

Thermal Dealkylation of 2,4-Bis(alkylamino)-6-chloro-*s*-triazines. Effect of Alkyl Group Structure. Part 2.¹

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Two series of *NN'*-dialkyl derivatives of 2,4-diamino-6-chloro-*s*-triazines (alkyl groups RCH₂CHMe and RCH₂CMe₂ where R = Me, Et, Prⁱ, or Bu^t) were thermally dealkylated, and the mixtures of olefinic products were analysed by g.l.c. In the series of secondary alkyl derivatives, alkyl group branching caused an increase in the *trans*- to *cis*-2-olefin ratio, while the 1-ene to 2-ene ratio remained practically unchanged. In the series of tertiary alkyl derivatives there was an increase in the 1-ene to 2-ene ratio. Both facts are interpreted in terms of increased non-bonding interactions of the alkyl groups on the α - and β -carbon atoms in the transition state.

In our previous papers,^{1,2} the thermal dealkylation of 2,4-bis(alkylamino)-6-chloro-*s*-triazines has been considered to be an intramolecular elimination (*E_i*) proceeding *via* a planar six-membered cyclic transition state. The proposed mechanism, like that of other similar β -*syn*-elimination reactions,³⁻⁶ required a β -hydrogen atom and the eliminating group to attain a *syn*-arrangement with respect to each other.^{7,8} The effect of alkyl group structure on the composition of the olefinic products when more than a single alkene was formed was discussed in Part 1.¹ It has been shown that with the gradual increase of β -carbon steric requirements the direction of elimination reflects steric, thermodynamic, and statistical control.^{1,9}

In an effort to assess the contribution of each of these

TABLE 1

Yields* and composition of olefins formed by thermal dealkylation of 2,4-bis(RCH₂CHMeNH)-6-chloro-*s*-triazines

R	1-Ene	2-Ene		1-Ene/ 2-Ene	<i>trans</i> / <i>cis</i>	Total amount (%)
		<i>cis</i>	<i>trans</i>			
Me ¹	19.5	20.8	59.8	0.24	2.87	25.4
Et	18.4	21.6	59.9	0.22	2.77	33.6
Pr ⁱ	14.9	9.6	75.4	0.18	7.85	34.5
Bu ^t	16.5	2.3	81.2	0.20	35.3	33.4

* Percentages throughout this paper were calculated on the basis of 2 mol of olefin to 1 mol of substrate.

factors, we planned experiments such that one factor would remain constant and the effect of the other two could be estimated more precisely. To achieve this, two series of 2,4-bis(alkylamino)-6-chloro-*s*-triazines bearing structurally related secondary and tertiary alkyl groups were studied. The statistical factor, determined by the number of β -hydrogen atoms, can be considered to be

¹ Part 1, M. D. Muškatirović and Ž. D. Tadić, *J.C.S. Perkin II*, 1975, 1701.

² Ž. D. Tadić and S. K. Ries, *J. Agric. Food Chem.*, 1971, **19**, 46.

³ C. D. Hurd and F. H. Blunck, *J. Amer. Chem. Soc.*, 1938, **60**, 2419.

⁴ C. H. DePuy and R. W. King, *Chem. Rev.*, 1960, **60**, 431.

constant. Steric requirements were successively increased by methylation on the γ - instead of β -carbon atom (*cf.* our previous paper).¹ The gradual branching

TABLE 2

Yields and composition of olefins formed by thermal dealkylation of 2,4-bis(RCH₂CMe₂NH)-6-chloro-*s*-triazines

R	1-Ene	2-Enc	1-Ene/ 2-Ene	Total amount (%)
Me	31.4	68.6	0.46	96.0
Et	38.9	61.1	0.64	79.7
Pr ⁱ	51.1	48.9	1.04	75.3
Bu ^t	77.3	22.6	3.42	95.0

of the alkyl group reduced the number of possible hyperconjugative structures which could stabilise the incipient double bond in the transition state, thus decreasing the effect of the thermodynamic factor.

