	2,26 (0,17)	–
(VIII)	4,09 (0,59)	–	1,30 (0,40)	4,27 (0,30)	2,31 (0,40)	–
(IX)	4,07 (0,56)	–	2,20 (0,25)	–	2,32 (0,37)	–
(XIIa)	3,93 (0,24)	–	3,13 (0,00) c	0,83 (0,38) d	0,91 (0,39) e	0,91 (0,16) f
(XIIb)	3,82 (0,12)	–	2,49 (0,17) c	0,82 (0,39) d	0,90 (0,33) e	0,87 (0,14) f
(XIIIa)	1,28 (0,20)	4,32 (0,09)	3,13 (–0,01) c	0,83 (0,37) d	0,91 (0,37) e	0,91 (0,14) f
(XIIIb)	1,23 (0,17)	4,06 (0,03)	2,58 (0,23) c	0,83 (0,35) d	0,91 (0,31) e	0,88 (0,15) f
(XIV)	1,27 (0,31)	4,59 (0,24)	3,85 (0,43)	–	3,85 (0,58)	–
(XV)	1,31 (0,42)	4,32 (0,46)	1,31 (0,42)	4,30 (0,24)	1,31 (0,56)	4,30 (0,36)
(XVI)	1,30 (0,31)	4,54 (0,22)	1,30 (0,40)	4,30 (0,23)	1,31 (0,58)	4,30 (0,42)
(XVII)	1,29 (0,29)	4,51 (0,29)	1,26 (0,36)	4,27 (0,22)	2,30 (0,35)	–
(XXI)	3,75 (–0,06)	–	1,71 (0,20)	–	1,75 (0,27)	–

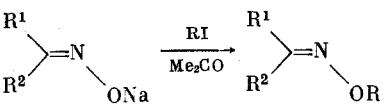
[a] $J_{CH_3-CH_2} = 6{,}75$, $J_{CH_3-CH} = 5{,}70$ Hz.
[b] $CHPh_2$.
[c] 4-H.
[d] 8-Me.
[e] 9-Me.
[f] 10-Me.



(8)

R=H (XII a,b), Me (XIII a, b)

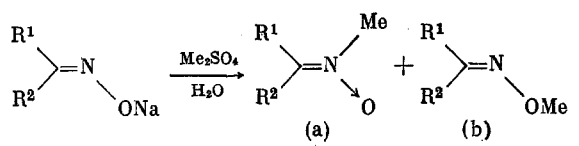
All the synthesized compounds except (IVa) have high thermal stability. For example, compound (IIa) distills under vacuum without change (controlled by PMR) when heated (150-160°C) for 1 h. The nitrones rapidly decompose under the influence of nucleophiles (sodium methoxide or methylamine in methanol at 20°C; triphenylphosphine in benzene at 80°C). Alkylation of the oximes in an alkaline medium, therefore, only gives O-ethers:



(9)

$R^1=R^2=CO_2Me$, R=Me (Ib), Et (IIb), *i*-Pr (XIV); $R^1=R^2=CO_2Et$, R=Me (IIIb), Et (XV), *i*-Pr (XVI); $R^1=CO_2Et$, $R^2=COMe$, R=Me (VIII), *i*-Pr (XVII)

However, the nitrone can be obtained where the products are insoluble in the reaction mixture and are isolated during formation:



(10)

$R^1=R^2=CO_2Me$ (Ia,b), CO_2Et (IIIa, b); $R^2=COMe$, $R^1=Me$ (VII); CO_2Et (VIII); $R^1=R^2=COPh$ (X)

Here, increase in the volume of the alkylating reagent and of the substituents in the initial oxime promotes O-alkylation (Table 1). Oxime O-ethers of such a type (IVb) and (VII) and o-alkyloximes of mesoxalamide [6], hydroxyiminocamphor [1], and epicamphor [6] and also that indicated in Scheme (2) have been described before [4]. The structure of the synthesized O-ethers was confirmed by the synthesis of 1-alkoxy-2,2-aziridinedicarboxylic esters from them [7], e.g., Scheme (11), and also by their IR (Table 1), PMR (Table 2), and mass spectra:

$$(\text{IIIb}) \xrightarrow{CH_2N_2} MeONCH_2C(CO_2Et)_2\ (\text{XVIII}) \qquad (11)$$

