[Contribution from the Department of Chemistry, Iowa State University]

Electronic Effects in Elimination Reactions. III. Sulfonylhydrazone Eliminations[1,2]

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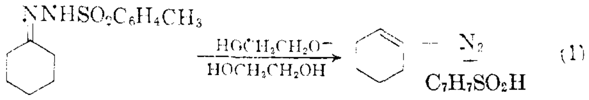
The olefinic products formed by the base-promoted decomposition of the *p*-toluenesulfonylhydrazones of several simple aliphatic ketones have been analyzed. The products are those predicted by the operation of the Saytzeff rule, and in one case extensive rearrangement of hydrogen occurred. The product distribution, the low *trans/cis* product ratio and the presence of rearranged product suggest an E_1 mechanism for the reaction. Appreciable amounts of saturated hydrocarbon are also produced in the reaction. The low yields (35%) of volatile products obtained in each case make the reaction rather unsuitable for the preparation of simple aliphatic olefins.

Introduction

Bamford and Stevens[3] discovered, several years ago, that *p*-toluenesulfonylhydrazones of many different types of ketones decomposed, on heating in base, to form olefins. As an example of the reaction, the tosylhydrazone of cyclohexanone gave cyclohexene in 100% yield when it was heated at reflux with sodium ethylene glycolate in ethylene glycol (eq. 1). Although a number of more complicated cases were examined, the only other simple aliphatic elimination studied was that of the tosylhydrazone of acetone, which gave propylene in undetermined yield.



(1)

Our interest in the factors which determine the direction of elimination in the formation of olefins[4] led us to an examination of the olefinic products formed when the tosylhydrazones of simple, unsymmetrical aliphatic ketones were decomposed. In addition to an interest in the mechanism and directing force we were interested in determining whether or not this reaction was generally suitable for the preparation of simple olefins or olefin mixtures in good yield, since the tosylhydrazones are nicely crystalline materials capable of ready purification, and many ketones are commercially available.

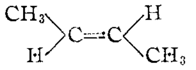
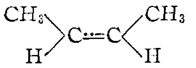
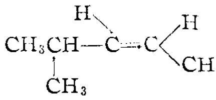
Results and Discussion

The decompositions were carried out by dissolving samples of the tosylhydrazones in ethylene glycol containing an excess of 1 *N* sodium ethyleneglycolate. The resultant solutions were heated at 170°, at which temperature nitrogen evolution was quite rapid. The condensable products were collected in a flask immersed in a Dry Ice-bath and estimated by the volume occupied at standard temperature and pressure. Nitrogen was measured in a gas buret. The product composition was determined by gas chromatography and in one case by mass spectrometry; the composition and yield of volatile products obtained were very reproducible and the results given are the average of several runs which did not differ from one another by more than 1 or 2%. A number of control experiments was run to determine that all the volatile material was collected and that the olefins which were produced in the reaction were stable to the reaction conditions.

The compositions of the volatile products from the decomposition of the *p*-toluenesulfonylhydrazones of 2-butanone, 3-methyl-2-butanone and 4-methyl-2-pentanone under these conditions are given in Table I. The first important observation about the reaction is that the yield of olefinic product formed is rather low, in each case amounting only to about 35%, although a quantitative amount of nitrogen was evolved. Obviously another product or products were being formed simultaneously. We have not isolated these products, but gas chromatographic analysis of the ethylene glycol after the completion of the reaction showed the pres-

Table I

Volatile Products from the Decomposition of Tosylhydrazones (170°)

