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# Product Ratio of Chlorocarbonylation of Substituted Adamantane (1)

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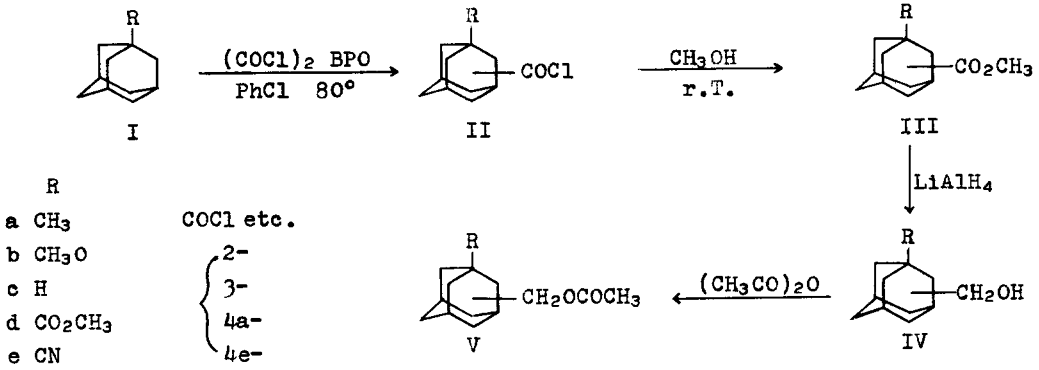
We have reported that in the halogenation of adamantane with various halogenating reagents, two observations were made; i) hydrogen abstraction by radical carriers from a bridgehead(BH) position was as normal as from a bridge(BR) position (estimated from the relative amounts of BH and BR products); while ii) the halogen abstraction by a BH radical was less selective than by a "normal" BR radical (estimated from the competitive halogen abstraction from a halogenating reagent and a solvent) (2). Similar results were also observed by Gleicher et al. (3). However, our unpublished results showed that radical halogenation does not seem a very good model reaction to investigate the reactivity problem (e.g., appreciable reverse halogen abstraction by a free radical took place) so that chlorocarbonylation was taken as a reference reaction to investigate the reactivity problem of polycyclics (4,5). In this article, we wish to report the results of chlorocarbonylation of substituted adamantanes, which was somewhat contrary to the reported results of halogenation (3,6).

Chlorocarbonylation was carried out in the following condition. Into a chlorobenzene solution of a substituted adamantane (n mole) was added dropweise oxalyl chloride (n mole) and benzoyl peroxide ($n/_{10}$ mole) dissolved in chlorobenzene at 80° under nitrogen. After stirring at 80° for 24 hours, the solution was cooled and into it was added a large excess amount of methanol. The solution was further stirred overnight.

Isolation of the products and determination of the product composition were as follows in the case of methyladamantane (similar procedures were taken for other substituted adamantanes). An isomeric mixture of methyl methyladamantanecarboxylates(IIIa) was obtained by distillation at 102-104°(6 mmHg) (52% preparative yield based on methyladamantane used and 93% based on the hydrocarbon consumed). The ester consisted of at least three components by VPC but VPC separation was not perfect as to be preparatively isolated (much better separation was observed for cyanoadamantanecarboxylates., methoxyadamantanecarboxylates and adamantanedicarboxylates). The ester mixture was reduced in practically quantitative yield with lithium aluminum hydride to methyladamantyl carbinols(IVa) (some minor side reactions were observed for cyanoadamantanecarboxylates and adamantanedicarboxylates). The alcohol mixture was further converted to the corresponding acetate mixture(Va). VPC separation was much better for the alcohols or the acetates than for the carboxylates.



VPC and nmr spectra of the carboxylates, alcohols or acetates allowed to estimate the ratio of the bridgehead product to the bridge products(BH/BR). Eg., the acetate mixture Va showed the absorption of α-methylene protons to oxygen; singlet at 6.38$\tau$ ($CCl_4$, TMS) and doublets at 5.96$\tau$, 5.89$\tau$ and 5.87$\tau$ (weak) (J's were practically the same, being ca 7 Hz). BH/BR ratio thus obtained for Ia was 2.3 : 1 . BH/BR ratio for substituted adamantanes were listed in the Table together with the reported results of halogenation.

Table Apparent BH and BR Product Composition

| Substituent | Chloro-[a] carbonylation | Bromination with[b] bromotrichloromethane | Bromination and chlorination[c] with NBS/$CCl_4$ |
|---|---|---|---|
| $CH_3$ | 2.3 | 6.7 | 2.0 |
| H[d] | 1.2 | 6.1 | 1.5 |
| $OCH_3$ | 5.7 | 5.7 | ... |
| $CO_2CH_3$ | 4.4 | 4.9 | 2.1 |
| CN | 1.4 | 2.8 | 0.87 |

a. This work; abstracting species: $\cdot Cl$
b. ref. 6; abstracting species: $\cdot CCl_3$
c. ref. 3; abstracting species: $\cdot N(COCH_2)_2$ and/or $\cdot Br$
d. without statistical correction

Authentic methyl 3-methyladamantane-1-carboxylate, 3-methyladamantyl-1-methanol were prepared from the relevantly synthesized 3-methyladamantane-1-carboxylic acid (7). Similarly were prepared: methyl 3-methoxyadamantane-1-carboxylate and 3-methoxyadamant-1-yl methanol from the known 3-methoxyadamantane-1-carboxylic acid (8), dimethyl ester of adamantane-1,3-dicarboxylic acid and 1,3-dihydroxymethyladamantane from the known adamantane-1,3-dicarboxylic acid (8).

The most interesting observation about chlorocarbonylation of substituted adamantanes was that the apparent "substituent effect" on BH/BR was different from that observed for bromination (3,6) (see the Table). The observed BH/BR ratio of bromination with bromotrichloromethane and bromination plus chlorination with N-bromosuccinimide in carbon tetrachloride were both in decreasing order with increasing $\sigma^*$, while in chlorocarbonylation, the ratio was qualitatively what is expected from steric ground (9).

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9. Model shows that a bulky group on 1-position gave much strain to 4-position than 3-position, although complete conformational analysis has not been made.