

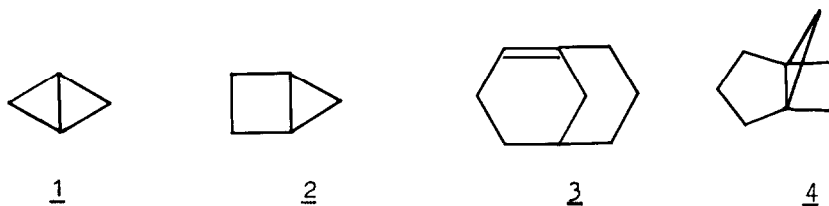
REACTIONS OF 1.3-DEHYDROADAMANTANE (3.3.1-PROPELLANE
SYSTEM) WITH CH- AND NH-ACIDS.

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Abstract: Reactions of 1.3-dehydroadamantane with aniline in the presence of its hydrochloride, p-toluenesulfamide, and malonic ester are investigated.

Strain or, more exactly, reactivity of strained molecules may be characterized by reactions of them with proton acids. There are few examples of addition of acetic acid to hydrocarbons in the absence of catalyst. Some of them are presented here (1-4)¹⁻⁴.



All compounds 1-4 are strained. Acetic acid is known to be the weakest proton acid added to hydrocarbons in direct reactions. We are interested in acidity decrease of acids, which are able to react with strained hydrocarbons under noncatalytic conditions.

During the course of our investigations concerning the small ring propellane chemistry⁵⁻⁷ we discovered recently that 1.3-dehydroadamantane 5 (DHA) reacts smoothly with some proton acids such as malonic ester 6, p-toluenesulfamide 7, and aniline hydrochloride in excess of aniline. All operations with DHA produced from 1.3-dichloroadamantane⁸ by the known method⁹ were carried out under argon atmosphere.

Treatment of DHA with excess of 6 (100°, 6 hr) followed by vacuum distillation afforded 1-adamantylmalonic ester 8 in 75% yield, b.p. 115-6°/0.15 torr, ref. b.p. 125-131°/0.25 torr¹⁰. The PMR spectrum is in agreement with structure 8.

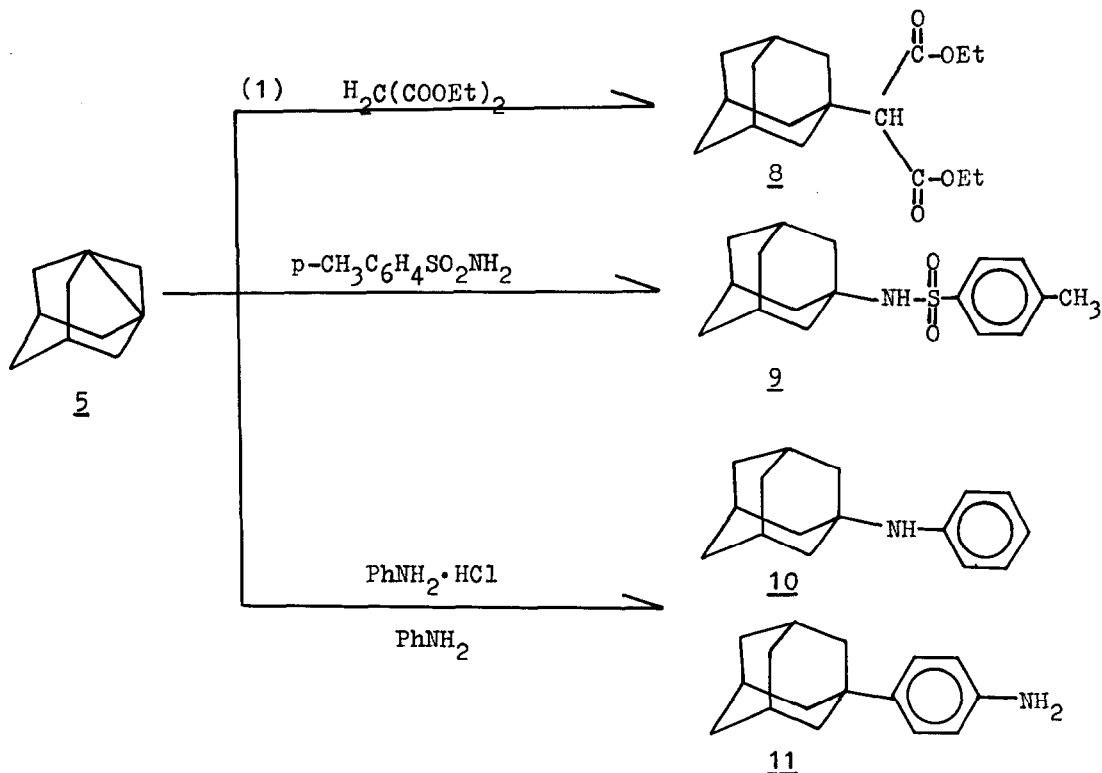
DHA reacted with 7 in boiling benzene for 14 hr and afforded N-(adamantyl)-p-toluenesulfamide 9 in 50% yield, m.p. 158-160°. PMR spectrum (60 MHz, CCl₄, δ): 7.77 and 7.23 (centres) AA'BB' system, J = 8 Hz 4H (benzene ring); 5.73 broadened singlet 1H (NH); 2.33 singlet 3H (CH₃); 1.93, 1.66 and 1.46 three multiplets 3H, 6H and 6H (adamantane fragment). Elemental analysis is consistent with formula C₁₇H₂₃NO₂S.

