821. *The Formation of Nitrosochlorides and Nitrosates.*

By N. THORNE.

In an investigation of the effect of structure on the ease of formation of nitrosochlorides and nitrosates by olefinic compounds it has been shown that, in general, structures which increase the availability of electrons at the double bond favour these addition reactions. Terminal double-bond compounds have been investigated in some detail.

THE addition of nitrosyl chloride to compounds containing carbon-to-carbon double bonds has been studied extensively, especially in the terpene series. Many double-bond compounds other than terpenes form nitrosochlorides, but some do not. Tilden and Sudborough [1] found that while trimethylethylene and styrene with nitrosyl chloride form crystalline dimeric nitrosochlorides, ethylene forms a dichloride, and propene and but-2-ene yield mixtures of dichloride and nitrosochloride. Tilden and Forster [2] showed that hex-2-ene and octene yield nitrosochlorides which were isolated in the form of monomeric blue oils, that stilbene and oleic acid form nitrosochlorides, but that β-nitrostyrene, phenanthrene, acenaphthylene, crotonic acid, but-3-enoic acid, maleic acid, fumaric acid, cinnamic acid, and ethyl cinnamate do not. They concluded that the proximity of a nitro- or carboxyl group to the ethylene carbon atoms seems to prevent the addition of nitrosyl chloride. A review on nitrosyl chloride [3] shows that nitrosochlorides of compounds such as ethylene have recently been prepared by utilising catalysts, and in some cases by working at very low temperatures.

In the work now described, the usual conditions for the preparation of nitrosochlorides and nitrosates were adopted, namely, mixing the olefin and pentyl nitrite, in a solvent if necessary, cooling in salt–ice, and adding fuming hydrochloric acid dropwise with stirring.

---

[1] Tilden and Sudborough, *J.*, 1893, **63**, 479.

[2] Tilden and Forster, *J.*, 1894, **65**, 324.

[3] Beckham, Fessler, and Kise, *Chem. Rev.*, 1951, **48**, 369.

In the preparation of nitrosates, the cooled mixture of the olefin and pentyl nitrite was allowed to react with concentrated nitric acid.

The extent to which the carboxyl group inhibits formation of nitrosochlorides was investigated for 4-phenylbut-3-enoic and 5-phenylpent-4-enoic acid. Neither of these forms a nitrosochloride or nitrosate, despite the fact that in the pentenoic acid the double bond and the carboxyl group are separated by two methylene groups. Oleic acid forms a nitrosochloride,[2] but in this case seven methylene groups intervene. It is therefore evident that a carboxyl group has a very marked effect, and that nitrosochloride formation does not take place unless the carboxyl group is well removed from the double bond.

Among hydrocarbons the position of the double bond in the carbon chain is found to affect the reaction. Allylbenzene does not form a nitrosochloride while propenylbenzene does. Hex-1-ene, hept-1-ene, and oct-1-ene do not form adducts, but hex-2-ene, hept-2-ene, oct-2-ene, and 4-methylpent-2-ene give low yields of monomeric nitrosochlorides. Nitrosate formation follows the same pattern, except that in the case of hex-2-ene a fair yield of the dimeric nitrosate is obtained. These results show that nitrosochlorides and nitrosates are not formed when the unsaturation is in the form of the allyl group $CH_2{:}CH{\cdot}CH_2{\cdot}$, although the propenyl structure $CH_3{\cdot}CH{:}CH$ permits their formation. This is supported by the researches of Tilden and Forster,[2] who showed that eugenol and safrol (allylic unsaturation) do not form nitrosochlorides, while anethole and *iso*safrole (propenylic unsaturation) do. It is found that hydrocarbons which possess a terminal double bond without conforming to the allylic structure usually form nitrosochlorides but not nitrosates. Thus 2 : 4 : 4-trimethylpent-1-ene readily forms a nitrosochloride but not a nitrosate; styrene forms a nitrosochloride, but allylbenzene (allylic structure) does not. The double bonds in the allyl and the propenyl structure are so similar in their other reactions that this difference is surprising.

Nitro-groups inhibit formation of the nitrosochloride since none of the nitro-substituted styrenes forms adducts.

