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THE ALKYL STRUCTURE-REACTIVITY RELATIONSHIP
IN COPE ELIMINATION OF ALKYLDIMETHYLAMINE OXIDES**

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The rate of Cope elimination was investigated in two homologous series of positionally isomeric open-chain amine oxides, $R.CHX.CH_2.C_5H_{11}$ and $R.CH_2.CHX.C_5H_{11}$ ($X = N(CH_3)_2 \rightarrow O$; $R = H$, CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, t-C_4H_9), and in a complementary series of α, β- and γ-methyl substituted 1-heptyldimethylamine oxides. The rates were found to increase with increasing alkyl substitution and extend over a range greater than six powers of ten. The principal factor affecting the rates appears to be related to the energy required for the C_α—N bond breaking in transition state. Although a satisfactory linear plot of logarithms of the rates vs Taft polar substituent constants, σ*, was obtained for the *trans*-alkene formation, further evidence from the subsidiary (Hammett) series of 1-arylbutylmethylamine oxides reveals that the alkyl substituent effect is not of the polar origin: relief of the ground-state strain is proposed to be the driving force in the reaction.

Recently, we examined kinetically the structure-reactivity relationship governing the *syn*-elimination processes in cycloalkyl series[3-7]. Novelty of results obtained from these studies prompted us now to examine analogously the course of corresponding processes in open-chain systems. As the first, we selected the Cope elimination[8-10] of alkyldimethylamines for such a scrutiny. The amine oxide elimination is known to proceed homogeneously in an intramolecular *syn*-fashion[11-15]; accordingly, interpretation of the rate data was expected to be a relatively simple matter which, in view of scarcity of relevant evidence available[15], should be of a considerable interest on its own right. Further, it was expected, from experience obtained in the cycloalkyl series, that the rate data would be useful, as reference values, for clarification of the mechanistically more involved *syn*-E2-processes[16-18] and a kinetic study of this reaction was therefore initiated.
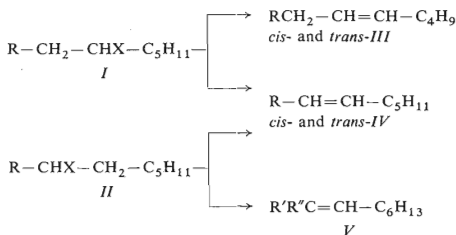
The Cope elimination is generally performed either by pyrolysis[10,15], or, at milder conditions, in a number of aprotic or weakly protic solvents[7,13]. Although the reaction affords usually the

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expected olefins in very high yields, appreciable amounts of basic by-products including the starting tertiary amines were noted at several occasions[19-21]. Similarly, we observed, in preliminary experiments performed in the solvent tert-butanol a sizeable de-oxidation of the amine oxides examined competing in a rather irreproducible manner with the olefin-forming reaction. Mechanism of the de-oxidation remains to be solved; however, we have found that it could be suppressed completely by addition of potassium tert-butoxide to the solvent, without affecting in any way the course of the elimination reaction.

In this paper we report the rates of formation of the *cis*- and *trans*-alkenes *III* and *IV*, and *IV* and *V*, arising respectively from the positionally isomeric amine oxides *I* and *II* (Scheme 1) in 0·1M solution of potassium tert-butoxide in tert-butanol and a less comp'ete set of corresponding rate data on the reaction performed in the solvent

$$R-CH_2-CHX-C_5H_{11} \xrightarrow{\hspace{1cm}} \begin{array}{l} RCH_2-CH=CH-C_4H_9 \\ \textit{cis- and trans-III} \\[1em] R-CH=CH-C_5H_{11} \\ \textit{cis- and trans-IV} \end{array}$$

$$I$$

$$R-CHX-CH_2-C_5H_{11} \xrightarrow{\hspace{1cm}} \begin{array}{l} R-CH=CH-C_5H_{11} \\ \textit{cis- and trans-IV} \\[1em] R'R''C=CH-C_6H_{13} \\ V \end{array}$$

$$II$$

X = N(CH_3)_2O

R = H, CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, t-C_4H_9

Scheme 1

dimethylformamide. We also report the rates of the olefin-forming reaction in a complementary series of α-, β- and γ-methyl substituted 1-heptyldimethylamine oxides, and in a Hammett series of 1-arylbutyldimethylamine oxides, measured under comparable conditions.

EXPERIMENTAL AND RESULTS

Alkylamines

The amines *I* and *II* (X = NH_2) were prepared from the *p*-toluenesulphonyl esters of the corresponding alcohols[22] by treatment with sodium azide in dimethyl sulphoxide and subsequent reduction of the resulting crude alkyl azides with lithium aluminium hydride in ether under standard conditions[17]. 2-Methyl-1-aminoheptane, 3-methyl-1-aminoheptane and 3,3-dimethyl-1-aminoheptane were prepared from the corresponding nitriles[23,24] by reduction with lithium alu-

minium hydride in ether. 2-Methyl-2-aminooctane was prepared by the Ritter reaction[25] from the corresponding alcohol[26] by treatment with sodium cyanide in a mixture of acetic-sulphuric acid. The crude amines were converted directly[27] into the corresponding dimethylamines.

Alkyldimethylamines

5-Decyl, 2,2-dimethyl-3-nonyl and 2,2-dimethyl-4-nonyl derivatives were reported by us previously[17,27]. The other dimethylamines were prepared from the above alkylamines by the Clarke-Eschweiler methylation in a usual manner[27]. The products were uniform according to vapour phase chromatography and afforded invariantly satisfactory elemental analyses (Table I).

TABLE I

Alkyldimethylamines, $RN(CH_3)_2$: Boiling Points and Elemental Analyses

Alkyl (R)	B.p., °C/Torr	Formula m.w.	Calculated/Found	
			% C	% H
1-Heptyl	66/20	$C_9H_{21}N$ (143·3)	75·45 75·13	14·77 14·51
2-Heptyl	75/35	$C_9H_{21}N$ (143·3)	75·45 75·63	14·77 14·72
2-Methyl-1-heptyl	68/20	$C_{10}H_{23}N$ (157·3)	76·36 76·75	14·74 14·90
3-Methyl-1-heptyl	70/20	$C_{10}H_{23}N$ (157·3)	76·36 76·77	14·74 14·81
2-Octyl	72/15	$C_{10}H_{23}N$ (157·3)	76·36 76·23	14·74 14·94
3-Octyl	71/15	$C_{10}H_{23}N$ (157·3)	76·36 76·52	14·74 14·69
3,3-Dimethyl-1-heptyl	80/20	$C_{11}H_{25}N$ (171·3)	77·12 76·99	14·71 14·85
2-Methyl-2-octyl	91/20	$C_{11}H_{25}N$ (171·3)	77·12 77·42	14·71 14·79
3-Nonyl	80/15	$C_{11}H_{25}N$ (171·3)	77·12 77·32	14·71 14·57
4-Nonyl	70/12	$C_{11}H_{25}N$ (171·3)	77·12 77·21	14·71 14·77
4-Decyl	98/15	$C_{12}H_{27}N$ (185·3)	77·75 77·84	14·68 14·63
2-Methyl-3-nonyl	96/15	$C_{12}H_{27}N$ (185·3)	77·75 77·74	14·68 14·47
2-Methyl-4-nonyl	95/15	$C_{12}H_{27}N$ (185·3)	77·75 78·03	14·68 14·77

