THE THERMAL DEALKYLATION OF 2-CHLORO-4,6-BIS(BORNYL- AND NORBORNYLAMINO)-s-TRIAZINES

Živorad D. Tadić, Bratislav Ž. Jovanović and Dušan G. Antonović

Department of Organic Chemistry, Faculty of Technology and Metallurgy,
*University of Belgrade, Karnegijeva 4, Belgrade, Yugoslavia*

Dedicated to Professor Otto Exner on the occasion of his 65th birthday.

The thermal dealkylation of 2-chloro-4,6-bis(isobornylamino)-s-triazine (*I*), 2-chloro-4,6-bis-(bornylamino)-s-triazine (*II*), 2-chloro-4,6-bis(*exo*-norbornylamino)-s-triazine (*III*) and 2-chloro--4,6-bis(*endo*-norbornylamino)-s-triazine (*IV*) was performed at 250°C. The high degree of dealkylation in the case of isobornyl derivative *I* was ascribed to a reaction via a seven-membered cyclic transition state, as well as to steric interaction of the dimethylmethylene group and the triazin ring. The presence of tricyclenes in the dealkylation products of this derivative also indicates that the reaction partially takes place with charge separation, i.e. by the anchimeric assistance of the C-6 atom. The lower degree of dealkylation of bornyl derivative *II* is in agreement with the lower reactivity of the *endo*-isomer and probably takes place via three different transition states yielding three products. The dealkylation of norbornyl derivatives (*exo-III* and *endo-IV*) was successful only in the case of the *exo*-isomer yielding the expected products, while the *endo*-isomer under these experimental conditions did not give any dealkylation products.

In our study of the thermal dealkylation of 2-chloro-4,6-bis(alkylamino)-s-triazines we have interpreted it as a reaction that takes place via an intramolecular six--membered cyclic transition state (Scheme 1), similar to other reactions of pyrolytic β-*cis*-elimination. The obtained results have confirmed that, at least in the case
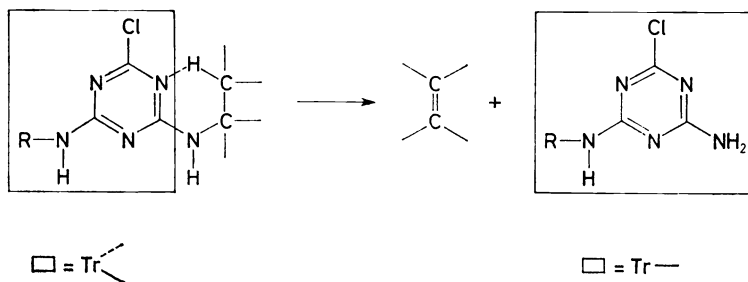
SCHEME 1

of alkylamino derivatives of s-triazine with a simpler alkylamino group, such a mechanism may be accepted[1]. Although the similarity of this reaction to other reactions of pyrolytic β-cis-elimination of esters and xanthates with the possibility of forming a six-membered cyclic transition state is considerable, the nature of the so called "leaving group" in these reactions is completely different.

As the character of the "leaving group" affects the mechanism of the reaction in this study we present the results of the thermal dealkylation of 2-chloro-4,6-bis-(isobornylamino)-s-triazine *(I)*, 2-chloro-4,6-bis(bornylamino)-s-triazine *(II)*, 2--chloro-4,6-bis(exo-norbornylamino)-s-triazine *(III)* and 2-chloro-4,6-bis(endo-nor-bornylamino)-s-triazine *(IV)* and compare them to the results of the thermal de-alkylation of 2-isobornyl and 2-bornyl xanthates and benzoates[2] using, to a con-siderable extent, the interpretations presented by the authors. The norbornyl deriva-tives *(exo-III* and *endo-IV)* were added to these investigations keeping in mind their structure, especially the absence of methyl groups on the methylene bridge.

EXPERIMENTAL

Thermal dealkylations. The experiments were performed in a static system (35 cm test tubes in a heated block with $\pm 0.5°C$ temperature regulation). The obtained deamination products were extracted by cyclopentane with cooling and the formed hydrocarbons determined by gas chroma-tography with a Varian Aerograph S-1400 instrument with the following column: 8% Carbo-wax 20M on Chromosorb G AW/DMCS, 80/100 mesh, $L = 3$ m, $d = 2$ mm, t_{col}^0. (tricyclene, camphene and bornene at 80°C; nortricyclene and norbornene at 70°C).