The four secondary alkyl derivatives 2,4-bis(RCH₂CHMeNH)-6-chloro-*s*-triazine (R = Me, Et, Prⁱ, or Bu^t) were thermally decomposed, giving mixtures of three positional and geometric isomers (alk-1-ene, *cis*-alk-2-ene, and *trans*-alk-2-ene). The four analogous tertiary alkyl derivatives 2,4-bis(RCH₂CMe₂NH)-6-chloro-*s*-triazine (R = Me, Et, Prⁱ, or Bu^t) yielded only two positional isomers. The olefin mixtures were analysed by g.l.c., and the results are summarized in Tables 1 and 2.

The data in Table 1 show that the thermal dealkylation of the secondary alkyl derivatives predominantly follows the Saytzeff rule.¹⁰ This is attributed to the hyperconjugative stabilization of the incipient double bond in the transition state leading to the more substituted olefin. The transition state that would lead to elimination according to the Saytzeff and Hofmann rule¹¹ could be as shown in Scheme 1.

⁵ A. C. Cope and E. R. Trumbell, *Org. Reactions*, 1960, **11**, 361.

⁶ H. R. Nace, *Org. Reactions*, 1962, **12**, 58.

⁷ W. Klyne and V. Prelog, *Experientia*, 1960, **16**, 521.

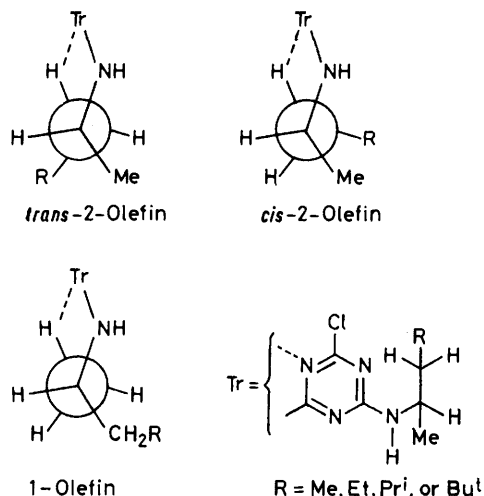
⁸ W. H. Saunders and A. F. Cockerill, 'Mechanisms of Elimination Reactions,' Wiley, New York, 1973, p. 380.

⁹ C. H. DePuy and R. W. King, *Chem. Rev.*, 1960, **60**, 435.

¹⁰ A. Saytzeff, *Annalen*, 1875, **179**, 296.

¹¹ A. W. Hofmann, *Annalen*, 1851, **78**, 253; 1851, **79**, 11.

On the basis of the variation of the steric and thermodynamic factors with increasing branching of R group, a slight increase in the ratio of 1- to 2-olefin was expected.



SCHEME 1

Table 1 shows that this ratio remains approximately constant throughout the series. The product distribution also illustrates the preference for *trans*- over *cis*-olefin formation and the increase of this olefin ratio with the successive replacement of γ -hydrogen atoms by methyl groups. The elimination leading to *cis*-isomer formation must proceed through an activated complex which requires the eclipsing of adjacent α - and β -substituents (Scheme 1). The Newman projections show that the alternative transition state leading to *trans*-olefin involves only a slight interaction between β -R and α -H and therefore is much more favoured. Although the *trans*-olefin comprises the major fraction, the presence of *cis*-olefin shows that this path of elimination is still possible. It becomes less and less favoured as the steric interaction between the adjacent eclipsing groups is increased.

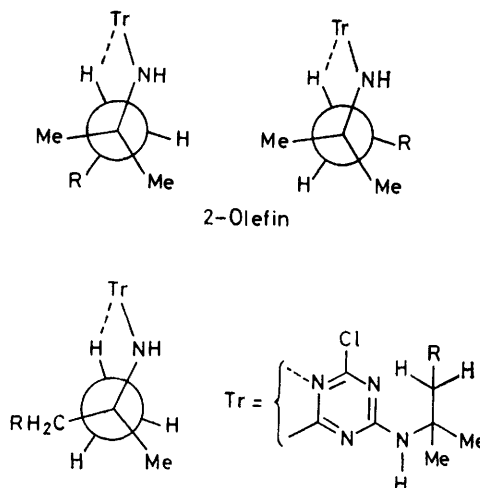
Thus in the series of secondary derivatives the *trans*- to *cis*-olefin ratio is controlled by the eclipsing effect. The 1- to 2-olefin ratio reflects the net effect of thermodynamic and steric factors. The latter is assumed to be of minor importance in this case, since it would tend to prevent the reaction from following the *trans*-path.