1-Aryl-1-aminobutanes

1-(p-Chlorophenyl)- and 1-(m-chlorophenyl)butylamine were prepared from p-toluenesulphonyl esters of the corresponding alcohols[28] by the azide synthesis[17] in a usual manner in 60—70% yield. The other 1-arylbutylamines were prepared by reduction of the oximes[28,29] with sodium in boiling ethanol in nearly quantitative yields. Boiling points and elemental analyses are summarised in Table II.

TABLE II

1-Aryl-1-aminobutanes: Boiling Points and Elemental Analyses

Aryl	B.p., °C/Torr	Formula (m.w.)	Calculated/Found		
			% C	% H	% N
C_6H_5	100—102/12	$C_{10}H_{15}N$ (149·2)	80·48 80·35	10·49 10·43	9·39 9·49
p-CH_3—C_6H_4	116—118/14	$C_{11}H_{17}N$ (163·2)	80·93 80·70	10·50 10·80	8·58 8·37
p-CH_3O—C_6H_4	140—142/12	$C_{11}H_{17}NO$ (179·2)	73·70 73·50	9·56 9·72	7·81 7·78
p-Cl-C_6H_4	125—127/12	$C_{10}H_{14}ClN$ (183·7)	65·39 65·47	7·68 7·76	7·63 7·34
m-Cl—C_6H_4	125—127/12	$C_{10}H_{14}ClN$ (183·7)	65·39 65·59	7·68 7·65	7·63 7·49

TABLE III

1-Aryl-1-dimethylaminobutanes: Boiling Points and Elemental Analyses

Aryl	B.p., °C/Torr	Formula (m.w.)	Calculated/Found		
			% C	% H	% N
C_6H_5	104—106/12	$C_{12}H_{19}N$ (117·3)	81·30 81·39	10·80 10·66	7·90 8·05
p-CH_3—C_6H_4	120—122/12	$C_{13}H_{21}N$ (191·3)	81·61 81·66	11·06 11·20	7·32 7·27
p-CH_3O—C_6H_4	134—135/14	$C_{13}H_{21}NO$ (207·3)	75·32 75·47	10·21 10·07	6·76 6·45
p-Cl-C_6H_4	128—130/12	$C_{12}H_{18}ClN$ (211·7)	68·07 67·96	8·57 8·29	6·61 6·74
m-Cl—C_6H_4	126/14	$C_{12}H_{18}ClN$ (211·7)	68·07 68·41	8·57 8·70	6·61 6·76

1-Aryl-1-dimethylaminobutanes

A) Clarke-Eschweiler methylation afforded the title amines in 60—70% yields, except for the *p*-methoxy derivative (0%). *B*) Modification of the procedure proposed by Vetter, Vetter and Biemann[30] afforded the title amines in practically quantitative yields: 1-Aryl-1-aminobutane (10 mmol) in methanol (10 ml) was treated with acetic acid (10 ml) and 30% aqueous formaldehyde (10 ml). Excess of sodium borohydride (5 g, 120 mmol) was added slowly under stirring to the reaction mixture, followed by 2·5M sodium hydroxide (50 ml). The product was taken in ether (4 × 50 ml), the extracts dried over solid potassium hydroxide, the solvent driven off and the residue distilled. Boiling points and elemental analyses are summarised in Table III.

Amine Oxides

A solution of the appropriate amine (500—1000 mg) in methanol (20 ml) was treated with 30% aqueous hydrogen peroxide (10 ml) at room temperature and allowed to stand for a week. The excess of hydrogen peroxide was decomposed under nitrogen by a careful addition of traces of platinum. After 72 h standing the solution was filtered, taken to dryness on a rotatory evaporator and the syrupous residue further dried on an oil pump (0·5 Torr) for 6 h at room temperature. According to vapour phase chromatography, the starting amines were completely absent in the products.

For the kinetic study, it was convenient to have known mixtures of several amine oxides (3—5) for simultaneous determination of the individual rate constants. These were prepared from the accurately weighted mixtures of the appropriate dimethylamines (about 100 mg of each) by the same procedure as described above for the individual compounds.

Reference Alkenes

General syntheses: The individual *cis*- and *trans*-alkenes *III* and *IV* (R = CH$_3$, C$_2$H$_5$, n-C$_3$H$_7$, t-C$_4$H$_9$) were prepared from the corresponding acetylenes[17,27,31] by the following procedures: *A*) Treatment of the acetylene with diborane prepared *in situ* from lithium aluminium hydride and boron trifluoride etherate in ether, followed by acetic acid, afforded the required *cis*-olefin[32]. According to vapour phase chromatography, the product was invariantly contamined by a small amount of the *trans*-isomer. *B*) Reduction of the acetylene with sodium in liquid ammonia[17,27,33] under standard conditions afforded the *trans*-olefin which according to vapour phase chromatography was completely pure. Terminal olefins (1-heptene and 1-octene) were synthetised from the corresponding acetylenes by the procedure *B*.

cis- *and* trans-2-*Methyl-4-nonene*: The following modifications of the Wittig-Schlosser olefin synthesis[34] were used for the preparation: *A*) Sodium hydride (1·2 g; 0·05 mol) was dissolved in dimethyl sulphoxide (50 ml) by stirring under nitrogen at 75°C for 45 min, the homogeneous solution cooled down in an ice-bath and treated with a solution of n-pentyltriphenylphosphonium bromide (20·7 g; 0·05 mol) in dimethyl sulphoxide (50 ml), followed after 10 min standing at room temperature by 3-methylbutanal (4,3 g, 0,05 mol). The reaction mixture was heated for 4 h at 40°C, diluted with a tenfold amount of water and the product taken up in pentane (2 × 50 ml). The pentane extracts were washed successively with 1M-HCl, 1M-NaOH and water, dried over magnesium sulphate and filtered through a column of alumina (II—III; 100 g). The column was eluted by additional pentane (200 ml) and the combined filtrates taken down. The residue was distilled at 70°C/15 Torr, yielding 3 g (43%) of the product, which according to vapour phase chromatography consisted of two isomers A and B in ratio 13 : 87.

