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The reaction between cis- and trans-decalin and EtOCON$_3$

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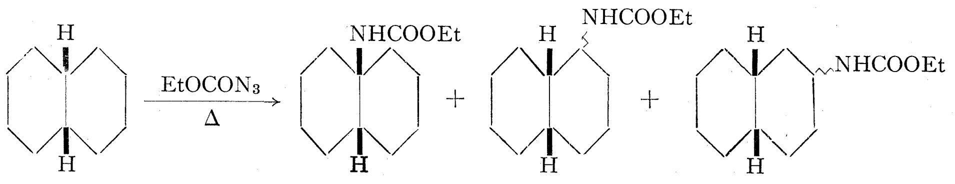
Chimica organica. — *The reaction between* cis– *and* trans–*decalin and* $\mathrm{EtOCON_3}$. Nota di PAOLO ANTONIO TARDELLA, presentata (*) dal Socio L. PANIZZI.

RIASSUNTO. — Si riportano i primi risultati relativi ad uno studio sulla reazione tra le decaline cis e trans e l'azidoformiato di etile.

La selettività d'inserzione su legami C—H secondari e terziari è diversa per i due isomeri. Il prodotto che risulta dall'inserzione sul C—H terziario ha la stessa stereochimica dell'idrocarburo posto a reagire.

The problem of insertion selectivities into C—H bonds in reactions of nitrenes with alkanes has been the object of recent interest [1].

In this paper we wish to report our results concerning the reaction between *cis* and *trans*–decalin and $\mathrm{EtOCO\dot{N}}$: generated from $\mathrm{EtOCON_3}$ [2].



I II III, IV V, VI

Reactions were carried out in a small Parr bomb (glass jacket) using a ratio 1 : 10 : 100 for $\mathrm{EtOCON_3}$: decalin: $\mathrm{CH_2Cl_2}$ (volumes; the ratio 1 : 10 = $\mathrm{EtOCON_3}$: decalin was maintained in reactions without solvent), under nitrogen, heating for 10–14 hrs at 120–125°.

Reaction mixtures, after residual solvent was removed, were diluted with equal volumes of $\mathrm{CHCl_3}$ and analyzed by VPC (glass column, 4 mm × 2 m, 20 % Carbowax on Celite $\mathrm{C_{22}}$) and components were compared (coinjection) with authentic samples prepared by standard procedures [3].

All urethanes (II, III, IV, V, VI and the corresponding *trans* compounds not reported in the above scheme) showed different retention times.

Results are collected in Table I. The product deriving from insertion into the ring junction C—H is, in both cases, only the one with the same stereochemistry as the starting hydrocarbon [4] and addition of the solvent does not change this stereospecificity [5].

(*) Nella seduta dell'11 aprile 1970.

TABLE I.

Decalin	Solvent (a)	Insertion products	
		yield (b) %	ratio 3°/2° (c)
cis	CH_2Cl_2 (d)	22	0.95
cis	CH_2Cl_2 (d)		1.6 (e)
trans	CH_2Cl_2 (d)		1.1
trans	CH_2Cl_2 (d)		1.0
cis	CH_2Cl_2 (f)		2.2
cis	CH_2Cl_2 (f)		2.5
trans	CH_2Cl_2 (f)		1.34
trans	CH_2Cl_2 (f)		1.32
cis	none		3.4
cis	none	47	3.2
trans	none		2.2
trans	none		2.2

(*a*) Pure grade ($\geq 99\%$ by VPC);

(*b*) Based on $EtOCON_3$: urethanes mixtures were separated by column chromatography and their IR and NMR spectra compared with that of authentic samples;

(*c*) Tertiary/secondary: calculated from peak areas and corrected for the number of hydrogens;

(*d*) Not degassed;

(*e*) Reactants ratio = 1 : 8 : 60 (volume);

(*f*) Degassed with N_2.

Concerning the relative reactivities of secondary and tertiary C—H bonds the noteworthy point is that for the cis isomer the usual ratio [6] tertiary/secondary was found (= 3.3) whereas the trans isomer gave a lower value (= 2.2).

Reactions in solution gave lower selectivity ratios, especially when not degassed (with N_2) solvent was used. Clearly the observed change might be due, at least in part, to oxygen dissolved in the solvent.

The influence of oxygen, known [7] to have a very high rate of reaction with alkyl radicals might support the step nature [8] of the process, not necessarily incompatible with the observed stereochemical results [9].

Experiments are in progress in order to make this point clear.

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REFERENCES.

[1] For a recent review cfr. W. LWOSKI, « Angew. Chem. Int. Ed. », *6*, 897 (1967).

[2] Decalin has been used as solvent for the study of decomposition of aryl-azides: P. A. S. SMITH *et al.*, « J. Amer. Chem. Soc. », *84*, 480 (1962); see L. KRBECHEK *et al.*, « J. Org. Chem. », *33*, 4286 (1968) too.

[3] Some urethanes are new compounds: all gave correct IR and NMR spectra and satisfactory elemental analysis: cfr. « C. A. », *31*, 4644^4 (1937).

[4] See ref. 1.

[5] Compare W. LWOSKI *et al.*, « J. Amer. Chem. Soc. », *91*, 5107 (1969).

[6] DAVID S. BRESLOW *et al.*, « J. Amer. Chem. Soc. », *90*, 7097 (1968) and ref. 1.

[7] C. WALLING, *Free radical in solution*, 418–436, J. Wiley, New York 1957.

[8] However, recent evidence, cfr. ref. 5, support the concerted nature of the process.

[9] P. D. BARTLETT *et al.*, « J. Amer. Chem. Soc. », *87*, 2590 (1965).