The structure of the nitrones was proved by cycloaddition reactions [Scheme (12)], their IR spectra (Table 1), and their PMR spectra (Table 2):

$$(\text{Ia}) \xrightarrow[3\text{ weeks}]{R_2C=CH_2} MeNOCR_2CH_2C(CO_2Me)_2 \qquad (12)$$

R = Me (XIX), CO_2Et (XX)

The presence of the MeN bond in (Ia) is confirmed by the broadening C [7] of the signal for the methyl protons on account of coupling with the ^{14}N nucleus ($C_{MeN/CO_2Me} = 1.38$) compared with MeON in (Ib) ($C_{MeON/CO_2Me} = 0.97$). The alternative oxaziridine structure is ruled by the absence of geminal nonequivalence of the CH_2N protons in (IIa).

In the mass spectra of (Ia)-(IIIa), (XIIa), and (XIIIa) there are (M — 16) (2-7%) and (M — 17) (2-18%) peaks characteristic of nitrones [8] and in the case of (IVa) (M — 18) (20%). In compounds (Ia)-(IIIa) general characteristic fragmentation practically absent in the case of the isomeric O-ethers is observed:

$$\left[\begin{array}{l} RO_2C \\ RO_2C \end{array}\!\!>C=\overset{+}{N}(O)R^1\right]^{+\cdot} \xrightarrow{-RO_2CO^{\cdot}} RO_2CC\equiv\overset{+}{N}R^1 \xrightarrow{-CO_2} RC\equiv\overset{+}{N}R^1 \qquad (13)$$

M^+

(Ia) *m/e* 175 (54%) *m/e* 100 (94%) *m/e* 56 (73%)
(IIa) *m/e* 189 (20%) *m/e* 114 (15%) *m/e* 70 (10,5%)
(IIIa) *m/e* 203 (4%) *m/e* 114 (21%) *m/e* 70 (12%)

The dissociation also differs substantially in (IVa) and (IVb):

$$m/e\ 29 \leftarrow\!\leftarrow [\text{IVa}]^{+\cdot} \xrightarrow{-H_2O} m/e\ 138 \xrightarrow[*]{-C_2H_4} m/e\ 110 \xrightarrow[*]{-CO} m/e\ 82 \xrightarrow[*]{-CH_2N\cdot} m/e\ 54 \qquad (14)$$

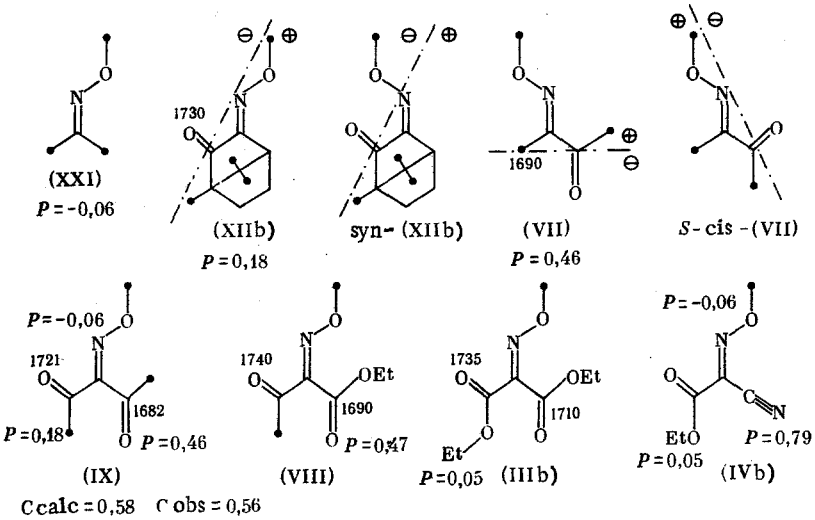
(100 %) *m/e* 156 (4 %) (20 %) (52 %) (24 %) (64 %)

$$m/e\ 28 \leftarrow\!\leftarrow [\text{IVb}]^{+\cdot} \xrightarrow{-MeO\cdot} m/e\ 125 \xrightarrow{-EtO_2C\cdot} m/e\ 52 \qquad (15)$$

(100 %) *m/e* 156 (15 %) (30%) (41 %)

According to the PMR spectra, the unsymmetrically substituted nitrones (IVa), (XIIa), and (XIIIa) and the oxime O-ethers (IVb), (VII), (VIII), (XIIb), and (XVII) are formed as one isomer, irrespective of the method of production (A, B, C, Table 1), i.e., alkylation takes place stereospecifically and, evidently, with retention of the configuration of the initial oxime.

