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EFFECT OF THE AMINE STRUCTURE ON THE COURSE OF LINEAR ANIONIC-COORDINATION DIMERIZATION OF ISOPRENE IN THE PRESENCE OF DIALKYLAMINE AND SODIUM

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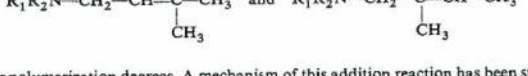
The effect was studied of the structure of the amine on the course of linear anionic-coordination dimerization of isoprene (2-methyl-1,3-butadiene) to β-myrcene (3-methylene-7-methyl-1,6-octadiene) in tetrahydrofuran solution in the presence of dialkylamine and sodium. The modified Taft–Pavelich equation was used to express this effect quantitatively. The selectivity of the reaction to β-myrcene was found to depend above all on the polar properties of the substituents R_1, R_2 of the dialkylamine use, described by the $\sum\sigma^*$ parameter, while the reaction rate of the formation of β-myrcene depended more on their steric properties, expressed by the $\sum E_s$ parameter.

In the work[1], the reaction of some dialkylamines with isoprene (*i.e.*, 2-methyl-1,3-butadiene) under the action of sodium was studied and found to lead to 1 : 1 adducts of the two reactants, of the types



$$R_1R_2N{-}CH_2{-}CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3 \quad \text{and} \quad R_1R_2N{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH_3$$

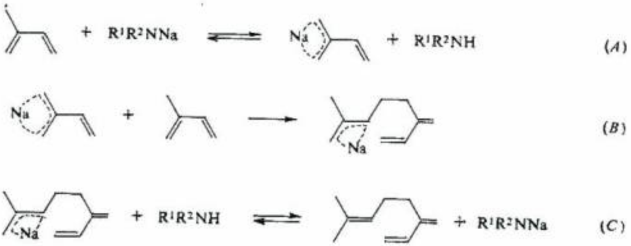
or with higher polymerization degrees. A mechanism of this addition reaction has been suggested[1]. By a side reaction, which became more involved as the isoprene-to-amine ratio was increased, isoprene dimerized to give β-myrcene (*i.e.*, 3-methylene-7-methyl-1,6-octadiene), an important intermediate product in the perfumery industry; this reaction was particularly pronounced when diisopropylamine was used as the reactant.

A synthesis of β-myrcene from isoprene under the action of sodium in the presence of a dialkylamine and tetrahydrofuran was first published by Japanese authors[2] in 1976, and shortly thereafter a preparation was described[3] using diisopropylamine, N,N,N′,N′-tetramethylethylenediamine, or triethylamine. No mention can be found in the papers[2,3] as to whether — in the conditions applied — the above adducts[1] were formed in addition too.

The synthesis of β-myrcene by dimerization of isoprene in the presence of various dialkylamines, under the action of sodium in tetrahydrofuran, was therefore studied in detail in[4]. In the experiments a homogeneous catalytic solution was used, made up of equimolar quantities of the amine, isoprene, and sodium in excess tetrahydrofuran (the alkali metal, introduced as a solid, usually passed into the solution); excess isoprene was then added to this solution to dimerize to β-myrcene.

The addition reactions affording the 1 : 1 adducts of isoprene with the amine took place with all the amines given in Table I except dicyclohexylamine. The highest reactivity in this respect was observed with N-methylisopropylamine, which reacted to give the adducts with isoprene even during the preparation of the catalytic solutions (and in this case a major part of the sodium remained in the solid state and no homogeneous catalytic solution emerged).

The dimerization of isoprene to β-myrcene can be described[5,6] by the pathway (*A*)–(*C*), in which R_1 and R_2 are alkyl or cycloalkyl groups:



In the present work the procedure for studying the reaction was modified so as to ensure consistent conditions at its beginning: the amine used as a constituent of the catalytic solution was invariably dicyclohexylamine (which reacts with isoprene only reluctantly), and the amine of interest was only added, together with isoprene, to the complete solution. The effect of dicyclohexylamine on the dimerization reactivity of isoprene in the mixture with the amine under study was disregarded.

EXPERIMENTAL

The chemicals used were purified as reported in ref.[5].