It can be seen from the Table that methyl- and methoxy-substituted olefins usually give high yields of nitrosochlorides. α-Methylstyrene gives a much higher yield than styrene, although α : 4-dimethylstyrene gives a lower yield. This may be due to the fact that α : 4-dimethylstyrene nitrosochloride is very unstable and therefore probably decomposes during its preparation. Methyl and methoxy-groups have little effect when in the *meta*-position, since 3-methylstyrene and styrene, and *m*-methoxypropenylbenzene and propenylbenzene give approximately the same yields of adducts.

Compound	Yield (%) of : nitrosochloride	Yield (%) of : nitrosate
Trimethylethylene	52	50
4-Phenylbut-3-enoic acid	—	—
5-Phenylpent-4-enoic acid	—	—
Allylbenzene	—	—
Propenylbenzene	32	—
Hex-1-ene	—	—
Hex-2-ene	4—5(monomer)	20
Hept-1-ene	—	—
Hept-2-ene	4—5(monomer)	4—5(monomer)
Oct-1-ene	—	—
Oct-2-ene	4—5(monomer)	4—5(monomer)
4-Methylpent-2-ene	4—5(monomer)	4—5(monomer)
2 : 4 : 4-Trimethylpent-1-ene	40	—
2 : 4 : 4-Trimethylpent-2-ene	68	47

Compound	Yield (%) of nitroso-chloride
Styrene	30 *
α-Methylstyrene	71
α : 4-Diethylstyrene	27
2-Methylstyrene	52
3-Methylstyrene	32
4-Methylstyrene	66
2 : 4 : 6-Trimethylstyrene	—
2-, 3-, and 4-Nitrostyrene	—
o-Methoxypropenylbenzene	60
m-Methoxypropenylbenzene	34
p-Methoxypropenylbenzene	79
1 : 1-Diphenylethylene	—
1 : 1-Di-*p*-methoxyphenylethylene	—

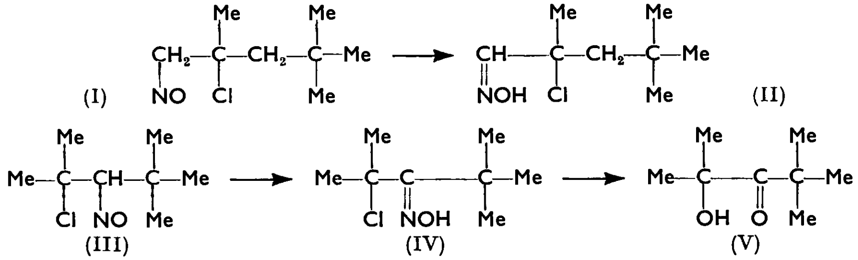
* None of the compounds in this column forms a nitrosate.

2 : 4 : 6-Trimethylstyrene does not form a nitrosochloride, probably owing to the steric effect of the two *o*-methyl groups. Similarly the steric effect of the phenyl groups in 1 : 1-diphenylethylene and 1 : 1-di-*p*-methoxyphenylethylene probably prevents these compounds from forming adducts.

In the case of the aliphatic olefins, low yields of adducts are isolated from hex-2-ene, hept-2-ene, oct-2-ene, and 4-methylpent-2-ene, but yields are better from trimethylethylene and 2 : 4 : 4-trimethylpent-1- and -2-ene. In the last compounds, the methyl groups increase the overall availability of electrons at the double bond. The same is true of the methyl and methoxy-substituted aryl olefins, especially when *ortho* or *para*. Nitro- and carboxyl groups have the reverse effect, and tend to reduce the electron-availability. It is therefore evident that nitrosochlorides are more readily formed by olefins containing groups which will reduce the reactivity of the double bond towards nucleophilic reagents, and increase it towards electrophilic reagents. It is reasonable to conclude that nitrosochlorides are formed by the combination of the electrophilic fragment NO^+, followed by the nucleophilic Cl^-.

None of the aryl olefins formed nitrosates under the conditions employed in the reaction.

Molecular-weight determinations have been carried out on all the solid nitrosochlorides and nitrosates obtained; these products are dimeric in benzene at about 5°, but in naphthalene at 80° are practically completely monomeric.