The reaction path to the 2-olefin in which eclipsing effects can be avoided is not available to the tertiary derivatives, which have two α -methyl groups. One of the two methyl groups interacts sterically with the β -alkyl group in both of the two possible eclipsing conformations leading to 2-olefin (Scheme 2). The statistical factor remains constant throughout the series. The ratio of the number of hyperconjugative structures which stabilise the incipient terminal double bond to the number of hyperconjugative structures stabilising the incipient internal double bond shows an increase of 50% (from 5:9 to 5:6) in going from the Me to the Bu^t derivative. In the analogous series of the secondary derivatives this ratio undergoes an increase of 100%

(from 2:6 to 2:3). Consequently the thermodynamic factor may be considered less variable in the series of the tertiary derivatives than in the secondary series; hence, the results of the experiments with tertiary derivatives would be expected to provide a more precise estimate of the effect of increasing steric requirements of R due to its eclipsing with one of the two α -methyl groups.

The results (Table 2) show an increase in 1- to 2-olefin ratio, becoming more and more pronounced, as the bulk of R increases, which can be explained in terms of the models for the transition states shown in Scheme 2. In the transition state leading to 2-olefin the steric interactions between α -Me and β -R are significant, whereas such interactions in the transition state leading to 1-olefin are much less pronounced. An increase of steric interaction in the transition state by an increase of the steric requirements of R should result in a decreased tendency to form the more alkylated olefin and an increased tendency to form the less alkylated one. The present data, being in agreement with this interpretation, suggest that such strains can overcome the effects of hyperconjugative stabilization of the incipient double bond and accomplish a transition from Saytzeff- to Hofmann-type elimination.

These studies of thermal dealkylation of *s*-triazine derivatives with constant statistical factor lead to the conclusion that steric effects in the transition state exercise an important control over product distribution.



SCHEME 2

The preferential and increasing formation of *trans*-olefin in the series of secondary alkyl derivatives establishes that the eclipsing effect strongly influences the reaction path. These data are in accord with the steric requirements of the eliminating groups and appear to constitute reliable evidence for the proposed cyclic transition state. An increase in steric requirements and consequently of eclipsing interactions in the tertiary series does result in an increased tendency towards Hofmann-type elimination. This is a strong indication of the occurrence of the planar or quasiplanar transition state proposed for the thermal dealkylation mechanism.

EXPERIMENTAL

The two series of new 2,4-bis(alkylamino)-6-chloro-*s*-triazines (Table 3 and 4) were synthesized by the modified procedure of Thurston from cyanuric chloride and the corresponding amines.¹²

Cyanuric chloride and *s*-butylamine were commercial samples (Fluka). Other secondary alkylamines of the type RCH₂CHMeNH₂ (R = Et, Prⁱ, or Bu^t) were prepared by a procedure similar to that of Mann and Porter.¹³ The synthesis of tertiary alkylamines RCH₂CMe₂NH₂ (R = Me, Et, Prⁱ, or Bu^t) was performed by the procedure of Ritter and Kalish.¹⁴

All *s*-triazine derivatives were crystallized from aqueous methanol and checked by t.l.c. for purity. Structures were proved by microanalyses and i.r. and mass spectra.

Mass Spectra.—(1) (90 °C) *m/e* 257 (*M*⁺), 242 [*M* - 15(·CH₃)], 228 [*M* - 29(·CH₂CH₃)], 202 [*M* - (55CH₂=CHCHCH₃)], 186 [*M* - 15(·CH₃) - 56(CH₂=CHCH₂CH₃)], 172 [*M* - 29(·CH₂CH₃) - 56(CH₂=CHCH₂CH₃)], and 146