Compound	Product	Yield, %[a]
$CH_3CH_2\underset{\underset{NNHSO_2C_6H_4CH_3}{\|}}{C}CH_3$	$CH_3CH_2CH{=}CH_2$	28
		37
		30
	$CH_3CH_2CH_2CH_3$	5
$(CH_3)_2CH\underset{\underset{NNHSO_2C_6H_4CH_3}{\|}}{C}CH_3$	$CH_3\underset{\underset{CH_3}{\vert}}{C}HCH{=}CH_2$	24
	$CH_3\underset{\underset{CH_3}{\vert}}{C}{=}CHCH_3$	56
	$CH_2{=}\underset{\underset{CH_3}{\vert}}{C}CH_2CH_3$	12
	$CH_3\underset{\underset{CH_3}{\vert}}{C}HCH_2CH_3$	8
$(CH_3)_2CHCH_2\underset{\underset{NNHSO_2C_6H_4CH_3}{\|}}{C}CH_3$	$CH_3\underset{\underset{CH_3}{\vert}}{C}HCH_2CH{=}CH_2$	32
		28
	trans	38
	$(CH_3)_2CHCH_2CH_2CH_3$	2

[a] Relative yields of products in the distillate. The total distillate in each case amounted to approximately 35% of theory.

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(1) This work was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of these funds.

(2) Paper II, C. H. DePuy and D. H. Froemsdorf, This Journal, **79**, 3710 (1957).

(3) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

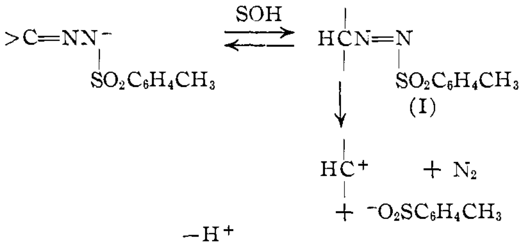
(4) D. H. Froemsdorf, C. H. Collins, G. S. Hammond and C. H. DePuy, This Journal, **81**, 643 (1959).

ence of some high-boiling material which may be the mono-ether of ethylene glycol. In any event the method is not an especially good one for the preparation of alicyclic olefins.

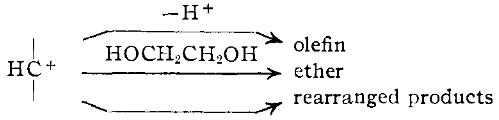
The olefinic products of the reaction are those to be expected by the operation of the Saytzeff rule,[5] *i.e.*, the more highly substituted olefins are formed in greatest amount. Thus the product from the elimination of the tosylhydrazone of 2-butanone contains 67% 2-butenes and 28% 1-butene. It is also pertinent that there is little selectivity in the formation of *cis*- and *trans*-2-olefins. *trans*- and *cis*-2-butene are formed in the ratio of 1.2 to 1. Although an E_2 elimination would be consistent with the formation of Saytzeff products, the low *trans/cis* ratio is more to be expected from an E_1 reaction. Thus while the solvolysis of *sec*-butyl tosylate gives a *trans/cis* ratio of 1.1 to 1,[6] the base-promoted dehydrobromination of *sec*-butyl bromide gives a ratio of 2.8 to 1,[4] and this is nearly the same as that found for the pyrolysis of *sec*-butyl acetate.[4,7]

An E_1 mechanism for the reaction is also strongly supported by the large amount of rearranged olefin formed in the elimination of the tosylhydrazone of 3-methyl-2-butanone. 2-Methyl-1-butene, which must have resulted from hydrogen migration, constituted 12% of the volatile products. The total amount of rearrangement must have been appreciably greater than 12%, however, for a carbonium ion formed by hydrogen rearrangement could also form 2-methyl-2-butene. Brown and Nakagawa[8] have shown that during the solvolysis of 2-methyl-2-bromopentane over twice as much 2-olefin is formed as 1-olefin. If this same ratio were to hold for this case it can be estimated that as much as 40% of the reaction proceeded by hydrogen migration. Bamford and Stevens[3] reported that rearrangement of carbons often occurred in these decompositions.