(I) $CH_2(NO)-CMe(Cl)-CH_2-CMe_3 \longrightarrow CH(=NOH)-CMe(Cl)-CH_2-CMe_3$ (II)

$Me-CMe(Cl)-CH(NO)-CMe_3 \longrightarrow Me-CMe(Cl)-C(=NOH)-CMe_3 \longrightarrow Me-CMe(OH)-C(=O)-CMe_3$

(III) (IV) (V)

Isomerisation of some of the nitrosochlorides to the corresponding chloro-oximes[4] has been carried out. 2 : 4 : 4-Trimethylpent-1-ene nitrosochloride (I) isomerised to 2-chloro-1-hydroxyimino-2 : 4 : 4-trimethylpentane (II), but 2 : 4 : 4-trimethylpent-2-ene nitrosochloride (III) gave 2-chloro-3-hydroxyimino-2 : 4 : 4-trimethylpentane (IV), which on hydrolysis with dilute acid yielded 2-hydroxy-2 : 4 : 4-trimethylpentan-3-one (V).

The structures of the nitrosochlorides (I) and (III) are based on their easy isomerisation to the respective oximes (II) and (IV). This type of reaction has been studied in the case of trimethylethylene nitrosochloride,[5] and the product identified beyond reasonable doubt. If 2 : 4 : 4-trimethylpent-1-ene nitrosochloride and 2 : 4 : 4-trimethylpent-2-ene nitrosochloride undergo this isomeric change, then the carbon atom carrying the nitroso-group must also carry a hydrogen atom. This condition is satisfied by the structures (I) and (III), but would not be fulfilled if the positions of the nitroso-group and the chlorine atom were interchanged. Confirmation is provided by the fact that the mechanism of the addition is such that the chlorine atom will become attached to the carbon atom carrying the least number of hydrogen atoms.

The piperidides from all the solid nitrosochlorides formed during this work have been prepared, and in the case of propenylbenzene nitrosochloride its reactions with other bases have also been studied.

EXPERIMENTAL

Propenylbenzene Nitrosochloride.—Fuming hydrochloric acid (40 c.c.) was added dropwise to a mixture of propenylbenzene (20 g.) and pentyl nitrite (40 c.c.) at <0°. The solution was stirred during the addition of the acid (1½ hr.). It became greenish-blue and slowly solidified. The crystals of *propenylbenzene nitrosochloride* were removed, and washed with ice-cold ethanol till white (10·5 g.), m. p. 128° [Found : C, 58·9; H, 5·5; N, 7·65; Cl, 18·9%; *M* (cryoscopic in benzene), 365; (cryoscopic in naphthalene), 207·0. $C_9H_{10}ONCl$ requires C, 58·84; H, 5·45; N, 7·6; Cl, 19·3%; *M*, 183·5]. The same conditions and quantities of reactants as in the above preparation were used in the preparation of the other nitrosochlorides.

Propenylbenzene Nitrolpiperidide.—Propenylbenzene nitrosochloride (1 g.) was heated with piperidine (1·5 g.) and alcohol (15 c.c.) for 10 min. Water was then added till the solution

---

[4] Thorne, *J.*, 1956, 2587.

[5] Schmidt, *Ber.*, 1902, **35**, 3729.

became faintly cloudy, and crystals of *propenylbenzene nitrolpiperidide* soon separated; recrystallised from alcohol it (1 g.) had m. p. 112° (Found: C, 72·7; H, 8·7; N, 12·2. $C_{14}H_{20}ON_2$ requires C, 72·4; H, 8·6; N, 12·1%). All the piperidides were prepared in this manner.

Propenylbenzene Nitrolanilide.—Prepared in the same way as the piperidide but with aniline (1 g.), this *compound* (1·2 g.) had m. p. 130° (Found: C, 75·3; H, 6·7; N, 11·8. $C_{15}H_{16}ON_2$ requires C, 75·0; H, 6·7; N, 11·7%).

Propenylbenzene Nitrolmethylanilide.—Prepared as above with methylaniline (1 g.), the *compound* (1·2 g.) had m. p. 148° (Found: C, 76·05; H, 7·1; N, 10·9. $C_{16}H_{18}ON_2$ requires C, 75·6; H, 7·1; N, 11·0%).