The percent of deamination was calculated in such a fashion that if one mole of the com-pound produced one mole of hydrocarbon the yield was considered to be 100%.

Materials. 2-Chloro-4,6-bis(2-isobornylamino)-s-triazine *(I)* and 2-chloro-4,6-bis(2-bornyl-amino)-s-triazine *(II)* were synthesized in the usual way[5] using $R(-)$isobornylamine hydro-chloride and $R(+)$-bornyl amine (Fluka). 2-Chloro-4,6-bis(exo-2-norbornylamino)-s-triazine *(III)* and 2-chloro-4,6-bis(endo-2-norbornylamino)-s-triazine *(IV)* were synthesized in the same way as the previous two. *Exo*-norbornyl amine was obtained from Fluka. *Endo*-norbornylamine was synthesized by Diels–Alder reaction from nitroethylene and cyclopentadiene[6]. *Endo*-2-nitro-norbornene obtained by this cyclization was then hydrogenated and reduced[7] by Fe powder to *endo*-2-aminonorbornene.

The tricyclene and camphene used as standards for GC were obtained from Fluka, while bornene[8] was synthesized starting from camphor which was transformed to bornyl amine. Bornyl amine was converted to trimethylbornyl ammonium iodide by exhaustive methylation and the obtained quaternary iodide transformed to the corresponding hydroxide on an ion ex-change column (this phase differs from the above mentioned method). Bornene was obtained by heating of the quaternary ammonium hydroxide. Nortricyclene was synthesized starting from norbornene using the procedure of Roberts and coworkers[9].

RESULTS AND DISCUSSION

The results of the thermal dealkylation of *I*, *II* and *III* are given in Scheme 2. The dealkylation of compound *I* gives a high yield of camphene *(V*, 40%) and somewhat

less tricyclene (*VI*, 16%), while the presence of bornene was not registered. It should be noted that bornene (*VII*) was also not detected in the thermal dealkylation of isobornyl benzoate, while in the dealkylation of isobornylmethyl xanthate it was registered in an amount of 38% (ref.[2]).
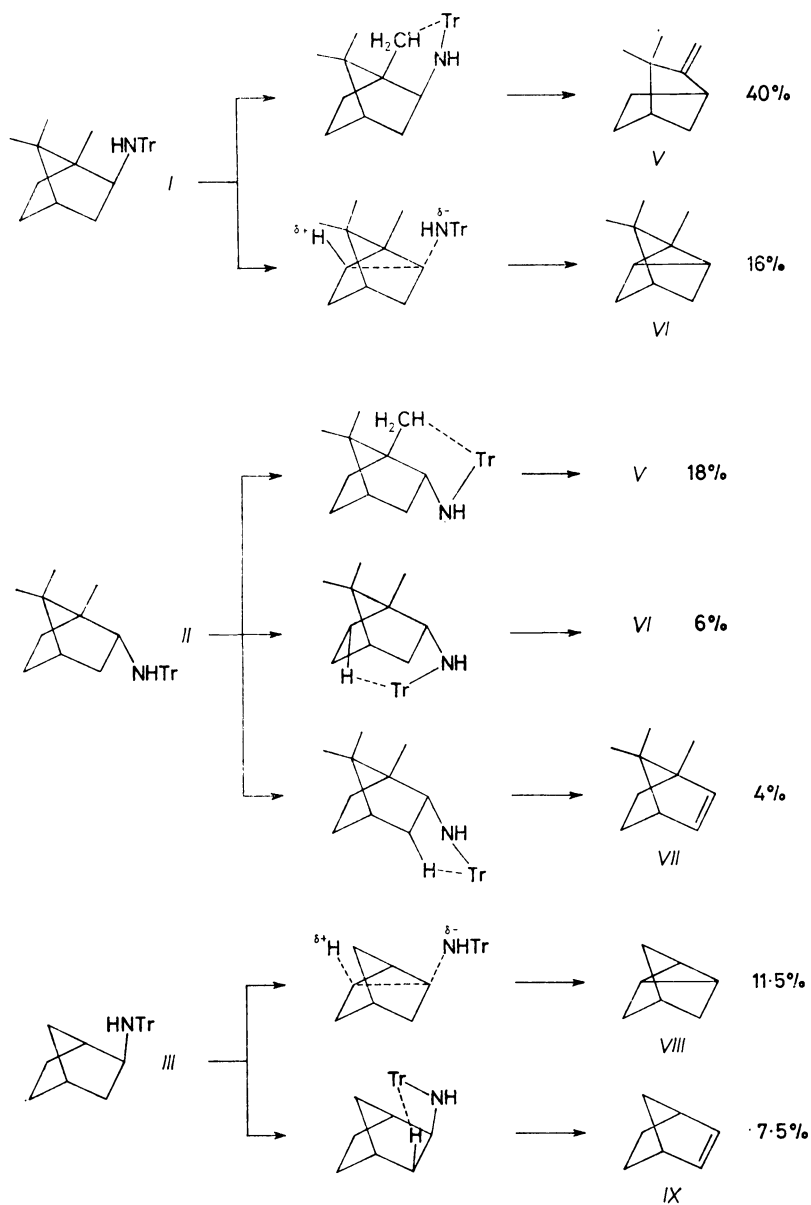
SCHEME 2