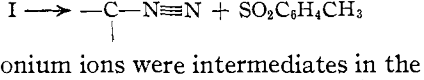
Corey and Sneen[9] have studied the decomposition of a steroidal tosylhydrazone and suggested, on the basis of the product formed, that the reaction had a great deal of E_1 character. The mechanism which we feel best fits the available data is given in equations 2 and 3, and is substantially the same as that proposed by Corey and Sneen. In this mechanism the tosylhydrazone, in its tautomeric form I, decomposes by an unimolecular process into nitrogen, *p*-toluenesulfinate ion and a carbonium ion. The carbonium ion may react in a number of different ways. It may give unrearranged olefins by the loss of a proton, it may rearrange, or it may form an ether by reaction with the solvent. The decomposition of I might also be imagined to proceed by way of the diazonium ion (eq. 4) and an analogy drawn to the amine nitrous acid reaction,[7] which also gives rise to extensive rearrangement. It is noteworthy, however, that the latter reaction shows much more discrimination in the formation of *cis*- and *trans*-2-butene. If this discrimination is due to the relative population of the ground-state conformations, as suggested by Streitwieser,[7] less discrimination would be expected at 170° and it is possible that this reaction amounts substantially to the base-catalyzed formation of a diazonium ion.



$$>C{=}N\underset{\displaystyle SO_2C_6H_4CH_3}{N^-} \overset{SOH}{\rightleftarrows} H\overset{|}{C}N{=}\underset{\displaystyle SO_2C_6H_4CH_3}{N}\ (I) \longrightarrow H\overset{|}{\underset{|}{C}}{}^+ + N_2 + {}^-O_2SC_6H_4CH_3 \qquad (2)$$



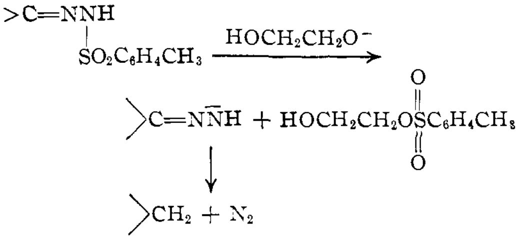
$$H\overset{|}{\underset{|}{C}}{}^+ \begin{cases} \xrightarrow{-H^+} \text{olefin} \\ \xrightarrow{HOCH_2CH_2OH} \text{ether} \\ \longrightarrow \text{rearranged products} \end{cases} \qquad (3)$$



$$I \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{+}{N}{\equiv}N + {}^-SO_2C_6H_4CH_3 \qquad (4)$$

If carbonium ions were intermediates in the reaction, it was thought that it might be possible to capture them if the reaction were run in the presence of a good nucleophile. When, however, the decomposition was run in the presence of an excess of sodium thiophenolate exactly the same total yield of volatile products was formed, and the composition of this mixture was the same as that formed in the absence of thiophenolate. If carbonium ions are formed, they must have a very short life-time.

The presence among the products of appreciable amounts of saturated hydrocarbons is also noteworthy. These compounds were identified by their retention time on gas chromatography columns and by their cracking patterns on mass spectral analysis. These hydrocarbons could conceivably have arisen by reduction of the carbonium ion intermediates by hydride transfer from the solvent. A more likely path is by sulfur–nitrogen fission of the tosylhydrazone, followed by Wolff–Kishner reduction of the resultant hydrazone (eq. 5).



$$>C{=}N\underset{\displaystyle SO_2C_6H_4CH_3}{N}H \xrightarrow{HOCH_2CH_2O^-} >C{=}N\bar{N}H + HOCH_2CH_2O\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}C_6H_4CH_3 \qquad (5)$$

$$\downarrow$$

$$>CH_2 + N_2$$

In summary, it may be said that in simple aliphatic cases the formation of olefins by the reaction of *p*-toluenesulfonylhydrazones with base is not a reaction which proceeds in especially good yield. The products obtained are likely to be complex mixtures of rearranged and unrearranged olefins together with some saturated hydrocarbon. At the present time the products formed seem to be best accommodated by a carbonium ion mechanism, and if this is indeed the case the reaction may provide a unique opportunity for the study of carbonium ion reactions with strong bases.