B) An ethereal solution of butyllithium (1M; 20 ml) was added dropwise under nitrogen to the stirred suspension of n-pentyltriphenylphosphonium bromide (8·26 g; 0·02 mol) in ether (50 ml). After 1 h stirring at room temperature, the homogenous solution was cooled down and treated with 3-methylbutanal (1·72 g; 0·02 mol) in ether (20 ml) at −60°C. The resulting betaine was kept 1 h at −30°C under continuous stirring and then converted into the betaine-ylide by dropwise addition of another portion of ethereal butyllithium (1M; 20 ml). The solution was stirred for 1 h at this temperature and decomposed by successive addition of tert-butanol (3 ml) in ether (30 ml) and solid potassium tert-butoxide (5·5 g; 0·05 mol). After 72 h standing at room temperature the reaction mixture was diluted with a tenfold amount of water, ethereal layer separated, washed with 1M-HCl, 1M-NaOH and water, dried and the solvent taken down. The residue was taken up in pentane (100 ml), placed into a column of alumina (II—III; 100 g) and the product eluted by pentane (400 ml). After a usual work-up it was obtained 1·4 g (35%) of the product containing the above isomers A and B in ratio 7 : 3. The isomers A and B were assigned *trans*- and *cis*-configuration, respectively, by analogy with the outcome reported by Schlosser and Christmann[34] for the closely related reactions.

cis- *and* trans-2-*Methyl*-3-*nonene*: Starting from n-hexyltriphenylphosphonium bromide and isobutyraldehyde the above procedure *A* and *B* afforded respectively a mixture of the title isomers C and D in ratio 9 : 91 and 51 : 49, b.p. 70°C/15 Torr. The isomers were assigned *trans*- (C) and *cis*- (D) configuration analogously as described above for the position isomers.

2-*Methyl*-2-*nonene*: Prepared from n-heptyltriphenylphosphonium bromide and acetone by the procedure *A* in 40% yield, b.p. 70°C/15 Torr. For $C_{10}H_{20}$ (140·3) calculated: 85·63% C, 14·37% H found: 85·57% C, 14·45% H.

2-*Methyl*-2-*octene*: Prepared analogously from n-hexyltriphenylphosphonium bromide and acetone in 45% yield, b.p. 80°C/65 Torr. For C_9H_{18} (126·2) calculated: 85·63% C, 14·37% H; found: 85·66% C, 14·29% H.

The Effect of Impurities on the Course of the Amine Oxides Decomposition

Decomposition of the alkyldimethylamine oxides in tert-butanol and also in dimethylformamide was found to proceed in a more complicated manner than anticipated. Aside from the expected alkenes, considerable amounts of the starting dimethylamines (in tert-butanol) and/or other unidentified basic products (in dimethylformamide) were formed in the course of the decomposition (Table IV), in proportions varying greatly in the individual runs.* Moreover, ratios of the alkene isomers varied in few cases with time (1-heptene *vs* cis- and trans-2-heptene; 1-octene *vs* cis- and trans-2-octene), and/or, on prolonged heating, their proportions decreased substantially. Unidentified impurities present in the starting mixtures of the amine oxides were found to cause the side reactions: passing the aqueous solution of the reactants through a column of Zerolith prior the reaction led to a very substantial decrease of the side products formation. The addition of a base to the solution of the amine oxides suppressed completely the side

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*   In each run, a mixture of several amine oxides was investigated simultaneously. Significantly, the proportions of the recovered starting amines were invariantly much higher, if the most reactive amine oxides *I* and *II* (R = t-C_4H_9) were present in the run. Although this observation has some analogy with the results reported by Cope and coworkers[19,20], the explanation of the American authors appears, at least in the present case untenable, on basis of the vpc evidence indicating that the amines were completely absent in the original amine oxides mixtures and were formed gradually in the course of the kinetic run.

reaction including the olefin isomerisation: in solution of tert-C_4H_9OK in tert-butanol, the decomposition of the amine oxides afforded the expected olefins as the sole products. Importantly, the course of the olefin forming reaction remained completely unaffected by the base: the ratios of the olefin isomers as well as the rate constants for the individual olefin formation were practically* the same in runs performed with or without the base. Accordingly, to minimize the experimental errors, we have used 0·1M solution of potassium tert-butoxide in tert-butanol as the solvent for the kinetic study.

TABLE IV

Decomposition of Alkyldimethylamine Oxides II, R.CH(N(CH$_3$)$_2$).C$_6$H$_{13}$, in tert-Butanol: Effect of Potassium tert-Butoxide on the Product Composition $\downarrow$ O

R	t-$C_4H_9OH^a$		0·1M t-C_4H_9OK in t-$C_4H_9OH^b$	
	% alkenes	% amine	% alkenes	% amine
H	2	>50^c	92	0
CH$_3$	24	50	93	0
C$_2$H$_5$	48	33	91	0
n-C$_3$H$_7$	54	26	92	0
i-C$_3$H$_7$	50	9	89	0
t-C$_4$H$_9$	25^d	12	50^d	0

^{a} The mixture of the amine oxides listed (about 0·03 mmol of each) was dissolved in 10 ml of tert-butanol and heated in sealed tube at 125°C/4 h; ^{b} performed analogously in presence of the base; ^{c} not determined quantitatively; ^{d} the low yield results presumably from partial decomposition of the very unstable amine oxide prior the experiment.

Rate Measurements

The tert-butanol used for the kinetic study was dried by repeated distillation with potassium; the solvent contained less than 0·01% of water. 0·1M Solution of potassium tert-butoxide in tert-butanol was prepared by dissolving the clean potassium metal in tert-butanol under nitrogen and the concentration determined titrimetrically. The dimethylformamide was dried over molecular sieves (3 Å) and distilled under reduced pressure.

Kinetic procedure: The overall rate constants were measured gas-chromatographically by determining the change in concentration of the reaction products with time using the method of internal standard. The rates of the partial processes (individual olefin isomer formation) were calculated from the overall rate constants and the proportions of the particular products in the reaction mixtures, as determined by gas chromatography.

* Formation of alkyldimethylamines in course of the amine oxides decomposition in tert-butanol did not follow the first-order kinetics and precluded therefore an accurate evaluation of the rate data of the olefin-forming processes.