The absence of bornene in the dealkylation of compound *I*, as well as in the case of isobornyl benzoate, can most probably be explained by the fact that it should be formed by classic β-*cis*-elimination via a six-membered cyclic transition state between the triazinyl and benzoyl group in the *exo* position and the *exo* H-atom in position 3. The formation of this cyclic transition state due to the steric interaction of the triazinyl group and the geminal dimethylmethylene group would be very difficult[3], so it probably does not occur.

The formation of camphene and tricyclene in the case of compound *I* also cannot be interpreted by classic β-*cis*-elimination. Bunton and coworkers[2] ascribed the formation of camphene to the dealkylation of isobornylmethyl xanthate according to a mechanism which involves the lowest activation energy, i.e. it takes place via a seven-membered cyclic transition state as the retention of configuration is maximal.

In the dealkylation of our compounds we did not follow the optical purity of the products, however, we assume that we can accept the same mechanisms for our case (reactions *I* → *VI*, *II* → *V* and *III* → *VIII*).

As a product of isobornyl benzoate dealkylation tricyclene is also formed in an amount of 13%. The formation of tricyclene is explained by the affinity of the benzoate to give the C-2 atom a cationic character in the course of dealkylation. In our case in the dealkylation of *I* beside camphene (*V*), tricyclene (*VI*) was also produced (16%). On the basis of the assumption that camphene (*V*) forms via seven-membered cyclic transition state and tricyclene (*VI*) by charge separation, we considered, keeping in mind that the second process requires a higher activation energy, that the camphene/tricyclene ratio should increase with temperature decrease. Therefore, we investigated the dealkylation of compound *I* at various temperatures and obtained ratios are given in Table I.

On the basis of the results of Table I it may be concluded that in the dealkylation of compound *I* there are basically two mechanisms as presented in Scheme 2. The absence of bornene (*VII*) in the dealkylation of compound *I*, as well as in the dealkylation of isobornyl benzoate, which could also occur via the carbocation, indicates that the assistance of the electron pair from the C-6 atom is a favoured process.

In the dealkylation of compound *II*, beside camphene (*V*) and tricyclene (*VI*), bornene (*VII*) was also obtained. The formation of bornene in the case of this isomer

TABLE I
Dependence of the camphene (*V*)/tricyclene (*VI*) ratio on temperature

t, °C	230	245	255	265
V/*VI*	5·9	4·8	4·3	3·9

(as compared to compound *I*), may be explained by the possibility of forming a classic cyclic transition state between the triazinyl residue in the *endo* position and the *endo* H-atom on C-3 (Scheme 2, reaction *II* → *VII*). Keeping in mind that Bunton[2] found that the bornene (*VII*) produced from *endo*-benzoate and *endo*-methyl xanthate has a high degree of optical purity and that as a consequence it could have formed by less drastic changes of the compound in the reaction, we also have accepted this interpretation for the formation of bornene (*VI*) in the case of compound *II*. The formation of camphene (*V*) and tricyclene (*VI*) can be explained by the formation of a seven-membered cyclic transition state (Scheme 2, reactions *II* → *V* and *II* → *VI*).

The results of compound *III* dealkylation confirm the assumption that steric factors are decisive for the formation of norbornene from the *exo*-isomer (Scheme 2, reaction *III* → *IX*) and indicate the possibility of forming a six-membered cyclic transition state because there are no methyl groups on the methylene bridge that would obstruct this formation. The formation of nortricyclene (*VIII*) (Scheme 2, reaction *III* → *VIII*) is possible by the same pathway as the production of tricyclene (Scheme 2, reaction *I* → *VI*).

As mentioned previously, compound *IV* does not dealkylate under these reaction conditions, which means that in the case of this norbornane alkylamino triazine the reactivity of the *endo*-substituent is considerably decreased[4].

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