Thermal Dealkylation of 2,4-Bisalkylamino-6-chloro-*s*-triazines. Effect of Alkyl Group Structure on Dealkylation

By **Milan D. Muškatirović,*** and **Živorad D. Tadić,** Department of Organic Chemistry, University of Beograd, Karnegieva 4, 11001 Beograd, Yugoslavia

A number of primary and secondary *NN'*-dialkyl derivatives of 2,4-diamino-6-chloro-*s*-triazines were thermally dealkylated at 250 and 280°. The amount of olefin formed increased in the series of primary derivatives (alkyl = Et, Pr, 2-methylpropyl, 2,3-dimethylpropyl) except for the last member. This trend was attributed to the increased hyperconjugative stabilization of the transition state for the reaction which was assumed to proceed *via* β-*cis*-elimination. The total amount of evolved olefins in the series of secondary derivatives (alkyl = Pr^i, Bu^s, 1,2-dimethylpropyl, 1,3,3-trimethylpropyl) decreases after the second member due to the predominance of steric and statistical factors over the thermodynamic one.

In our previous paper on thermal dealkylation of 2,4-bisalkylamino-6-chloro-*s*-triazines it was proposed that this reaction presents an example of pyrolytic elimination, proceeding *via* a cyclic intramolecular six-membered ring transition state.[†,1] Assuming the similarity of dealkylation of alkylamino-substituted *s*-triazines to other pyrolytic eliminations[2–6] and having in mind the effect of the structure of the alkyl group in these reactions,[5a] this paper presents an investigation of the effect of the structure of the alkylamino-groups in 2,4-bisalkylamino-6-chloro-*s*-triazines on olefin formation and on the extent of dealkylation.

DISCUSSION

The increase of the amount of olefin for the first three members of the primary alkylamino-series (alkyl = Me, Et, and 2-methylpropyl), and can be attributed to hyperconjugative stabilization of the transition state in the olefin-forming reaction with the increase of alkyl group branching (Table 1).[5a,c,7]

TABLE 1

Yield * and composition of olefins formed by thermal dealkylation of 2,4-bis($\mathrm{RCH_2NH}$)-6-chloro-*s*-triazines

		Olefin (%)	
R	Olefins †	250°	280°
Me	$\mathrm{CH_2{=}CH_2}$	3.30	10.12
Et	$\mathrm{CH_2{=}CHMe}$	12.50	19.97
Pr^i	$\mathrm{CH_2{=}CMe_2}$	29.70	39.00
Bu^t	$\mathrm{MeCH{=}CMe_2}$	3.10	3.44
	$\mathrm{EtCMe{=}CH_2}$	0.80	0.98

* Percentages throughout this paper were calculated on the basis of 1 mol of olefin to 1 mol of substrate. † T.l.c. analysis showed that in all cases only two derivatives were present in the residue: 2-alkylamino-4-amino-6-chloro-*s*-triazine and unchanged starting material.

The correlation of the transition state stabilization and the stability of the products of the reaction, as the function of the number of hydrogen atoms available for hyperconjugative stabilization, points out the highly olefinic character of the transition state.[8] Apart from the thermodynamic factor, the increase of the amount of olefins formed is probably also influenced by the increase of driving force for the elimination reaction with increased branching of the alkyl group due to the enhanced decrease of *B*-strain on going from the substrate with a bond angle of 109° to the transition state with the bond angle approaching 120°.

The products of dealkylation of the neopentyl derivative indicate that the reaction most probably proceeds by a mechanism which involves the detachment of α- and γ-hydrogen atoms respectively, and the formation of a double bond between α- and β- and β- and γ-carbon atoms, respectively, with the simultaneous migration of methyl group from a β- to an α-carbon atom. It is interesting to note that the temperature of the reaction does not influence the dealkylation of the neopentyl derivative within experimental error (Table 1).

Though it is beyond the scope of the present work it should be noted that the substitution of chlorine in the triazine ring with iodine caused a marked increase in the amount of dealkylation for all other primary compounds, except for the neopentyl derivative.