Determination of overall rate constants of decomposition, k_1 decomp.: A mixture of appropriate amine oxides (about 100 mg of each; *cf.* the above synthesis) was dissolved in 0·1M tert-C_4H_9OK in tert-butanol (75 ml) containing a known amount of the internal standard (n-propylcyclopentane). The solution was distributed into carefully dried ampoules (4 ml lots), the ampoules were flushed with nitrogen, sealed and placed into a thermostated bath. In appropriate time intervals the ampoules were withdrawn and the reaction quenched by an immediate pouring the contents into 50 ml volumetric flasks containing 1M-KOH in saturated aqueous sodium chloride solution (20 ml) and pentane (1 ml). The volume was made up to mark with water, the contents were thoroughly shaken and a sample of the pentane layer injected directly into the gas chromatograph.

Vapour phase chromatography: The measurements were performed on a Carlo Erba Fractovap GT chromatograph with a digital integrator. With few exceptions given below, the isomeric alkenes were cleanly separated on a capillary (50 m) coated with di-n-butyl tetrachlorophthalate under the described conditions[34,35]. Only incomplete separation of the isomeric 3-, 4- and 5-decenes was reached on this as well as other capillaries, in agreement with the results reported by Ryba[35]. The isomeric *cis*- and *trans*-2-methylnon-4-enes were separated on a capillary (50 m) coated with Apiezone at 65°C. The isomer olefin composition data obtained from decomposition of the amine oxides *I* and *II* are summarised in the Tables V and VI, respectively.

Evaluation of the rate data: The first-order rate constants of the amine oxide decomposition, $k_1^{decomp.}$, were calculated from the values of R_t and R_∞, expressing the ratio of the integrated areas corresponding to the sum of olefins formed from a particular reactant, and to the internal standard, respectively, at time $t(R_t)$ or at the end of the reaction (R_∞), as determined by vapour phase chromatography. The rate constants were evaluated numerically from the equation (*1*):

$$k_1^{decomp.} = 2\cdot303/t \cdot \log R_\infty/(R_\infty - R_t) \,. \tag{1}$$

The decomposition was measured on average up to 80% completion and the corresponding rate values were found to be constant within the error of measurement (usually less than 5%). The data are summarised in the Tables VII—X.

For evaluation of the partial rate constants of formation of the individual olefin isomers, it was necessary to determine the amounts of the particular products resulting from the decomposition of the amine oxide mixtures. This was accomplished also by gas chromatography using the equation (*2*):

$$[P^i] = f \cdot R_\infty^i \cdot [IS] \,, \tag{2}$$

where $[P^i]$ is a concentration of the individual product at the end of the reaction, f is experimentally determined correction factor for the chromatographical values of R_∞^i corresponding to the ratio of areas due to the given product and the internal standard, respectively, and [IS] the concentration of the internal standard. From the determined amounts of the products, the contributions (% P^i) of the corresponding partial processes were calculated; accordingly, the overall rate constants, $k_1^{decomp.}$ were separated into the partial constants for the individual product formation, k_1^i, using the equation (*3*):

$$k_1^i = k_1^{decomp.} \cdot \% P^i/100 \tag{3}$$

The partial rate constants, k_1^i, expressed in s^{-1}, are summarised in Tables VII—X.

TABLE V

Olefin Isomer Composition from the Elimination Reaction of the Alkyldimethylamine Oxides I, R.CH$_2$CH(N(CH$_3$)$_2$).C$_5$H$_{11}$, in 0·1M Potassium tert-Butoxide–tert-Butanol Solution at 70°C
$\downarrow$
O

R	% $E_i^{tot\ a}$	RCH$_2$CH=CHC$_4$H$_9$		RCH=CHC$_5$H$_{11}$	
		% trans	% cis	% trans	% cis
t-C$_4$H$_9$	95	35·7	3·4	60·7	0·16
i-C$_3$H$_7$	93	39·5	5·2	52·8	2·4
n-C$_3$H$_7$	92	42·3^b	8·3^b	41·7^b	7·7^b
C$_2$H$_5$	93	44·2	8·9	39·2	7·7
CH$_3$	89	49·4	9·2	30·0	11·4
H	91	30·0	11·8	58·2	

^{a} Determined at 125°C; ^{b} the values are less accurate in view of the incomplete separation of the isomeric 4- and 5-decenes.

TABLE VI

Olefin Isomer Composition from the Elimination Reaction of the Alkyldimethylamine Oxides II, RCH(N(CH$_3$)$_2$).C$_6$H$_{13}$, in 0·1M Potassium tert-Butoxide–tert-Butanol Solution at 70°C
$\downarrow$
O

R	% $E_i^{tot\ a}$	RCH=CHC$_5$H$_{11}$		R^{1}R^{2}C=CHC$_6$H$_{13}$	
		% trans	% cis	% trans	% cis
t-C$_4$H$_9$	∼ 50	99·8	0·2	—	—
i-C$_3$H$_7$	89	62·5	2·5	35·0^b	
n-C$_3$H$_7$	92	44·0^c	6·0^c	44·0^{c,d}	6·0^{c,d}
C$_2$H$_5$	91	49·8	9·2	30·0^e	11·0^e
CH$_3$	93	30·1	10·7	59·2^f	
H	92	100		—	—

^{a} Determined at 125°C; ^{b} R^1 = R^2 = CH$_3$; ^{c} the values are less accurate in view of the incomplete separation of cis-4- and trans-3-isomer; ^{d} R^1 = C$_2$H$_5$, R^2 = H; ^{e} R^1 = CH$_3$, R^2 = H; ^{f} R^1 = R^2 = H.

TABLE VII
Partial Rate Constants of the Elimination of the Alkyldimethylamine Oxides *I*, RCH₂CH.
.(N(CH₃)₂).C₅H₁₁, in 0·1M Potassium tert-Butoxide–tert-Butanol Solution at 70°C
↓
O

R	$k_{E_1}^{tot\ a} \cdot 10^7$	RCH₂CH=CHC₄H₉		RCH=CHC₅H₁₁	
		$k_{E_1}^{trans} \cdot 10^7$	$k_{E_1}^{cis} \cdot 10^7$	$k_{E_1}^{trans} \cdot 10^7$	$k_{E_1}^{cis} \cdot 10^7$
t-C₄H₉	6 280	2 240	214·0	3 816	10·0
i-C₃H₇	626	247·0	34·0	330·0	15·0
n-C₃H₇	260	~110·0[b]	~21·5[b]	~108·5[b]	~20·0[b]
C₂H₅	255	113·0	23·0	100·0	19·0
CH₃	166	82·0	15·3	49·8	18·9
H	17·3	5·2	2·0	10·1	

[a] Calculated from the experimentally determined rate constants of decomposition, $k_1^{decomp.}$, using the data of Table V; [b] less accurate data (*cf.* footnote b in Table V).