70(Me₂C=CHCH₃), and 146 [*M* - 69(Me₂C=CCH₃) - 70(Me₂C=CHCH₃)]; (6) (60 °C) *m/e* 313 (*M*⁺), 298 [*M* - 15(·CH₃)], 284 [*M* - 29(·CH₂CH₃)], 270 [*M* - 43(·CH₂CH₂CH₃)], 230 [*M* - 83(Me₂C=CCH₂CH₃)], 214 [*M* - 15(·CH₃) - 84(Me₂C=CHCH₂CH₃)], 200 [*M* - 29(·CH₂CH₃) - 84(Me₂C=CHCH₂CH₃)], 186 [*M* - 43(·CH₂CH₂CH₃) - 84(Me₂C=CHCH₂CH₃)], and 146 [*M* - 83(Me₂C=CCH₂CH₃) - 84(Me₂C=CHCH₂CH₃)]; (7) (190 °C) *m/e* 341 (*M*⁺), 326 [*M* - 15(·CH₃)], 298 [*M* - 43(·CHMe₂)], 284 [*M* - 57(·CH₂CHMe₂)], 244 [*M* - 97(Me₂C=CCHMe₂)], 228 [*M* - 15(·CH₃) - 98(Me₂C=CHCHMe₂)], 186 [*M* - 43(·CHMe₂) - 98(Me₂C=CHCHMe₂)], 172 [*M* - 57(·CH₂CHMe₂) - 98(Me₂C=CHCHMe₂)], and 146 [*M* - 97(Me₂C=CCHMe₂) - 98(Me₂C=CHCHMe₂)]; (8) (190 °C) *m/e* 369 (*M*⁺), 354 [*M* - 15(·CH₃)], 312 [*M* - 57(·CMe₃)], 298 [*M* - 71(·CH₂CMe₃)], 258 [*M* - 111(Me₂C=CMe₃)], 242 [*M* - 15(·CH₃) - 112(Me₂C=CHCMe₃)], 200 [*M* - 57(·CMe₃) - 112(Me₂C=CHCMe₃)], 186 [*M* - 71(·CH₂CMe₃) - 112(Me₂C=CHCMe₃)], and 146 [*M* - 111(Me₂C=CMe₃) - 112(Me₂C=CHCMe₃)].

TABLE 3
2,4-Bis(RCH₂CHMeNH)-6-chloro-*s*-triazines

	R	Yield (%)	M.p. (°C)	Formula	%C		%H		%N	
					Reqd.	Found	Reqd.	Found	Reqd.	Found
(1)	Me	95	216	C ₁₁ H ₂₀ ClN ₅	51.25	51.0	7.8	7.8	27.15	26.75
(2)	Et	92	149—150	C ₁₈ H ₃₄ ClN ₅	54.6	54.7	8.45	8.3	24.5	24.25
(3)	Pr ⁱ	75	171—172	C ₁₅ H ₂₈ ClN ₅	57.4	57.45	9.0	8.9	22.3	22.1
(4)	Bu ^t	30	200	C ₁₇ H ₃₂ ClN ₅	59.7	58.85	9.45	8.95	20.5	20.6

TABLE 4
2,4-Bis(RCH₂CMe₂NH)-6-chloro-*s*-triazines

	R	Yield (%)	M.p. (°C)	Formula	%C		%H		%N	
					Reqd.	Found	Reqd.	Found	Reqd.	Found
(5)	Me	95	160—161	C ₁₈ H ₂₄ ClN ₅	54.6	54.05	8.45	8.75	24.5	23.05
(6)	Et	80	109—110	C ₁₅ H ₂₈ ClN ₅	57.4	56.15	9.0	8.8	22.3	21.65
(7)	Pr ⁱ	73	118	C ₁₇ H ₃₂ ClN ₅	59.7	59.85	9.95	9.4	20.5	20.6
(8)	Bu ^t	55	153—155	C ₁₉ H ₃₆ ClN ₅	61.7	60.65	9.8	9.35	18.95	18.25

