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HIGH TEMPERATURE HETEROGENOUS REACTIONS THE DEHYDROHALOGENATION OF 2,3-DIBROMOBICYCLO [2.2 1] HEPTANE AND 2,7-DIBROMOBICYCLO [2.2.1] HEPTANE

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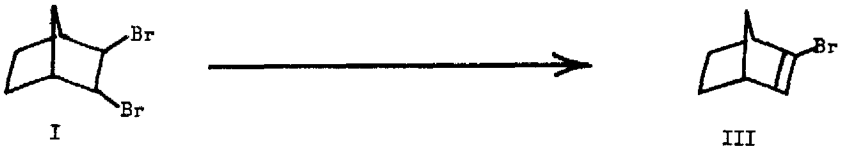
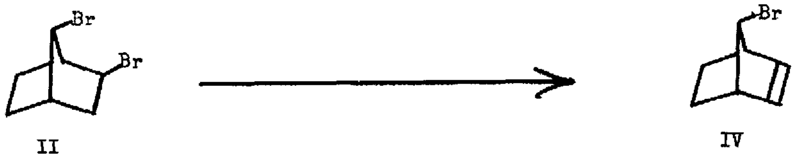
Recently there have been a series of detailed studies which have examined heterogenous reactions involving gas and solid phase reagents.[1,2] These studies have focused on the rigid crystalline structure of the solid phase reagent, and its influence on the interactions between the reagents which are required for reaction [3] These studies have provided important information about these reactions, however, there are few instances which justify laboratory application of gas/solid heterogenous reactions as a viable alternative to the more traditional solution chemistry [4]

We would like to report a high temperature heterogenous reaction which is a practical alternative to a common solution reaction, i e , dehydrohalogenation These dehydrohalogenations are commonly carried out in an alcohol solvent with the corresponding alkoxide serving as the base However, since many of the usual bases employed to effect these reactions are stable at high temperatures (200° - 300°C) they are suitable to serve as the solid substrate in a heterogenous system Also, at these temperatures many alkyl halides are volatile enough to be added in the vapor phase. In this system the reaction is extremely fast, the volatile reagents and products are added and removed continuously in a nitrogen flow system, and the products may be isolated with a minimum of effort (usually rotary evaporation or extraction to remove the alcohol formed in the reaction)

The specific reactions thus far examined are the dehydrohalogenation of 2,3-dibromobicyclo [2 2 1] heptane (I) and 2,7-dibromobicyclo [2 2 1] heptane (II) with strong base (NaOMe or t-BuOK) to yield 2-bromobicyclo [2.2 1] hept-2-ene (III) and 7-bromobicyclo [2 2.1] hept-2-ene (IV) respectively, Eq 1a and 1b The products of these reactions have been



Eq. 1a



Eq. 1b

used extensively as a source of many substituted bicyclo [2 2 1] heptane systems.[5] The solution dehydrohalogenation reactions involve long reaction times, yields of about 50%, and cumbersome work-up procedures.[6] The principal advantages of the high temperature heterogenous reaction system are 1) short reaction times, 2) good yields, and 3) facile product work-up. We have found that these advantages are sufficient to warrant the use of the heterogenous system in the preparation of III and IV.

The basic design of the apparatus consists of a 50 x 2 5 cm pyrex tube fitted with a S24/40 joint at one end and a S18/9 ball-joint at the other with indentations in the tube 35 cm from the S24/40 end to allow positioning of the solid charge The S24/40 end is attached to a joint containing a nitrogen inlet This joint also contains a septum inlet for the syringe addition of the liquid reagent The tube fits into a Lindberg Model 54031 Tube Furnace with the joints extending out of the furnace about 2 cm on each end The furnace is mounted with an incline of 15° from the horizontal. The alkyl halide is added <u>via</u> syringe through the septum. Thus, the liquid rolls down the incline into the heated zone and is vaporized The solid phase reagent (base) is packed in the tube at the indentations between glass wool plugs. The positioning of the solid is about 30cm into the heated zone to insure that the alkyl halide has completely vaporized before contact with the solid base. A cold trap condenser cooled in Dry Ice/acetone is attached to the tube as it exits the furnace to collect the volatile products. The entire system is continuously purged with a 60 ml/min. flow of nitrogen gas. Note it is essential to use an inert carrier gas since the alkoxide bases burn in the atmosphere at the temperatures of these experiments.

A typical reaction was run according to the general description which follows. The apparatus was assembled as described above using a 5 to 10 g charge of solid base. The system was allowed to equilibrate for 15 minutes at the reaction temperature while the system was purged with nitrogen to remove any residual alcohol. Using a syringe fitted with a stopcock 2.1 g of the halide were added dropwise The addition was carried out over a 10 minute time interval. Following the addition of the halide the system was rinsed by the similar addition of a 1 ml portion of pentane. After the addition of pentane, 15 minutes were allowed to insure the removal of the volatile products from the tube. The cold trap was removed, warmed to room temperature, and the condensate transferred to a flask. The methanol and pentane were removed by rotary evaporation leaving the product as the residue. The purity of the product was determined by NMR and GLC analyses. When potassium t-butoxide was used as the base, the t-butanol formed was removed by adding 10 ml of pentane to the condensate and extracting with four 10 ml portions of water The pentane layer was separated, dried over $MgSO_4$, filtered and the pentane removed by rotary evaporation.

The results of the reactions of I and II with sodium methoxide and potassium t-butoxide are shown in the table below. Reactions 2 and 4 give 55 and 40 percent yields of III and IV respectively with no other contaminants present after work-up In these reactions the yields are comparable to the solution reactions; however, the time involved in doing the reaction and isolating the desired product is significantly reduced (~ 1 hr. vs. ~ 2 days) When sodium methoxide is used as the base (reactions 1 and 3) the starting material is not completely consumed and the isolation of III and IV requires a vacuum distillation. However, even with this addition to the procedure the yields and reaction times justify the heterogenous reaction.

Table: RESULTS OF HIGH TEMPERATURE HETEROGENOUS DEHYDROHALOGENATIONS

RXN	ALKYL HALIDE	BASE	TEMP. °C	% YIELD	%UNREACTED STARTING MATERIAL
1	I	NaOMe	200	87	10
2	I	t-BuOK	200	55	0
3	II	NaOMe	225	56	15
4	II	t-BuOK	225	40	0

The fact that I reacts at lower temperatures than II is also consistent with the same reactions in solution[6] Also, in reactions 2 and 4 there is a significant material loss after regular work-up. This can be accounted for by the formation of some polymeric material which remains in the furnace, and the formation of other volatile hydrocarbons which are lost in the course of the work-up

Our efforts to investigate the details of this system and its potential application are continuing and will be the subject of later reports

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