TABLE VIII
Partial Rate Constants of the Elimination of the Alkyldimethylamine Oxides *II*, RCH(N(CH₃)₂).
.C₆H₁₃, in 0·1M Potassium tert-Butoxide–tert-Butanol Solution at 70°C
↓
O

R	$k_{E_1}^{tot\ a} \cdot 10^7$	RCH=CHC₅H₁₁		R¹R²C=CC₆H₁₃	
		$k_{E_1}^{trans} \cdot 10^7$	$k_{E_1}^{cis} \cdot 10^7$	$k_{E_1}^{trans} \cdot 10^7$	$k_{E_1}^{cis} \cdot 10^7$
t-C₄H₉	~500·000	~500·000	~1·000	—	—
i-C₃H₇	2·450	1·530	62	858[b]	
n-C₃H₇	257	113[c]	15·5[c]	113[c,d]	15·5[c,d]
C₂H₅	167	83·2	15·3	50·1[e]	18·4[e]
CH₃	18·0	5·4	1·9	10·7[f]	
H	~0·5	0·5		—	—

[a] Calculated from the overall rate constants of decomposition, $k_1^{decomp.}$, using the data of Table VI; [b] R¹ = R² = CH₃; [c] less accurate data (*cf.* footnote b in Table VI); [d] R¹ = C₂H₅, R² = H; [e] R¹ = CH₃, R² = H; [f] R¹ = R² = H.

TABLE IX

Decomposition of 1-Heptyldimethylamine Oxide (*VI*) and the α-, β- and γ-Methyl substituted Homologues in 0·1M Potassium tert-Butoxide–tert-Butanol Solution at 110°C

Reactant	% E_i	$k_1^{decomp.} . 10^6$	$k_{E_i}^{tot} . 10^6$	$(k_{E_i}^{term.} . 10^6)^a$
VI	86·6	9·2	8·0	4·0
γ-CH$_3$-*VI*	90·2	17·4	15·7	7·8
γ,γ-(CH$_3$)$_2$-*VI*	90·0	24·7	22·3	11·1
β-CH$_3$-*VI*	70·4	50·0	35·3	35·3
α-CH$_3$-*VI*	90·0^b	~333^d	~300	59·2
α,α-(CH$_3$)$_2$-*VI*	55·4^c	~70 000^d	~39 000	4 840

^{a} Rate constants for the terminal isomer formation divided by number of available hydrogens; ^{b} olefin mixture consisting of 59·2% 1-octene, 30·1% *trans*-2-octene and 10·7% *cis*-2-octene; ^{c} olefin mixture consisting of 74·4% 2-methyloct-1-ene and 25·6% 2-methyloct-2-ene; ^{d} calculated from the measurements at lower temperature (70°C).

TABLE X

Rate Constants of Elimination of the 1-Arylbutyldimethylamine Oxides, X-C$_6$H$_4$.CH(NMe$_2$O). .C$_3$H$_7$ in tert-Butanol at 60°C

X^a	*m*-Cl	*p*-Cl	H	*p*-CH$_3$	*p*-OCH$_3$
$k_{E_i} . 10^4$	3·70	2·94	2·27	1·39	1·21

^{a} The runs were performed in absence of tert-C$_4$H$_9$OK in order to avoid base-catalysed isomerisation of the products. The decomposition afforded practically pure *trans*-olefins (less than 1% of the *cis*-isomers) in almost quantitative yields.

Elimination in Dimethylformamide

In addition to the complete study performed in 0·1M solution of potassium tert-butoxide in tert-butanol, we also examined the course of the amine oxide decomposition in the solvent dimethyl-formamide. In both the solvents compared, the olefin isomer composition was found to be almost identical. The yields of the alkenes in dimethylformamide were in some cases also rather low (Table XI), similarly as noted above for the reaction performed in tert-butanol without the base (Table IV). However, the alkyldimethylamine formation represented only a minor, if any, part of the side reactions which led mainly to formation of unidentified higher boiling products. Also, we have measured the rates of elimination of two selected series of amine oxides in dimethyl-formamide by the above procedure and found a very similar spread of rate values (Table XI) as obtained for the reaction in the solvent tert-butanol.

Decomposition of Alkyldimethylamine Oxides *I* and *II* in Dimethylformamide at 50°C: Yields of Alkenes and Overall Rate Constants of Elimination

R	$RCH_2CH[N(CH_3)_2O].C_5H_{11}$		$RCH[N(CH_3)_2O].CH_2C_5H_{11}$	
	% E_i	$k_{E_i}^{tot} . 10^7$	% E_i	$k_{E_i}^{tot} . 10^7$
i-C_3H_7	70	371	44·5	4 230
n-C_3H_7	66	273	39·7	500
C_2H_5	69	314	38·7	374
CH_3	63	237	32·7	52·2
H	28·5	38·7	5·5	1·6

DISCUSSION

Rate constants of formation of the alkenes *trans-* and *cis-III*, and *trans-* and *cis-IV* arising respectively from reaction of the amine oxides *I* and *II* in tert-butanol are plotted as a function of the substituent R on Fig. 1. It is immediately apparent from
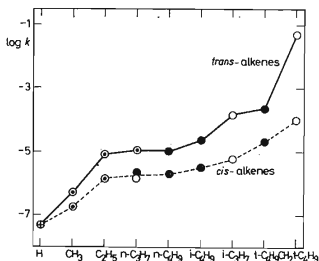

Fig. 1

Effect of Alkyl Substituent, R^α, on Rates of Olefin Formation from Amine Oxides *I* and *II*

● *trans*-Alkene *III* from Amine Oxide *I* ($R^\alpha = R.CH_2$); ○ *trans*-Alkene *IV* from Amine Oxide *II* ($R^\alpha = R$); ⊕ 1-Heptene from *II*, $R^\alpha = H$.

the Figure that the curves representing the dependence of rate on alkyl structure for the *trans-* and *cis*-alkene formation in direction "away" from the substituent R are of the same general type. The rates of the *trans-* as well as *cis*-alkenes formation increase very pronouncedly with the increasing complexity of R, the former being, however, more sensitive towards the structural change. The overall spread of the rates is unexpectedly large and extends over a range greater than six power of ten, with alkenes *IV*; R = H and R = t-C_4H_9 (*trans-*) from the corresponding amine

oxides *II*; R = H and R = t-C_4H_9 being formed, respectively, most slowly and most rapidly in this process. Similar trends may be found (Table VII and VIII) also for the alkenes *IV* and *V* arising from the same amine oxides (*I* and *II*, respectively) in the opposite direction, "towards" the substituent R.