The configuration and approximate conformation of the O-ethers were determined by means of the ASIS effect [7] of the MeON group, due to the carbonyl group [9] (Table 2). Assuming that the contributions (P, ppm) from the various functional groups to the observed ASIS effect of the MeON group are additive, we determined the true contribution of the C=NO group in the model compound (XXI) (Scheme 16). The contribution from the anti-S-cis-CO group was established on the rigid system (XIIb); the observed ASIS effect is given by $C = P_{CNO} + P_{CO}$, from which according to the data in Table 2 $P_{CO} = C - P_{CNO} = 0.12 + 0.06 = 0.18$. It can be seen that according to [9] a negative value of P_{CO} must be expected for syn-(XIIb). Similar treatment of the nonrigid system (VII) leads to the S-trans conformation. The C value of 0.58 for (IX) calculated on the basis of these values agrees well with the observed value of 0.56 (Table 2). The contributions P from the CO_2Et and CN groups were determined similarly from the C values for (VIII), (IIIb), and (Vb). The consistent changes in the values of the corresponding ν_{CO} bands are also indicated in Scheme (16):



(16)

Thus, contrary to published data, only O- and N-alkylation of the activated oximes is observed in all the investigated cases. A check on Scheme (1) showed that 2-hydroxyiminoindanedione does not react with diazomethane under the conditions in [3] and it only gives the O-ether in reaction with $MeCHN_2$ in ethanol [Scheme (7)]. We were unable to check Scheme (2) [4] on account of the nonreproducibility of the synthesis of trismethylsulfonylnitromethane [10]. It can be supposed that the product postulated in [4] as 1-hydroxyaziridine is a nitrone. In all known cases of N-alkylation under the influence of diazoalkanes the proton is localized at the nitrogen [11-14]. In our case, therefore, it can be represented through the intermediate NH-nitrone, the formation of which was supposed in [15]. The absence of N-alkylation in the oximes is then explained by the impossibility of transition from the stabilized OH form to NH.

EXPERIMENTAL

The PMR spectra were measured on Jeol JNM-C60-HL (60 MHz) and Tesla BS-487C (80 MHz) spectrometers. The IR spectra were recorded on a UR-20 spectrometer. The mass spectra were recorded on an MKh-1303 mass spectrometer at 30 eV.

The synthesis of the initial oximes and the assignment of the configuration of the unsymmetrical oximes will be published separately. Diacetyl monooxime was identified with a sample having the known E configuration by means of its melting point [16].

Alkylation of Oximes by Diazoalkanes

α,α-Dimethoxycarbonyl-N-methyl Nitrone (Ia) and Dimethyl Mesoxalate O-Methyloxime (Ib). To a solution of 37.8 g (0.24 mole) of dimethyl hydroxyiminomalonate in 100 ml of ether at 0°C we gradually added an ether solution of diazomethane until the release of gas had ceased and a stable yellow color had formed. The ether was removed, and the residue was chromatographed on a column of silica gel L100/160 μ in chloroform to remove the unreacted oxime. The liquid mixture of products was treated with ether at −5 to 0°C, and the crystals were separated by filtration and washed thoroughly with cold ether. A 28-g yield (66.6%) of compound (Ia) was obtained. From the ether solution after threefold distillation we obtained 2.8 g (6.7%) of compound (Ib) (Table 1).

Compounds (IIa) and (IIb) were obtained similarly. Compounds (IIIa) and (IIIb) and compounds (IVa) and (IVb) were separated by column chromatography with silica gel L100/160 μ in benzene with subsequent threefold vacuum distillation.