Acknowledgment.—We wish to express our gratitude to Prof. H. J. Svec and Mr. J. Capellen for the mass spectral analysis.

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(5) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., p. 427.

(6) H. C. Brown and M. Nakagawa, THIS JOURNAL, **77**, 3614 (1955).

(7) The importance of the *trans/cis* olefin ratio has been discussed by A. Streitwieser, Jr. and W. D. Schaeffer, *ibid.*, **79**, 2888 (1957).

(8) H. C. Brown and M. Nakagawa, *ibid.*, **77**, 3610 (1955).

(9) E. J. Corey and R. A. Sneen, *ibid.*, **78**, 6269 (1956).

Experimental

***p*-Toluenesulfonylhydrazine.**—*p*-Toluenesulfonylchloride (100 g.) was dissolved in the least possible amount of benzene and a mixture of 60 g. of hydrazine hydrate and 10 ml. of water was added with cooling and stirring. After the initial vigorous reaction had subsided, the mixture was allowed to stand for 3 hours and the crystalline hydrazine filtered. Rapid recrystallization from water yielded the hydrazine, m.p. 109–110°, reported[10] m.p. 112°. Unless the recrystallization is done rapidly a considerable loss of product results.

Preparation of Tosylhydrazones. (a) **2-Butanone Tosylhydrazone.**—The *p*-toluenesulfonylhydrazine, 10 g., was dissolved in 125 ml. of 1 *N* HCl and an equimolar amount of 2-butanone added with stirring. After standing for one hour the reaction mixture was filtered and the product recrystallized from an ethanol–water mixture to give an 85% yield of white crystalline hydrazone, m.p. 123–124°.

(b) **3-Methyl-2-butanone Tosylhydrazone.**—The *p*-toluenesulfonylhydrazine, 8 g., was dissolved in 100 ml. of 1% ethanolic HCl and an equimolar amount of the ketone was added. The solution was heated at reflux for 0.5 hour and, after cooling, an equal volume of water was added and the solution cooled to −10°. The product was collected and recrystallized from ethanol-water, m.p. 121–122°.

(c) **4-Methyl-2-pentanone tosylhydrazone**, which was prepared by method b, melted at 116–117°.

Decomposition of the Hydrazones.—The decompositions in each case were carried out by heating a sample of the hydrazone in ethylene glycol containing an excess of 1 *N* sodium ethyleneglycolate. The decomposition of the hydrazone of 2-butanone is typical. The hydrazone (1.00 g., 0.004 mole) was dissolved in 20 ml. of 1 *N* sodium ethyleneglycolate in ethylene glycol. The mixture was heated to 170° in an oil-bath, at which temperature nitrogen evolution became rapid. The hydrocarbon products were collected in a flask which was cooled in a Dry Ice-bath and the nitrogen was collected in a gas buret. The hydrocarbons occupied a volume of 33.1 ml. at standard temperature and pressure (35% yield) and 93 ml. of nitrogen was collected.

Analysis of Products.—The condensable products were analyzed by gas chromatography. The butenes were separated on a 12.5 foot column of N,N-dibutylformamide on Celite, the pentenes on a similar 4.5 foot column and the hexenes on a 4.5 foot silver nitrate–ethylene glycol column. Identifications were made by comparison with authentic samples or mixtures. Triplicate analyses gave precisely concordant results. The butenes also were analyzed by mass spectrometry and the results were in excellent agreement with those obtained by gas chromatography.

Butenes.—1-Butene was obtained by the pyrolysis of *n*-butyl acetate.[4] *cis*- and *trans*-2-butene were obtained by the pyrolysis of *sec*-butyl acetate.[4] *n*-Butane was obtained from the Matheson Co.