An analogous situation is found also for the terminal alkene formation from the methyl substituted series of 1-heptyldimethylamine oxides. As may be seen from Table IX, successive introduction of methyl groups into the heptyl chain of the parent system leads to gradual increase of rates (10^3) in order γ-CH_3 < γ,γ-di-CH_3 < < β-CH_3 < α-CH_3 < α,α-di-CH_3 paralleling thus the rate pattern for the internal alkenes from the amine oxides *I* and *II*. It follows from the rate trends* that alkyl structure effects operate very generally in the olefin-formation and are felt strongly already in the most simple systems. In this way, these findings disprove the very common though never soundly documented view** that such effects are inessential[9] in the reaction, except for the eclipsing effect leading to predominance of *trans*-over *cis*-alkenes when such isomerism is possible.

Before entering the detailed examination of these results, we have to consider possible modes in which the alkyl structure may affect the rates in the reaction. The amine oxide elimination has been shown to be an intramolecular *syn*-elimination process[10] and a nearly *syn*-periplanar arrangement of the groups involved is therefore required in the transition state (Scheme 2); accordingly, the energy necessary for attainement of this unfavourable arrangement should depend on the bulk of the adjacent alkyl groups. Further, some breaking of the C_α—N and/or C_β—H bond will occur on going to the transition state and, conceivably, both steric as well as polar properties of the alkyl substituents could assist in the bond fissions. Hence, a complex operation of several factors may be anticipated in the reaction, the relative importance of which will be analysed in subsequent sections of this paper.
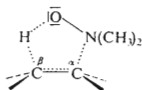
SCHEME 2

* A very similar pattern of rate data for amine oxides *I* and *II* found in dimethylformamide (Table XI) lends further significance to the present observations.
** The erroneous view is based entirely on product composition data. Cope and his co-workers[15] found in elimination of the unsymmetrical amine oxides of the type $R^1R^2CH_3N{\rightarrow}O$ a nearly statistical olefin distribution, regardless of α or β branching. Although the original investigators restrained themselves from drawing any definite conclusion from the kinetically unsupported data, the results were later taken as an evidence of a balance of individually small polar and steric effects.

Eclipsing Effects

Energy required to bring about *syn*-periplanarity is assumed to increase with increasing bulk of neighbouring groups; correspondingly, a gradual and pronounced decrease of rates by successive alkyl substitution of the amine oxides would be expected to result from prevalent operation of this factor in the olefin-forming reaction. While an exactly opposite rate trend actually found (Fig. 1) shows that different factors must be of a greater importance in both the *trans*- as well as *cis*-alkene formation, the role played by the eclipsing effects is apparent from the values of the *trans*- to *cis*-alkene ratios (Table XII). Significantly, two exceptions from the general "upward" rate trend may be found in the reaction (Table VII) concerning the *cis*-alkene formation in the sterically very demanding situations (*I*; R = i-C$_3$H$_7$ and t-C$_4$H$_9$). These, obviously, may be accounted well by the eclipsing effect.

TABLE XII

trans- to *cis*-Isomer Ratios in Formation of the Alkene R^1.CH=CH.R^2 from Amine Oxides R^1.CHX.CH$_2$.R^2 (X = N(CH$_3$)$_2$O)

R^1	t-Bu[a]	i-Pr[b]	Neope[c]	s-Bu[b]	Pr[e]	Et[f]	Pr[e]	Et[f]	Me[g]	Me[g]
R^2	Pe[h]	Pe[h]	Bu[i]	Bu[i]	Pe[h]	Pe[h]	Bu[i]	Bu[i]	Pe[h]	Bu[i]
trans/cis[j]	500	25	10.5	7.6	7.3	5.4	5.0	5.4	2.8	2.5
$\Delta\Delta F^{\neq}$[k]	4.2	2.2	1.6	1.4	1.3$_5$	1.1$_5$	1.0	1.1$_5$	0.7	0.6

[a] tert-Butyl; [b] isopropyl; [c] neopentyl; [d] sec-butyl; [e] n-propyl; [f] ethyl; [g] methyl; [h] n-pentyl; [i] n-butyl; [j] in 0.1M t-C$_4$H$_9$OK in tert-butanol at 70°C; [k] in kcal/mol.

The Alkyl Effect on the C$_\alpha$—N and C$_\beta$—H Bond Fission

The values of carbonyl stretching frequencies, ν(C=O), of ketones (or aldehydes) may serve as a measure of easiness of bond-fission processes on the related carbon atom. This was demonstrated first by Foote[36] and Schleyer[37] who found a surprisingly good linear correlation between the rates of solvolysis of arenesulphonates and the values of ν(C=O) of the corresponding carbonyl derivatives. Recently, we brought further evidence suggesting that such a relationship may hold also for the more complex processes involving in the transition state bond changes on two neighbouring carbon atoms. Thus, in homologous series of cycloalkyl derivatives differing in ring size (n = 5 − 16) we found[3,4,7] for several *syn*-elimination processes (including the Cope elimination) a reasonable correlation between the rates and the ν(C=O) values of the corresponding cycloalkanones. A quite analogous situation is now found

in the elimination of the open-chain amine oxides as demonstrated by plotting the values of log k for the formation of alkenes *trans-* and *cis-IV* against the values[38,39] of $\nu(C{=}O)$ of the closely related* carbonyl compounds $RCOC_2H_5$. As the Fig. 2
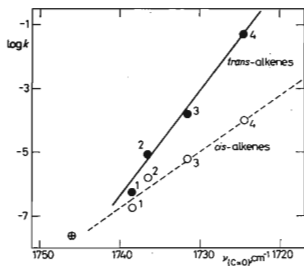

Fig. 2

Relationship between Rates of Alkene Formation from Amine Oxides *II* and Values of $\nu_{(C=O)}$ of Compounds $RCOC_2H_5$

● *trans-*Alkenes *IV*; ○ *cis-*alkenes *IV*; ⊕ 1-heptene (R = H; the rate was corrected for unequal number of available hydrogens); 1: R = CH_3; 2: R = C_2H_5; 3: R = i-C_3H_7; 4: R = t-C_4H_9.

shows, two straight lines may be drawn in the plot encompassing respectively the rate data for the *trans-* and *cis-*isomers. Neglecting the difference in slopes of the two lines, accountable by the eclipsing effect, the reasonable fit of the data lends a support to the view that the substituent effect observed in the open-chain systems results mainly from assistance in the C_α—N and/or C_β—H bond loosening accompanying the incipient double bond formation. An intriguing question arises in this context concerning the relative importance of the bond changes on the alternative C_α and C_β carbon atoms. Substituent effects observed in the two positions may afford a valuable information on the subtle problem: evidence along these lines is obtained from the rate data for the *trans-*alkenes *III* and *IV* formation from the positionally isomeric amine oxides *I* and *II* (Table XIII).