Hydroxyiminomalonodinitrile O-Methyl Ether (Vb). To a solution of 37.6 g (0.4 mole) of hydroxyiminomalonodinitrile in 200 ml of ether at 0°C we slowly added an ether solution of diazomethane until the release of gas had ceased. The mixture acquired a dark-red color. After removal of the ether the crystals were separated by filtration, washed with ether, and recrystallized three times from isopropanol. A 7.4-g yield (17.5%) of a product melting at 170-173°C (decomp.) was obtained. The PMR spectrum in deuteromethanol contained a singlet at 4.19 ppm; according to analysis, the product is evidently an oligomer of the respective nitrone. Found %: C 44.02; H 2.78; N 38.49. $C_4H_3N_3O$. Calculated %: C 44.04; H 2.77; N 38.53. From the filtrate and ether after washing by threefold distillation we obtained 7 g (17.1%) of compound (Vb).

Dimethyl Mesoxalate O-Benzhydryloxime (VI). To a solution of 8.1 g (0.05 mole) of dimethyl hydroxyiminomalonate in 50 ml of ether we added a solution of 9.7 g (0.05 mole) of diphenyldiazomethane in 200 ml of ether. The solvent was gradually distilled. The intense red-violet color of the solution became lighter and changed into pink. The obtained crystalline mass was washed with cold ether and recrystallized from a 3:1 mixture of hexane and benzene. A 9.7-g yield (33.3%) of (VI) was obtained.

Diacetyl Monooxime O-Methyl Ether (VII). To a solution of 11.1 g (0.11 mole) of diacetyl monoxime in 200 ml of ether at 0°C we added an excess of an ether solution of diazomethane. The reaction mass was kept at 20°C for 2 weeks. The solvent was removed, and the residue was distilled under vacuum. We obtained 5.0 g of the initial oxime and 3 g of (VII). The yield was 43.2% calculated on the reacted oxime.

Hydroxyiminoacetoacetic Ester O-Methyl Ether (VIII). To a solution of 15.9 g (0.1 mole) of hydroxyiminoacetoacetic ester in 100 ml of ether at 0°C we slowly added an ether solution of diazomethane until the release of gas had ceased. The ether was distilled, and the residue was distilled under vacuum. An 8.7-g yield (50%) of compound (VIII) was obtained.

Compound (IX) was obtained similarly (Table 1).

Hydroxyiminodibenzoylmethane O-Methyl Ether (X). To a suspension of 3.6 g (14 mole) of hydroxyiminodibenzoylmethane in 100 ml of ether we slowly added an ether solution of diazomethane until the release of gas had ceased. The ether was distilled, and the residue in the form of a dark-green viscous oil crystallized when rubbed in hexane. A 2.3-g yield (64.3%) of (X) was obtained (Table 1). PMR spectrum (benzene, δ, ppm): 3.37 (Me).

2-Ethoxyimino-1,3-indanedione (XI). To a solution of 0.9 g (5 mmole) of 2-hydroxyimino-1,3-indanedione in 15 ml of ethanol we slowly added an ether solution of diazoethane until the release of gas had ceased. The solvent was removed, and the residue was chromatographed on a column of silica gel L4/50 μ in chloroform. After recrystallization from a 1:1 mixture of benzene and hexane we obtained 0.5 g of yellow crystals of (XI). PMR spectrum (carbon tetrachloride, δ, ppm): 1.45 (Me, J_{HH} = 7 Hz), 4.62 (CH_2), 7.95-8.35 (C_6H_4).

By the action of diazomethane under analogous conditions we obtained a mixture of unidentified products.

anti-3-Hydroxyiminocamphor N-Methylnitrone (XIIa) and O-Methyl Ether (XIIb). A 5-g sample (0.03 mole) of anti-3-hydroxyiminocamphor was kept for a week in an excess of an ether solution of diazomethane. The ether was distilled, and the residue was chromatographed on a column of silica gel L4/50 μ in chloroform. A 0.8-g yield (13.8%) of (XIIb) (the more mobile fraction) and 2.0 g (33.3%) of (XIIa) were obtained. Compounds (XIIIa) and (XIIIb) were obtained similarly (Table 1).