Preparation of the Catalytic Solution

Tetrahydrofuran (39 mmol), sodium (3 mmol), dicyclohexylamine (3 mmol), and isoprene (3 mmol) were delivered, against a nitrogen stream, into a 50 ml reactor prior dried and flushed with nitrogen. The mixture was stirred at 20°C for 30 min, during which period all the sodium passed into solution.

Measurement

To the catalytic solution in the reactor was added isoprene (45 mmol) together with the dialkylamine (3 mmol). The reactor was submerged in a bath at 10°C, and 0·1 ml samples for gas chromatographic analysis were drawn through a Teflon seal by means of a syringe.

Analytical Methods

The reaction system was analyzed gas chromatographically on a Chrom 4 instrument equipped with a flame ionization detector. A glass column 2·5 m long, *i.d.* 2 mm, packed with 15% Apiezon L and 3% NaOH on Chromaton N-AW-HMDS was employed. The injected volume was 3 μl. The concentrations of isoprene, β-myrcene, and the 1 : 1 adduct of isoprene with the amine were read from calibration graphs. The concentrations of isoprene oligomers and of adducts of the amine with isoprene of a higher polymerization degree were calculated as the balance between the total conversion of isoprene and the concentrations of β-myrcene and the 1 : 1 adduct, and expressed as the isoprene dimer concentration. The initial rates of loss of isoprene and formation of β-myrcene, the isoprene–amine 1 : 1 adduct, and isoprene oligomers, in the time $t = 0$ that isoprene and the dialkylamine of choice were added to the catalytic solution, were determined as the tangents to the curves in the time dependences of the corresponding concentrations.

RESULTS AND DISCUSSION

In the dimerization of isoprene under the catalytic action of sodium in the presence of a dialkylamine, the effect was examined of the amine substituents R_1, R_2 on the initial rate of loss of isoprene (I) and formation of β-myrcene (M) and the amine–isoprene 1 : 1 adducts (A). The initial reaction rates were correlated by the modified Taft–Pavelich equation[6]

$$\log (r/r_0) = \varrho^* \sum \sigma^* + \delta \sum E_s \,, \qquad (1)$$

where r is the initial reaction rate, r_0 is the corresponding value for $R_1 = R_2 = CH_3$ $\sum\sigma^* = 0, \sum E_s = 0$), $\sum\sigma^*$ is the sum of the polar effects of the substituents R_1 and R_2, $\sum E_s$ is the sum of their steric effects, and ϱ^* and δ are parameters expressing the susceptibility of the reaction to variations in the polar and steric properties respectively. The $\sum\sigma^*$ and $\sum E_s$ values, taken from ref.[8], are given in Table I.

TABLE I

Values of the $\sum\sigma^*$ and $\sum E_s$ parameters for the dialkylamines examined[8]

Amine	$\sum\sigma^*$	$\sum E_s$
N-Methylisopropylamine	−0·19	−0·47
N-Ethylisopropylamine	−0·29	−0·54
N-Propylisopropylamine	−0·305	−0·83
N-Butylisopropylamine	−0·32	−0·86
Dipropylamine	−0·23	−0·72
Diisopropylamine	−0·38	−0·94
N-Isopropylcyclohexylamine[a]	−0·45	−1·26
Dicyclohexylamine[a]	−0·52	−1·58

[a] Ref.[9].

The initial rates, for the various amines tested, are given in Table II. By double regression correlation of the logarithm of the initial rate of isoprene loss according to Eq. (*1*), the dependence

$$\log r_I = 2{\cdot}17 \sum\sigma^* + 0{\cdot}47 \sum E_s + 2{\cdot}9 \qquad (2)$$

was obtained with a correlation coefficient 0·98. It will be clear that the initial rate of isoprene loss is more susceptible to variations in the polar properties of the amine substituents than to variations in their steric properties.

Similarly, the initial rate of formation of the isoprene–amine 1 : 1 adduct correlates as

$$\log r_A = 3{\cdot}97 \sum\sigma^* + 0{\cdot}74 \sum E_s + 3{\cdot}26 \qquad (3)$$

(correlation coefficient 0·97) if dicyclohexylamine ($r \approx 0$) is omitted. The initial rate of formation of β-myrcene obeys the relation

$$\log 2r_M = 0{\cdot}16 \sum\sigma^* + 0{\cdot}49 \sum E_s + 1{\cdot}9 \qquad (4)$$

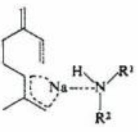
with a correlation coefficient 0·95. Hence, while the addition reaction of isoprene with dialkylamine is more susceptible to changes in the polar properties of the substituents, the dimerization reaction leading to β-myrcene is susceptible rather to changes in their steric properties.