*Propenylbenzene Nitrol-*o*-toluidide.*—The *compound* (1 g.), obtained from *o*-toluidine (1 g.), had m. p. 124° (Found: C, 75·6; H, 7·1; N, 11·1. $C_{16}H_{18}ON_2$ requires C, 75·6; H, 7·1; N, 11·0%).

*Propenylbenzene Nitrol-*m*-toluidide.*—This *compound* (1·2 g.) had m. p. 143° (Found: C, 75·6; H, 7·7; N, 11·2%), and the *p-isomer* m. p. 142° (Found: C, 75·7; H, 7·0; N, 11·0%).

Hex-2-ene Nitrosate.—Nitric acid (35 c.c.) was added during 1½ hr. to hex-2-ene (20 g.) and pentyl nitrite (40 c.c.) at $<0°$. The liquid became blue, and slowly solidified. The crystals of *nitrosate* were removed and washed with alcohol till white (8 g.); they had m. p. 110° (decomp.) [Found: C, 41·3; H, 6·95; N, 15·9%; *M* (cryoscopic in benzene), 350·0; (cryoscopic in naphthalene), 195·4. $C_6H_{12}O_4N_2$ requires C, 40·9; H, 6·8; N, 15·9%; *M*, 176].

The other nitrosates were prepared in the above manner.

Hex-2-ene Nitrolpiperidide.—Prepared from hex-2-ene nitrosate (1 g.) and recrystallised from alcohol–water this *compound* (1·3 g.) had m. p. 94° (Found: C, 66·4; H, 11·0; N, 13·9. $C_{11}H_{22}ON_2$ requires C, 66·6; H, 11·1; N, 14·15%).

Hex-2-ene Nitrosochloride.—The nitrosochloride was obtained from the organic layer as a blue oil (2 g.), by drying ($CaCl_2$) and removal of other materials under reduced pressure. The oil decomposed on distillation, even under reduced pressure (Found: N, 8·9; Cl, 21·7. Calc. for $C_6H_{12}ONCl$: N, 9·4; Cl, 23·5%). On exposure to moist air it deposited crystals of hydroxylamine hydrochloride.

Hept-2-ene Nitrosochloride.—The nitrosochloride was obtained as an unstable blue oil (2 g.) (Found: N, 8·3; Cl, 19·85. Calc. for $C_7H_{14}ONCl$: N, 8·6; Cl, 21·7%).

Hept-2-ene Nitrosate.—The nitrosate was isolated as a blue-green oil (2 g.), which decomposed on distillation (Found: N, 13·8. Calc. for $C_7H_{14}O_4N_2$: N, 14·7%).

Oct-2-ene Nitrosochloride.—The nitrosochloride was isolated as an unstable blue oil (2 g.) (Found: N, 6·8; Cl, 18·5. Calc. for $C_8H_{16}ONCl$: N, 7·9; Cl, 20·0%).

Oct-2-ene Nitrosate.—The nitrosate was isolated as a blue-green unstable oil (2 g.) (Found: N, 12·8. Calc. for $C_8H_{16}O_4N_2$: N, 13·7%).

4-Methylpent-2-ene nitrosochloride (Found: N, 8·7; Cl, 21·7. Calc. for $C_6H_{12}ONCl$: N, 9·4; Cl, 23·5%) and nitrosate (Found: N, 14·5. Calc. for $C_6H_{12}O_4N_2$: N, 15·9%) were also unstable.

2 : 4 : 4-*Trimethylpent-*1-*ene nitrosochloride* was obtained as white crystals, m. p. 78° (from ethanol) [Found: C, 53·8; H, 8·9; N, 8·05; Cl, 20·2%; *M* (cryoscopic in benzene), 351; (cryoscopic in naphthalene), 186. $C_8H_{16}ONCl$ requires C, 54·1; H, 9·1; N, 7·9; Cl, 20·0%; *M*, 177·5].

Isomerisation of 2 : 4 : 4-*Trimethylpent-*1-*ene Nitrosochloride.*—A solution of this nitrosochloride (5 g.) in ethanol (50 c.c.) was heated carefully to the b. p. A vigorous reaction occurred, and the colour changed from blue to yellow. The alcohol was removed, and the solid was recrystallised from alcohol–water, giving colourless 2-*chloro-*2-*hydroxyimino-*2 : 4 : 4-*trimethylpentane* (4·5 g.), m. p. 134° (Found: C, 53·9; H, 9·1; N, 8·0; Cl, 19·8. $C_8H_{16}ONCl$ requires C, 54·1; H, 9·0; N, 7·9; Cl, 20·0%).