[*M* - 55(CH₂=CHCHCH₃) - 56(CH₂=CHCH₂CH₃)]; (2) (190 °C) *m/e* 285 (*M*⁺), 270 [*M* - 15(·CH₃)], 256 [*M* - 29(·CH₂CH₃)], 242 [*M* - 43(·CH₂CH₂CH₃)], 216 [*M* - 69(CH₂=CHCHCH₂CH₃)], 200 [*M* - 15(·CH₃) - 70(CH₂=CHCH₂CH₂CH₃)], 186 [*M* - 29(·CH₂CH₃) - 70(CH₂=CHCH₂CH₂CH₃)], 172 [*M* - 43(·CH₂CH₂CH₃) - 70(CH₂=CHCH₂CH₂CH₃)], and 146 [*M* - 69(CH₂=CHCHCH₂CH₃) - 70(CH₂=CHCH₂CH₂CH₃)]; (3) (190 °C) *m/e* 313 (*M*⁺), 298 [*M* - 15(·CH₃)], 270 [*M* - 43(·CHMe₂)], 256 [*M* - 57(·CH₂CHMe₂)], 230 [*M* - 83(CH₂=CHCHCHMe₂)], 214 [*M* - 15(·CH₃) - 84(CH₂=CHCH₂CHMe₂)], 186 [*M* - 43(·CHMe₂) - 84(CH₂=CHCH₂CHMe₂)], 172 [*M* - 57(·CH₂CHMe₂) - 84(CH₂=CHCH₂CHMe₂)], and 146 [*M* - 83(CH₂=CHCHCHMe₂) - 84(CH₂=CHCH₂CHMe₂)]; (4) (190 °C) *m/e* 341 (*M*⁺), 326 [*M* - 15(·CH₃)], 284 [*M* - 57(·CMe₃)], 270 [*M* - 71(·CH₂CMe₃)], 244 [*M* - 97(CH₂=CHCHCMe₃)], 228 [*M* - 15(·CH₃) - 98(CH₂=CHCH₂CMe₃)], 186 [*M* - 57(·CMe₃) - 98(CH₂=CHCH₂CMe₃)], 172 [*M* - 57(·CMe₃) - 98(CH₂=CHCH₂CMe₃)], and 146 [*M* - 97(CH₂=CHCHCMe₃) - 98(CH₂=CHCH₂CMe₃)].

(5) (90 °C) *m/e* 285 (*M*⁺), 270 [*M* - 15(·CH₃)], 256 [*M* - 29(·CH₂CH₃)], 216 [*M* - 69(Me₂C=CCH₃)], 200 [*M* - 15(·CH₃) - 70(Me₂C=CHCH₃)], 186 [*M* - 29(·CH₂CH₃) -

Thermal Dealkylation and G.l.c. Analysis of the Resulting Olefins.—All the thermal decompositions were conducted by heating the substrate (0.5 mmol at 250 °C) in a thermostatted oil-bath (±1 °C) for 1 h in an apparatus similar to the one previously described.² The gaseous products were transported by nitrogen to a thermostatted burette (80 °C), from which the mixtures of olefins were taken and analysed (Varian Aerograph 1400). The olefins used as standards were commercially available (Fluka). A 13 ft × 1/4 in column of 15% (w/w) squalane on Chromosorb P (80—100 mesh) with nitrogen as carrier gas at 30 or 50 °C was used for g.l.c. analysis of the products from the *s*-alkylamino derivatives (2)—(4); the products from the derivative (1) were analysed on dibenzyl ether on Celite at 25 °C. The olefins from the *t*-alkylamino-derivatives (5)—(8) were analysed on a 6.5 ft × 1/8 in column of 30% (w/w) diethylene glycol-silver nitrate on Chromosorb R (60—80 mesh) at 50 °C with nitrogen as carrier gas.

This work was supported by the Serbian Republic Research Fund. We thank Dr. D. Jeremić for the interpretation of mass spectra.

[6/1418 Received, 19th July, 1976]

¹² J. T. Thurston, J. R. Dudley, D. W. Kaiser, J. Hechenbleikner, F. C. Schaefer, and D. Holm-Hansen, *J. Amer. Chem. Soc.*, 1951, **73**, 2983.

¹³ F. G. Mann and J. F. Porter, *J. Chem. Soc.*, 1944, 456.

¹⁴ J. J. Ritter and J. Kalish, *J. Amer. Chem. Soc.*, 1948, **70**, 4048.