

## Effect of Leaving Group in $\gamma$ -Elimination Reactions

By CARL L. BUMGARDNER

(Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27607, U.S.A.)

CONTINUING our study of the competition between  $\beta$ - and  $\gamma$ -elimination reactions,<sup>1</sup> we examined the effect of changing the leaving group, X, on the mode of reaction of 3-phenylpropyl derivatives with sodium amide in liquid ammonia.

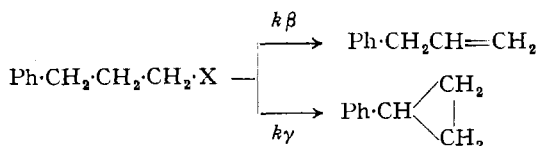


Table I summarizes the results.

TABLE I  
Effect of Leaving Group

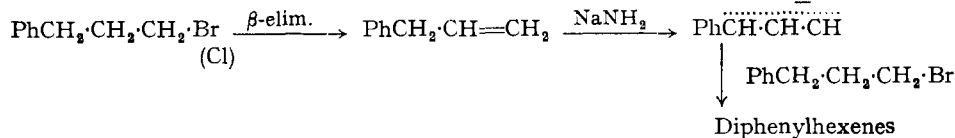
Nature of Group	Hydrocarbon Products	Type Elimination
X = Br	Diphenylhexenes	$\beta$ (+ alkylation)
X = Cl	Phenylcyclopropane + Diphenylhexenes	$\gamma$ + $\beta$ (+ alkylation)
X = F	Phenylcyclopropane	$\gamma$
X = OTs	Phenylcyclopropane	$\gamma$
X = N <sup>+</sup> Me <sub>3</sub>	Phenylcyclopropane	$\gamma$

Under the reaction conditions, 3-phenylpropyl bromide gives no phenylcyclopropane but a mixture of diphenylhexenes which arise by a sequence beginning with  $\beta$ -elimination followed by

alkylation of the sodium salt of propenylbenzene.<sup>2</sup> In contrast, 3-phenylpropyl fluoride, tosylate, and trimethylammonium iodide yield exclusively phenylcyclopropane. From 3-phenylpropyl chloride a mixture of the diphenylhexenes and phenylcyclopropane is obtained. The products were separated by distillation and gas-phase chromatography and characterized by infrared, ultraviolet, and nuclear magnetic resonance spectra.

The fact that the  $k\beta/k\gamma$  ratio decreases in the order Br > Cl > F leads us to suggest that  $k\beta$  is more sensitive to the leaving group than is  $k\gamma$ . Thus, with the easily polarizable bromine atom,  $\beta$ -elimination is promoted more than  $\gamma$ -elimination; whereas with the non-polarizable fluorine atom, both  $\beta$ - and  $\gamma$ -eliminations are slowed, but the former process is slowed to a greater extent. The poorer leaving groups, F and N<sup>+</sup>Me<sub>3</sub>, therefore, are to be used when  $\gamma$ -elimination is desired.

Particularly noteworthy is the position of tosylate, normally a good leaving group, which joins F and N<sup>+</sup>Me<sub>3</sub> as a group favouring  $\gamma$ -elimination. This result may be another manifestation of the resistance of tosylate to undergoing  $\beta$ -elimination<sup>3,4</sup> or an example of an unusually facile (possibly concerted)  $\gamma$ -elimination.



(Received, July 12th, 1965; Com. 439.)

<sup>1</sup> C. L. Bumgardner, *J. Org. Chem.*, 1964, **29**, 767 and references cited therein.

<sup>2</sup> This sequence and the mixture of diphenylhexenes will be discussed in detail in the full paper.

<sup>3</sup> H. M. Walborsky and C. G. Pitt, *J. Amer. Chem. Soc.*, 1962, **84**, 4831.

<sup>4</sup> P. Veeravague, R. T. Arnold, and E. W. Eigenmann, *J. Amer. Chem. Soc.*, 1964, **86**, 3072.