2 : 4 : 4-*Trimethylpent-*1-*ene Nitrolpiperidide.*—2 : 4 : 4-Trimethylpent-1-ene nitrosochloride (1 g.) gave this *compound* (0·8 g.), m. p. 92° (from alcohol–water) (Found: C, 69·2; H, 11·3; N, 12·2. $C_{13}H_{26}ON_2$ requires C, 69·0; H, 11·5; N, 12·4%).

2 : 4 : 4-*Trimethylpent-*2-*ene Nitrosochloride.*—The *nitrosochloride* was obtained as colourless crystals (21 g.), m. p. 113°, from ethanol [Found: C, 54·3; H, 9·1; N, 8·05; Cl, 19·8%; *M* (cryoscopic in benzene) 353·5; (cryoscopic in naphthalene), 192·3].

A solution of it (5 g.) in ethanol (50 c.c.) was heated and worked up as above, giving 2-*chloro-*3-*hydroxyimino-*2 : 4 : 4-*trimethylpentane* as an oil (4 g.), which decomposed on distillation (Found: C, 53·8; H, 9·2; N, 7·7; Cl, 19·6%).

2-*Hydroxy-*2 : 4 : 4-*trimethylpentan-*3-*one.*—2 : 4 : 4-Trimethylpent-2-ene nitrosochloride

(20 g.), hydrochloric acid (200 c.c.), water (200 c.c.), and ethanol (200 c.c.) were heated under reflux for 3 hr. Water (500 c.c.) was then added, and the whole was extracted six times with ether. The ethereal solution was dried (K_2CO_3) and distilled, giving the *ketol* (5 g.), b. p. 185—187° (Found : C, 66·0; H, 11·8. $C_8H_{16}O_2$ requires C, 66·7; H, 11·1%).

A sample with 2 : 4-dinitrophenylhydrazine in warm sulphuric acid–alcohol gave the *dinitrophenylhydrazone*, red needles (from ethanol), m. p. 230° (decomp.) (Found : C, 51·7; H, 6·2; N, 17·4. $C_{14}H_{20}O_5N_4$ requires C, 51·9; H, 6·2; N, 17·3%).

2 : 4 : 4-*Trimethylpent*-2-*ene Nitrolpiperidide*.—The nitrosochloride (1 g.) gave the *nitrolpiperidide* (1·2 g.), m. p. 112° (from alcohol–water) (Found : C, 69·1; H, 11·4; N, 11·9. $C_{13}H_{26}ON_2$ requires C, 69·0; H, 11·5; N, 12·4%).

2 : 4 : 4-*Trimethylpent*-2-*ene Nitrosate*.—The *nitrosate* was isolated as white crystals (17 g.), m. p. 124°, from ethanol [Found : C, 47·1; H, 7·8; N, 13·6%; *M* (cryoscopic in benzene), 406·5; (cryoscopic in naphthalene), 229·9. $C_8H_{16}O_4N_2$ requires C, 47·1; H, 7·8; N, 13·7%; *M*, 204].

Styrene Nitrosochloride.—This was isolated as white crystals, m. p. 103° (decomp.), from ethanol [Found : C, 56·65; H, 4·6; N, 8·15; Cl, 21·1%; *M* (cryoscopic in benzene), 343·0; (cryoscopic in naphthalene), 185·1. Calc. for C_8H_8ONCl : C, 56·6; H, 4·7; N, 8·3; Cl, 20·9%; *M*, 169·5].

Styrene nitrolpiperidide, recrystallised from alcohol–water, had m. p. 136° (Found : C, 71·6; H, 8·3; N, 13·1. $C_{13}H_{18}ON_2$ requires C, 71·55; H, 8·3; N, 12·8%).