As comparison of the rates of the *trans-IV*-alkene formation from the amine oxides *I* and *II* shows, there is a considerably greater spread of the rate values within the series *II* which has the "variable" substituent R on C_α (six powers of ten); in the series *I* the spread of rates is only about three powers of ten, indicating thus a substantially less powerful influence of the substituent located on the carbon C_β. Although these differences undoubtedly show that stretching of the C_α—N bond is more influenced by the alkyl substitution than that of the C_β—H bond, no direct conclusion concerning the actual substituent effect on the two individual bond changes can be drawn from a simple comparison of the effects observed in the two series. Conceivably, the substituent located on the C_α as well as that on the C_β affects simul-

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*   The data for the parent ketones $RCOCH_2C_5H_{11}$ are not available in literature.

TABLE XIII

Relative Rates of *trans-III* and *trans-IV* Alkene Formation from Amine Oxides *I* and *II*

R	$k(II \rightarrow trans\text{-}IV)$	$k(I \rightarrow trans\text{-}IV)$	$k(I \rightarrow trans\text{-}III)$	$\dfrac{k(I \rightarrow trans\text{-}IV)}{k(I \rightarrow trans\text{-}III)}$
H	$1\cdot0^a$	$1\cdot3 \cdot 10^{1\ a}$	$2\cdot1 \cdot 10^1$	0·6
CH_3	$2\cdot2 \cdot 10^1$	$2\cdot0 \cdot 10^2$	$3\cdot3 \cdot 10^2$	0·6
C_2H_5	$3\cdot3 \cdot 10^2$	$4\cdot0 \cdot 10^2$	$4\cdot5 \cdot 10^2$	0·9
$n\text{-}C_3H_7$	$4\cdot5 \cdot 10^2$	$4\cdot3 \cdot 10^2$	$4\cdot4 \cdot 10^2$	1·0
$i\text{-}C_3H_7$	$6\cdot1 \cdot 10^3$	$1\cdot3 \cdot 10^3$	$9\cdot9 \cdot 10^2$	1·3
$t\text{-}C_4H_9$	$2\cdot0 \cdot 10^6$	$1\cdot5 \cdot 10^4$	$9\cdot0 \cdot 10^3$	1·7

^{a} Corrected for unequal number of available hydrogens.

taneously both the C_α—N and C_β—H bond fission and further data are therefore required for dissection of the two partial effects. The substituent effect on the C_α—N bond has to be nearly cancelled in the ratios of position-isomeric alkenes arising from individual amine oxides: accordingly, the values of the *trans-IV/trans-III* ratios in the amine oxide series *I* can be used as a measure of the effect of the alkyl substituent in the C—H bond fission.

It may be seen from the data of Table XIII that the rates of formation of both the *trans*-isomers increase substantially with increasing alkyl substitution of the amine oxide *I*. By contrast, the values of the ratios of the corresponding rates (*trans-IV* : : *trans-III*) remain very close to unity within the series, the overall increase of the values being less than 3. It follows therefore that the substituent located on C_β exerts only a slight effect on the C_β—H bond, the greatest part of its influence being transmitted on the more remote carbon C_α. In other words, a conclusion can be drawn from this finding that the substituent effect observed in the olefin-forming reaction is displayed almost exclusively on the C_α—N bond: the C—H bond fission, if any in the transition state,* appears to be insensitive towards the alkyl substitution.

Steric Origin of the Alkyl Effect: Evidence from a Subsidiary (Hammett) Series

Although bond changes on the reaction site (C_α—N) account reasonably well for similarity of trends which exists between carbonyl frequencies and the reaction rates, some uncertainty still persists concerning the origin of the substituent effect. In principle, both steric as well as polar properties of the alkyl substituent may affect the bond changes and some arguments may be found in support of importance of either of them.

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*   The possibility that the Cope elimination is a two-step rather than concerted process, however remote, cannot be completely excluded on basis of the available evidence.

In is expected usually that a steric effect, once it starts, builds up very rapidly[40,41], with increasing alkyl substitution about the reaction site. Accordingly, a telescope form of reactivity variation is predicted[40] to distinguish a steric control, in contrast to the monotonous form resulting generally from predominance of polar effects[40,41]. In actual fact, it is the "polar" form of variation which is observed for the *trans*-alkene formation from the open-chain amine oxides now examined: indeed, a surprisingly good linear correlation is obtained, by plotting the logarithms of the rates for the *trans-III* and *trans-IV*-alkene formation against the Taft polar substituent constants, σ^*, (Fig. 3a) which gives an apparent value of $\varrho^* \sim -10$ suggesting a powerfull operation of the electron-releasing substituent effect. However, an entirely different picture emerges from the rate data obtained in the related Hammett series of p- and m-substituted 1-fenylbutyldimethylamine oxides (Table X). As Fig. 3b shows, a straight line is again obtained by plotting the logarithms of rates for 1-arylbutene formation against the σ values; however, in contrary to the result from the aliphatic series *I* and *II*, the slope gives a value of ϱ which is low and positive ($\varrho \sim 2$) indicating that the electron-withdrawal rather than electron-release supports the olefin formation.