Treatment of DHA with aniline in the presence of its hydrochloride (12 hr, 100°) followed by preparative TLC (silicagel, benzene-ethylacetate 9:1) afforded the products of aniline alkylation on aminogroup and on para-position to it in ratio 4:1 in 55% total yield. N-(1-adamantyl)-aniline 10, m.p. 74-9°, ref. m.p. 75-82°¹¹; p-(1-adamantyl)-aniline 11, m.p. 98-104°, ref. m.p. 99-105°¹¹. The PMR spectra are consistent with structures 10 and 11.

Adamantyl-cation is likely to be intermediate in the reactions because, in particular, similar distribution of adamantylanilines found in the reaction of 1-bromoadamantane with aniline¹¹ is likely to correspond to formation of the same intermediate. One plausible suggestion is that firstly proton is removed slowly from undissociated acid molecule by DHA and then the formed adamantyl-cation rapidly adds to a nucleophile.

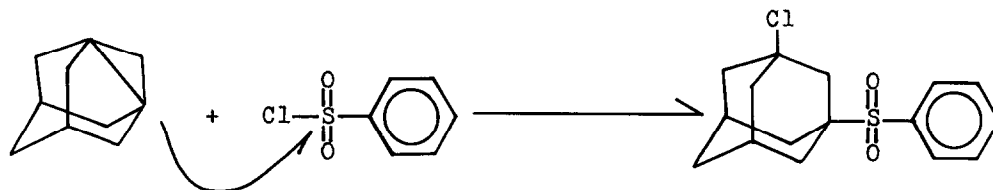
As far as we know, the reaction (1) is the first example of direct addition of weak CH-acid (pK_a 13 in water¹²) to hydrocarbon. The same is true for p-toluenesulfamide, that acts here as an NH-acid (pK_a 10 in water¹²). Let us distinguish between unstrained alkenes and small ring propellanes. Unstrained alkenes don't react with acetic acid (pK_a 5 in water¹²) without catalyst. Evidently, they will not react with malonic ester and p-toluenesulfamide in direct reaction either. Similar suggestion does not appear true a priori for aniline hydrochloride (pK_a 4 in water¹²).

Although Roberts and Caserio suggested that alkenes would not react with



ammonia in presence of its sulfate¹³ we carried out special experiment because amiline and ammonia may be different reagents and different media. We chose p-toluidine as amine to exclude C-alkylation of the latter, i.e. to simplify the work up of the reaction mixture. Cyclohexene was used as alkene. After treatment of cyclohexene with p-toluidine and its hydrochloride in sealed tube (100°, 24 hr) no products of amine alkylation were detected by PMR. This is likely to be explained by low basicity of alkene. Now, DHA is the stronger base, and it can compete for proton with such bases as aniline and anions of diethylmalonate and p-toluenesulfamide.

There is a correlation between a basicity and a nucleophilicity, as a rule. In particular, easy addition of benzenesulfonyl chloride to DHA in the absence of catalyst⁵ may be interpreted as a nucleophilic substitution at sulfur atom with DHA in nucleophile role. Radical mechanism of the latter reaction should not be excluded, however.



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