TABLE II

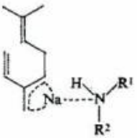
Initial rates (mmol dm^{-3} min^{-1}) of loss of isoprene (r_I) and formation of β-myrcene (r_M), the isoprene–amine 1 : 1 adducts (r_A), and isoprene oligomers (r_0), for the dialkylamines examined

Amine	r_I	r_M	r_A	r_0
N-Methylisopropylamine	222	23	125	25
N-Ethylisopropylamine	105	18	53	7
N-Propylisopropylamine	85	17	49	1
N-Butylisopropylamine	57	17	21	1
Dipropylamine	99	14	57	7
Diisopropylamine	42	13	10	3
N-Isopropylcyclohexylamine	17	7	3	0·2
Dicyclohexylamine	12	6	0	0·1

Previously we discussed[5] the mechanism of the dimerization reaction in relation with the presence of the coloured complexes



I



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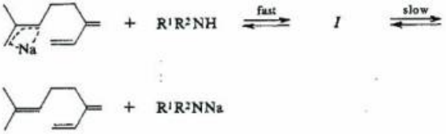
whose formation affects the selectivity of the reaction. Eq. (*4*) indicates that the mechanism of the dimerization reaction involves a step which is very sensitive to the steric properties of the substituents R_1, R_2, this step being probably the slowest reaction step:



(*D*)

The formation of complex *I* is obviously fast, because, as the data of Table II demonstrate, for dicyclohexylamine the initial rate of isoprene loss equals that of formation

TABLE III

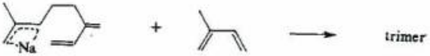
Selectivity values for the reaction of isoprene under the action of sodium in the presence of dialkylamine to β-myrcene (S_M) and to the 1 : 1 adduct with the amine (S_A)

Amine	S_M	S_A
N-Methylisopropylamine	0·21	0·56
N-Ethylisopropylamine	0·34	0·50
N-Propylisopropylamine	0·40	0·57
N-Butylisopropylamine	0·59	0·36
Dipropylamine	0·28	0·57
Diisopropylamine	0·62	0·24
N-Isopropylcyclohexylamine	0·82	0·18
Dicyclohexylamine	1	0

of β-myrcene taking into account the change in the mole number during the reaction

(E)

The formation of complex *I* is faster than the competitive reactions



(F)

The slowest reaction step seems to be the transmetallation of (3-methylene-7-methyl-1,6-octadien)ylnatrium to β-myrcene.

Table III gives the selectivities of the reaction to β-myrcene (S_M) and to the isoprene–amine 1 : 1 adduct (S_A), defined as

$$S_M = 2r_M/r_1\,; \quad S_A = r_A/r_1\,. \tag{5a,b}$$

Combining Eqs (*4*) and (*2*) or (*3*) and (*2*) we obtain

$$\log S_M = -2\cdot01 \sum\sigma^* + 0\cdot02 \sum E_s - 1 \tag{6a}$$

$$\log S_A = 1\cdot8 \sum\sigma^* + 0\cdot27 \sum E_s + 0\cdot36 \tag{6b}$$

Thus, the effect of the polarity of the substituents, expressed by the $\sum\sigma^*$ parametre, on the logarithm of selectivity of the isoprene dimerization exceeds by two orders of magnitude the effect of the steric properties, expressed by the $\sum E_s$ parameter; for dicyclohexylamine ($\sum\sigma^* = -0\cdot5$), $\log S_M = 0$. The absolute term in Eq. (*6b*), which should be less than or equal to zero because $S_A \leqq 1$, obviously involves an error of measurement. The logarithm of selectivity of the addition reaction is also affected by the substituent polarity by an order of magnitude more than by the steric properties. As the $\sum\sigma^*$ parameter decreases, the reaction becomes rather one of isoprene metallation with a consecutive addition of a next isoprene unit and transmetallation yielding β-myrcene, whereas as the $\sum\sigma^*$ and $\sum E_s$ parameters increase, the addition reaction of isoprene with the amine becomes increasingly involved.

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