Some examples are admittedly known in literature[42] that profound mechanistic changes may occur even within a single reaction series and revert eventually a sign of the ϱ value; in principle, it might be argued to be so also in the present case.
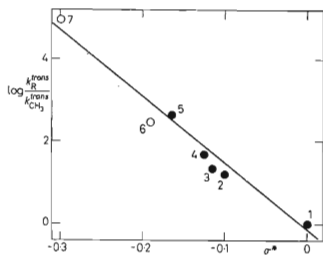

FIG. 3a

Relationship between Rates of Alkene Formation from Amine Oxides *I* and *II*, and Taft Polar Substituent Constants, σ^*, for R^α

● *trans-III* from *I* ($R^\alpha = RCH_2$); ○ *trans-IV* from *II* ($R^\alpha = R$); 1: $R^\alpha = CH_3$; 2: $R^\alpha = C_2H_5$; 3: $R^\alpha = n\text{-}C_3H_7$; 4: $R^\alpha = i\text{-}C_4H_9$; 5: $R^\alpha = C_4H_9CH_2$; 6: $R^\alpha = i\text{-}C_3H_7$; 7: $R^\alpha = t\text{-}C_4H_9$.
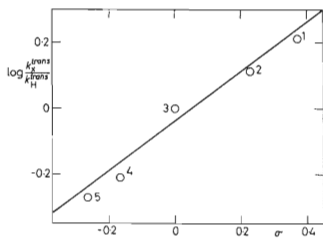
FIG. 3b

Relationship between Rates of 1-Arylbutene Formation from p- and m-Substituted 1-Phenylbutyldimethylamine Oxides and Hammett Polar Substituent Constants (σ)

1: X = H; 2: X = m-Cl; 3: X = p-Cl; 4: X = p-CH$_3$; 5: X = p-OCH$_3$.

However, the linearity of the present correlations speaks strongly against such a possibility and suggests that the mechanism of the olefin-forming reaction does not change substantially within the compared series. A conclusion appears therefore justified from the opposite results in the Taft and the Hammett series that the substituent effect in the former is despite the "polar" form of variation of a steric origin: then, relief of ground-state strain by the C_α—N bond stretching must be the most important factor in the reaction.

It has been already pointed out[43] that much of accomodation of a molecule to strain is accomplished by adjustment of bond angles. Accordingly, bond angle strain rather than non-bonded interactions may be viewed to be the main component of the strain to be relieved in the olefin formation. This, presumably, accounts for the unusual pattern of the alkyl substituent effect observed in the reaction, for, in contrast to the steep bank in energy curve for non-bonded interactions, the bond angle strain is expected[43] to be subjected to a more gentle form of variation.

REFERENCES

1. Závada J., Pánková M., Svoboda M., Schlosser M.: J. Chem. Soc., Chem. Comm. *1973*, 168.
2. Pánková M., Závada J.: Tetrahedron Letters, in press.
3. Sicher J., Závada J.: This Journal *32*, 2122 (1967).
4. Závada J., Krupička J., Sicher J.: This Journal *33*, 1393 (1968).
5. Závada J., Sicher J.: This Journal *32*, 3701 (1967).
6. Sicher J., Závada J.: This Journal *33*, 1278 (1968).
7. Závada J., Krupička J., Sicher J.: This Journal *31*, 4273 (1966).
8. Banthorpe D. V.: *Elimination Reactions*. Elsevier, Amsterdam 1963.
9. DePuy C. H., King R. W.: Chem. Rev. *60*, 431 (1960).
10. Cope A. C., Trumbull E. R.: *Organic Reactions*, Vol. 11, p. 317. Wiley, New York 1960.
11. Cram D. J., McCarty J. E.: J. Am. Chem. Soc. *76*, 5740 (1954).
12. Cope A. C., Acton E. M.: J. Am. Chem. Soc. *80*, 355 (1958).
13. Cram D. J., Sahyun M. R. V.: J. Am. Chem. Soc. *85*, 1263 (1963).
14. Závada J., Svoboda M., Sicher J.: This Journal *33*, 4027 (1968).
15. Cope A. C., LeBel N. A., Lee H. H., Moore W. R.: J. Am. Chem. Soc. *79*, 4720 (1957).
16. Sicher J.: Angew. Chem. *84*, 177 (1972).
17. Závada J., Pánková M., Sicher J.: This Journal *37*, 2414 (1972).
18. Pánková M., Vítek A., Vašíčková S., Řeřicha R., Závada J.: This Journal *37*, 3456 (1972).
19. Cope A. C., Ciganek E., Howell C. F., Schweizer E. E.: J. Am. Chem. Soc. *82*, 4663 (1960).
20. Cope A. C., Ross D. L.: J. Am. Chem. Soc. *83*, 3854 (1961).
21. Cope A. C., Ciganek E.: Org. Syn. *39*, 40 (1959).
22. Calingaert G., Soroos H.: J. Am. Chem. Soc. *58*, 635 (1936).
23. Mosher W. A., Berger P. W., Foldi A. P., Kelle T. J., Nebel C. J.: J. Chem. Soc. (C) *1969*, 12.
24. Cope A. C., Hofmann C. M., Wyckoff C., Hardenbergh E.: J. Am. Chem. Soc. *63*, 3452 (1941).
25. Ritter J. J., Kalish J.: J. Am. Chem. Soc. *70*, 4048 (1948).
26. Whitmore F. C., Southgate H. A.: J. Am. Chem. Soc. *60*, 2571 (1938).
27. Sicher J., Závada J., Pánková M.: This Journal *36*, 3140 (1971).

28. Morgan F. T., Hickinbottom W. J.: J. Chem. Soc. *119*, 1879 (1921).
29. Noller C. R., Adams R.: J. Am. Chem. Soc. *46*, 1889 (1924).
30. Vetter W., Vetter H., Biemann K. in the book: *Mass Spectrometry; Organic Chemical Applications* (K. Biemann, Ed.), p. 358. McGraw-Hill, New York 1962.
31. Bried E. A., Henion G. F.: J. Am. Chem. Soc. *59*, 1310 (1937).
32. Brown H. C., Zweifel G.: J. Am. Chem. Soc. *81*, 1512 (1959).
33. Henne A. L., Greenlee K. W.: J. Am. Chem. Soc. *65*, 2020 (1943).
34. Schlosser M., Christmann K. F.: Ann. *708*, 1 (1967).
35. Ryba M.: Chromatographia *5*, 23 (1972).
36. Foote C. S.: J. Am. Chem. Soc. *86*, 1853 (1964).
37. Schleyer P. von R.: J. Am. Chem. Soc. *86*, 1854 (1964).
38. Morgan K. J., Unwin N.: J. Chem. Soc. (B) *1967*, 1336.
39. Depireux J.: Bull. Soc. Chim. Belges *66*, 218 (1957).
40. Banthorpe D. V., Hughes E. D., Ingold C.: J. Chem. Soc. *1960*, 4054.
41. Taft R. W. in the book: *Steric Effects in Organic Chemistry*, (M. Newman, Ed.). Wiley, New York 1956.
42. Streitwieser A.: Chem. Rev. *56*, 571 (1956).
43. Hendrickson J.: J. Am. Chem. Soc. *83*, 4537 (1961).

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