The composition and the ratio of the products of dealkylation of the s-butyl derivative can be attributed to two effects: hyperconjugative stabilization of the transition state already mentioned for the series of primary derivatives favouring the formation of internal olefin and the steric effect of the eclipsed methyl groups in the transition state which favours the formation of terminal olefin (Table 2)[7,9–12]

On the basis of the data of Brown and his co-workers[5a] it would be expected that the third member of the series of secondary derivatives, on consideration of the higher

---

[†] The stereochemical proof of this mechanism is presently under investigation.

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

[2] M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. Mandow, G. A. Maw, and L. I. Woolf, *J. Chem. Soc.*, 1948, 2093.

[3] E. D. Hughes, C. K. Ingold, and V. J. Shiner, jun., *J. Chem. Soc.*, 1953, 3827.

[4] C. H. Schramm, *Science*, 1950, 112, 367.

[5] (*a*) H. C. Brown, I. Moritani, and M. Nakagawa, *J. Amer. Chem. Soc.*, 1956, **78**, 2190; (*b*) H. C. Brown and N. Nakahawa, *ibid.*, p. 2197; (*c*) H. C. Brown, I. Moritani, and Y. Okamoto, *ibid.*, p. 2193; (*d*) H. C. Brown and O. H. Wheeler, *ibid.*, p. 2199.

[6] C. H. De Puy and R. W. King, *Chem. Rev.*, 1960, **60**, 431.

[7] D. H. Froemsdorf, C. H. Collins, G. S. Hammond, and C. H. De Puy, *J. Amer. Chem. Soc.*, 1959, **81**, 643.

[8] H. C. Brown and I. Moritani, *J. Amer. Chem. Soc.*, 1956, **78**, 2203.

[9] A. C. Cope, N. A. Le Bel, H. H. Lee, and W. R. Moore, *J. Amer. Chem. Soc.*, 1957, **79**, 4720.

[10] J. Sicher and J. Zavada, *Coll. Czech. Chem. Comm.*, 1968, **33**, 1278.

[11] W. H. Saunders, jun., and D. S. Bailey, *J. Amer. Chem. Soc.*, 1970, **92**, 6904.

[12] W. H. Saunders, jun., D. S. Bailey, F. C. Montgomery, and G. W. Chodak, *J. Amer. Chem. Soc.*, 1970, **92**, 6911.

degree of branching, should yield an increased ratio of terminal : internal olefin compared with the s-butyl derivative. Our data on the basis of these two members of the series, which were the only two which could be compared in this manner, are not in agreement with this conclusion since, contrary to Brown's experiments where the number of β-hydrogen atoms was constant throughout the series, in our investigation the hydrogens on one methyl group were succesively substituted with methyl groups which probably caused the discrepancy with Brown's results. Evolution of 2-methylbut-1-ene could be explained by a concerted mechanism involving the simultaneous formation of an olefinic bond between the β- and γ-carbon atoms and hydride transfer from β- to α-carbon.

Table 2

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

		Olefin (%)	
R	Olefins	250°	280°
Me	CH_2=CHMe	40.80	51.73
Et	CH_2=CHEt	9.90	13.70
	MeCH=CHMe (*cis*)	10.60	13.90
	MeCH=CHMe (*trans*)	30.40	40.70
Pr^i	Me_2C=CHMe	36.85	47.24
	EtCMe=CH_2	4.74	6.25
	CH_2=$CHPr^i$	4.28	7.06
Bu^t	CH_2=$CHBu^t$	12.97	22.28
	Me_2C=CMe_2	7.42	11.49
	Pr^iCMe=CH_2	10.36	12.66

In the dealkylation of the fourth member of the series, 3,3-dimethylbut-1-ene is formed as the sole product of β-*cis*-elimination.

The production of 2,3-dimethylbut-2-ene and 2,3-dimethylbut-1-ene in the same reaction is due to the same mechanism as previously described for 2-methylbut-1-ene, except that methyl group shifts instead of hydride ion.

In conclusion, it can be stated that the thermal dealkylation of alkylamino-*s*-triazines is a reaction governed by thermodynamic, steric, and statistical factors.

The ratio of olefins formed in the dealkylation of 1-methylpropyl derivatives indicates the important contribution of steric effects arising from the eclipsing of non-participating methyl groups in the transition state. This also proves that the molecule is rigid in the transition state although it involves a six-membered ring.