Similarly were prepared : α-*methylstyrene nitrosochloride*, white crystals (22 g.), m. p. 90° (decomp.) (from ethanol) [Found : C, 58·4; H, 5·6; N, 7·8; Cl, 19·3%; *M* (cryoscopic in benzene), 370·5; (cryoscopic in naphthalene), 198·0. $C_9H_{10}ONCl$ requires C, 58·8; H, 5·45; N, 7·6; Cl, 19·3%; *M*, 183·5], and *nitrolpiperidide*, m. p. 123° (from ethanol) (Found : C, 72·4; H, 8·7; N, 11·9. $C_{14}H_{20}ON_2$ requires C, 72·4; H, 8·6; N, 12·1%); 2-*methylstyrene nitrosochloride*, m. p. 98° (decomp.) (from ethanol) [Found : C, 58·8; H, 5·5; N, 7·8; Cl, 19·5%; *M* (cryoscopic in benzene), 370·9; (cryoscopic in naphthalene), 207·7. $C_9H_{10}ONCl$ requires C, 58·8; H, 5·45; N, 7·6; Cl, 19·3%; *M* 183·5], and *nitrolpiperidide*, m. p. 132° (from ethanol) (Found : C, 72·6; H, 8·8; N, 12·1. $C_{14}H_{20}ON_2$ requires C, 72·4; H, 8·6; N, 12·1%); the 3-*methyl analogues*, m. p. 104° (decomp.) (from ethanol) [Found : C, 59·0; H, 5·5; N, 7·7; Cl, 19·2%; *M* (cryoscopic in benzene), 371·9; (cryoscopic in naphthalene), 215·7], and m. p. 138° (Found : C, 71 92; H, 8·69; N, 12·2%), respectively; the 4-*methyl analogues*, m. p. 102° (decomp.) [Found : C, 59·0; H, 5·6; N, 7·7; Cl, 19·35%; *M* (cryoscopic in benzene), 358·2; (cryoscopic in naphthalene), 217·0], and m. p. 162° (Found : C, 72·5; H, 8·8; N, 11·9%), respectively; α : 4-*dimethylstyrene nitrosochloride*, m. p. 97° (from ethanol) [Found : C, 60·9; H, 6·1; N, 7·2; Cl, 18·1%; *M* (cryoscopic in benzene), 401·8; (cryoscopic in naphthalene), 210·5. $C_{10}H_{12}ONCl$ requires C, 60·75; H, 6·1; N, 7·1; Cl, 18·0%; *M*, 197·5], and *nitrolpiperidide*, m. p. 107° (from aqueous ethanol) (Found : C, 73·0; H, 8·9; N, 10·7. $C_{15}H_{22}ON_2$ requires C, 73·2; H, 8·9; N, 11·4%); o-*methoxypropenylbenzene nitrosochloride*, m. p. 124° (from alcohol) [Found : C, 56·0; H, 5·7; N, 6·45; Cl, 16·6%; *M* (cryoscopic in benzene), 425·8; (cryoscopic in naphthalene), 238·8. $C_{10}H_{12}O_2NCl$ requires C, 56·2; H, 5·6; N, 6·6; Cl, 16·65%; *M*, 213·5], and m. p. 142° (Found : C, 68·6; H, 8·4; N, 10·8. $C_{15}H_{22}O_2N_2$ requires C, 68·7; H, 8·4; N, 10·7%); the m-*methoxy-analogues*, m. p. 134° (from ethanol) [Found : C, 56·4; H, 5·7; N, 6·7; Cl, 16·8%; *M* (cryoscopic in benzene), 432·7; (cryoscopic in naphthalene), 234·1], and *nitrolpiperidide*, m. p. 148° (from alcohol) (Found : C, 68·8; H, 8·5; N, 10·5%), respectively; and the p-*methoxy-analogues*, m. p. 126° (from ethanol) [Found : C, 56·1; H, 5·6; N, 6·6; Cl, 16·5%; *M* (cryoscopic in benzene), 431·7; (cryoscopic in naphthalene), 235·3], and m. p. 117° (Found : C, 68·9; H, 8·4; N, 10·4%), respectively.

The author thanks Imperial Chemical Industries Limited for gifts of pure olefins.

THE TATEM LABORATORIES, UNIVERSITY COLLEGE,
CATHAYS PARK, CARDIFF.

[*Received, June 6th*, 1956.]