Alkylation of Oximes by Alkyl Halides

Diethyl Mesoxalate O-Methyl Oxime (IIIb). An 18.9-g sample (0.1 mole) of diethyl hydroxyiminomalonate was treated with a solution of 2.3 g (0.1 mole) of sodium in ethanol, and the solvent was removed. A mixture of the obtained salt and 14.2 g (0.1 mole) of methyl iodide in 200 ml of acetone was boiled for 5 days. The solvent was removed, and the product was extracted with ether and distilled. A 6.9-g yield (33.0%) of (IIIb) was obtained.

Compounds (Ib), (IIb), and (XIV-XVII) were obtained similarly (Table 1). When acetone was replaced by acetonitrile, the yield of (IIIb) was increased to 41.3%, and when it was replaced by methanol the yield decreased to 25.9%.

Alkylation of the Oximes by Dialkyl Sulfates

α,α-Diethoxycarbonyl-N-methylnitrone (IIIa) and Diethyl Mesoxalate O-Methyloxime (IIIb). To 18.9 g (0.1 mole) of hydroxyiminomalonic ester and 5.6 g (0.1 mole) of potassium hydroxide in 100 ml of water we added 15.4 g (0.1 mole) of dimethyl sulfate. The mixture was stirred until the alkaline reaction disappeared. The product was extracted with ether (3 × 100 ml), and the solvent was removed. After threefold distillation we obtained 4.5 g (20%) of (IIIb) and 5.7 g (28%) of (IIIa).

Compounds (VII), (VIII), (X), and (XV) were obtained similarly (Table 1).

1-Methoxy-2,2-aziridinedicarboxylic Ester (XVIII). A mixture of 10.2 g (50 mmole) of (IIIb) with an excess of diazomethane in ether was kept at 20°C for one month. The solvent was removed, and the residue was distilled under vacuum. A 7.4-g yield (68%) of (XVIII) was obtained; bp 97-98°C (2 mm Hg); n_D^{20} 1.4419 (cf. [7]).

Dimethyl 2,5,5-Trimethyl-3,3-isoxazolidinedicarboxylate (XIX). A solution of 0.5 g (3 mmole) of (Ia) in 3 ml of isobutylene was kept in a sealed tube at 20°C for 3 weeks. After column chromatography on silica gel L100/160 μ in chloroform we obtained 0.52 g (77.6%) of (XIX) in the form of a colorless viscous liquid; n_D^{20} 1.4558. PMR spectrum (benzene, δ, ppm): 1.28 (MeC), 2.53 (CH_2), 2.83 (MeN), 3.3 (MeO); M^+, m/e 231. IR spectrum (ν, cm^{-1}, molecular layer): 1730 (CO). Found %: C 51.97; H 7.44 N 6.1. $C_{10}H_{17}NO_5$. Calculated %: C 51.94; H 7.41; N 6.06.

3,3-Dimethyl 5,5-Diethyl 2-Methyl-3,3,5,5-oxazolidinetetracarboxylate (XX). From 0.5 g (3 mmole) of compound (Ia) and 0.5 g (3 mmole) of methylenemalonic ester in 5 ml of absolute benzene we similarly obtained 0.92 g (92%) of compound (XX); n_D^{20} 1.4548. PMR spectrum (benzene, δ, ppm): 0.83 and 3.91 (EtO), 2.85 (MeN), 3.3 (MeO), 3.7 (CH_2); M^+, m/e 347. IR spectrum (ν, cm^{-1}, molecular layer): 1750 (CO). Found %: C 48.38; H 6.17; N 3.99. $C_{14}H_{21}NO_9$. Calculated %: C 48.42; H 6.09; N 4.03.

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CONCLUSIONS

1. Under the influence of diazoalkanes oximes activated by carbonyl and nitrile substituents form N- and O-alkylated products. Steric hindrances in the oxime and in the diazoalkane lead to a decrease in the yield of the N-alkylation products.

2. O-Alkylation of unsymmetrically substituted oximes occurs with retention of the configuration. The additivity of the contributions from the functional groups to the observed ASIS effect of the MeON group is proposed as a method for determination of the configurations and approximate conformations of O-alkyl oximes.

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