N-Alkyltriazines with β-hydrogen atoms in the alkyl portion of the molecule react most probably *via* a cyclic intramolecular six-membered ring transition state with an energy of activation much lower by comparison with the energy of activation for the reaction of derivatives without a β-hydrogen atom in the alkyl portion of the molecule.[13-15]

EXPERIMENTAL

Materials.—Cyanuric chloride and amines used, except 1,3-dimethylpropylamine which was synthesised in the usual manner from isopropyl methyl ketone, and the olefins used as standards, were commercial samples (Fluka).

All triazines except 2-chloro-4,6-bisethylamino-*s*-triazine (simazine) and 2-chloro-4,6-bis(isopropylamino)-*s*-triazine (propazine) which were commercially available (Geigy) were synthesised by the general procedure of Thurston.[16] The purity of recrystallised compounds (from ethyl acetate) was checked by t.l.c. 2-*Chloro*-4,6-*bispropylamino*-s-*triazine* had m.p. 219° (Found: C, 47.55; H, 7.2; N, 31.0. $C_9H_{16}N_5Cl$ requires C, 47.05; H, 7.0; N, 30.45%). 2-*Chloro*-4,6-*bis*-2-*methylpropylamino*-s-*triazine* had m.p. 222° (Found: C, 51.7; H, 7.75; N, 26.4. $C_{11}H_{20}N_5Cl$ requires C, 51.25; H, 7.8; N, 27.15%). 2-*Chloro*-4,6-*bis*-2,2-*dimethylpropylamino*-s-*triazine* had m.p. 203° (Found: C, 54.4; H, 8.6; N, 24.2. $C_{13}H_{24}N_5Cl$ requires C, 54.65; H, 8.45; N, 24.5%). 2-*Chloro*-4,6-*bis*-1-*methylpropylamino*-s-*triazine* had m.p. 216° (Found: C, 51.0; H, 7.8; N, 26.75. $C_{11}H_{20}N_5Cl$ requires C, 51.25; H, 7.8; N, 27.15%). 2-*Chloro*-4,6-*bis*-1,3-*dimethylpropylamino*-s-*triazine* had m.p. 176° (Found: C, 54.85; H, 8.4; N, 23.85. $C_{13}H_{24}N_5Cl$ requires C, 54.65; H, 8.45; N, 24.5%). 2-*Chloro*-4,6-*bis*-1,3,3-*trimethylpropylamino*-s-*triazine* had m.p. 220° (Found: C, 57.15; H, 8.9; N, 22.4. $C_{15}H_{28}N_5Cl$ requires C, 57.4; H, 9.0; N, 22.3%).

Dealkylations.—Substrate (1 mmol) was dealkylated by heating at 250 and 280° in the apparatus similar to that described previously.[1] The reaction vessel was modified to avoid losses due to sublimation. The reaction was performed in the thermostatted oil-bath (±1°) over 1 h. The gaseous products were transported by the low nitrogen flow to the burette (1 l), for g.l.c. analysis. Standards were prepared by adding 200—400 μl of olefins per 1 l.

G.l.c.—The gases evolved were analysed on a Perkin-Elmer Fractometer F-7. Ethylene, propene, and isobutene were analysed on Al_2O_3 at 100, 100, and 120°, respectively. But-1-ene, *cis*-but-2-ene, and *trans*-but-2-ene were analysed on dibenzyl ether on Celite at 25°, 2-methyl-but-2-ene, 2-methylbut-1-ene, 3-methylbut-1-ene, 2,3-dimethyl-but-2-ene, 3,3-dimethyl-but-1-ene, and 2,3-dimethylbut-1-ene were analysed on β,β′-oxydipropiononitrile on Celite 545 (80—100) at 25°.

We thank the Serbian Republic Research Fund for support.

[5/438 *Received*, 3*rd March*, 1975]

---

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

[14] A. C. Cope, T. T. Foster, and P. H. Towle, *J. Amer. Chem. Soc.*, 1949, **71**, 3929.

[15] R. T. Arnold, G. G. Smith, and R. N. Dodson, *J. Org. Chem.*, 1950, **15**, 1256.

[16] J. T. Thurston, J. R. Dudley, D. W. Kaiser, I. Hechenbleikuer, F. C. Schaefer, and D. Holm-Hausen, *J. Amer. Chem. Soc.*, 1951, **73**, 2983.