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OXIDATION OF N-ALKYL-N'-TOSYLHYDRAZINES.
A NEW, CONVENIENT SYNTHESIS OF HYDROPEROXIDES.

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The N-alkyl-N'-tosylhydrazines are easily oxidized by hydrogen peroxide and sodium peroxide to give with high yields (90-95%) the corresponding hydroperoxides, in agreement with the following possible reaction schema:

$$\mathrm{R{-}NH{-}NH{-}Ts} \xrightarrow[\text{THF, r.t.}]{H_2O_2/Na_2O_2} \underset{\text{ION PAIR}}{\left[\mathrm{R{-}}\overset{+}{\mathrm{N}}{\equiv}\mathrm{N} \quad \mathrm{Ts}^-\right]} \longrightarrow \mathrm{R{-}OOH}$$

The results obtained are reported in the following table(1):

R-	R-NH-NH-Ts	m.p.	R-OOH	m.p.	Yield %
2,2-Dimethylpropyl-	(1)	82-4°	(1a), oil		87
n-Hexadecyl-	(2)(2)		(2a)(4)		95
Cyclohexyl-	(3)(3)		(3a)(5)		92
2-Methylcyclohexyl-	cis-isomer (4)	106-8°	(4a, 4b)[a], oil		90 (85)
5α-Cholestan-3β-yl-	(5)	128-35°	3α-isomer (5a)	158-60°	95 (88)
			3β-isomer (5b)	104-5°	
17β-Hydroxy-androstan-3-yl-	(6)[b]		(6a, 6b)[b]		93
17β-Acetoxy-androstan-3-yl-	(7)[b]		(7a, 7b)[b]		95

[a] The product contained about 50% trans and 50% cis isomer

[b] Mixture of the 3α and 3β isomers

The alkyl-tosylhydrazines employed are obtained in turn by reducing with B_2H_6 or with $NaBH_4$ corresponding tosylhydrazides or tosylhydrazones(2,3) and characterized on the basis of analytical and spectroscopic data. Specifically, N-(5α-cholestan-3β-yl)-N'-tosylhydrazine (5) and cis,N-(2-methylcyclohexyl)-N'-tosylhydrazine (4) were obtained as the main products by reduction of the corresponding tosylhydrazones and were purified *through the fractional crystallisation* of the reaction mixture.

The hydroperoxides were characterized by $LiAlH_4$-reduction to the corresponding alcohols and on the basis of the analytical data, of the IR data (ν_{H-O_2-} 3450, ν_{-O-O-} 830-890 cm^{-1})(6,7) and of the signals of the ^1H-NMR spectrum(8). Particularly, a mixture of the hydroperoxide isomers 3α (5a) and 3β (5b) is obtained in the oxidation of the N-(5α-cholestan-3β-yl)-N'-tosylhydrazine (5) in a ratio of approximately 1:1. This result may be interpreted as a racemization at the asymmetric center to which the tosylhydrazinic residue is bound. Furthermore a mixture of the hydroperoxide isomers cis (4a) and trans (4b) (see table) is obtained in the oxidation of the cis,N-(2-methylcyclohexyl)-N'-tosylhydrazine (4), while no significant amounts of the product of transposition: 1-methylcyclohexyl hydroperoxide is observed, which could be the result of the intermediate formation of a carbocation.

On the basis of the preliminary results and of the spectroscopic findings, it is possible to formulate the hypothesis that the reaction may proceed through the formation of the tosylazoalkane, which is present in the reaction medium in the form of an ion-pair. The same hydroperoxides may be directly obtained starting from tosylhydrazides or tosylhydrazones without isolating the intermediate N-alkyl-N'-tosylhydrazines; the yields related to the hydroperoxides obtained through this one-step procedure are reported in brackets in the table. The method above described points to a new way for synthesizing the primary and secondary hydroperoxides, starting from carbonylic compounds or carboxylic acids under mild conditions and with high yields and may offer an alternative to the methods of preparation of the hydroperoxides already described(4,5,9,10)

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1) The yields are calculated by way of HPLC (Column Hibar LiChrosorb Si60 (7μ), 25 cm; eluent: hexane-ethyl acetate 85:15 v:v; detector RI)
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8) The characteristic signal of the hydroperoxidic proton with chemical shift within fields ranging between 8 and 9 δ is always present in the latter(7). The configurational isomers are characterized, whenever necessary, on the basis of the value of the chemical shift and of the J of the proton on α-carbon with respect to the hydroperoxidic group $(-\underset{\alpha}{\overset{|}{C}}H-OOH)$
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