Pentenes.—3-Methyl-1-butene was obtained by the pyrolysis of 3-methyl-1-butyl acetate.[4] 2-Methyl-1-butene and 2-methyl-2-butene were obtained by the pyrolysis of *t*-amyl acetate.[4]

Hexenes.—Pyrolysis of 4-methyl-2-pentyl acetate gave a mixture of three products. Careful fractionation of the mixture through a 30-plate column separated it into a lower boiling fraction which was mainly 4-methyl-1-pentene, and a mixture of *cis*- and *trans*-4-methyl-2-pentene. It was assumed that the *cis* isomer, the higher boiling of the two, which is formed in smaller amount during the pyrolysis and which would be expected to form a stronger complex with silver nitrate, would be eluted later during the chromatography.

Decomposition of the Hydrazone in the Pressure of Thiophenoxide.—The tosylhydrazone of 2-butanone, 1.00 g., was placed in 20 ml. of 1 *N* sodium ethyleneglycolate solution which was 0.5 *N* in thiophenoxide ion. A slow stream of nitrogen was passed through the solution and the mixture was heated at 170°. The volatile products were collected, and their volume measured under standard conditions. The yield was 33.4%. Gas phase chromatography of these products showed that the same ratio of products had been formed.

Control Experiments.—Pure olefins, or olefin mixtures differing in composition from those produced in the reaction, were slowly introduced below the surface of the reaction mixture at 170°. In no case did any detectable isomerization take place.

AMES, IOWA

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[10] K. Freudenberg and F. Blummel, *Ann.*, **440**, 51 (1924).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Synthesis of 1-Acetyl-4-Isopropenyl-1-Cyclopentene

BY JOSEPH WOLINSKY AND WALTER BARKER

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The synthesis of 1-acetyl-4-isopropenyl-1-cyclopentene (IV) from limonene monoxide is described. This substance proved to be identical with a ketone isolated from Spanish *Eucalyptus globulus*, thus necessitating a minor revision of the previously accepted structure for the naturally occurring ketone.

The related terpene lactones isolated from various Iridomyrmex species of ants[1] and from oil of catnip[2] have been the subject of considerable interest in recent years. While the preparation of iridomyrmecin, from ants, has been recently reported,[3] nepetalactone, from catnip, has not yet been synthesized. It was our original intention to undertake the preparation of these compounds, but, as it developed, our plan was not fulfilled; for reasons which will become apparent from the sequel, we instead synthesized 1-acetyl-4-isopropenyl-1-cyclopentene, a substance which proved to be identical with an unusual terpene ketone found in Spanish *Eucalyptus globulus*.[4]

Our approach, outlined in Chart I, began with the acid-catalyzed hydrolysis of limonene monoxide. Cleavage of the resulting diol I with sodium metaperiodate led to the keto-aldehyde II as indicated by the infrared spectrum of the resulting oil which displayed a maximum at 3.7 μ associated with an aldehydic hydrogen atom, in addition to a very strong carbonyl band at 5.8 μ and terminal methylene absorption at 6.08 and 11.25 μ. The presence of a medium band at 3.0 μ probably stemmed from the starting diol I since treatment of the crude cleavage product with Brady reagent[5] afforded a single derivative corre-

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[1] R. Fusco, R. Trave and A. Vercellone, *Chim. e Industr.*, **37**, 251 (1955); G. W. K. Cavill, D. L. Ford and H. D. Locksley, *Austr. J. Chem.*, **9**, 288 (1956); *Chemistry & Industry*, 465 (1956); G. W. K. Cavill and H. D. Locksley, *Austr. J. Chem.*, **10**, 352 (1957).

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[3] F. Korte, J. Falbe and A. Zschocke, *Tetrahedron*, **6**, 201 (1959); F. J. Clark, G. I. Fray, R. H. Jaeger and R. Robinson, *ibid.*, **6**, 217 (1959).

[4] H. Schmidt, *Ber.*, **80**, 528 (1947); **80**, 533 (1947).

[5] O. L. Brady, *J. Chem. Soc.*, 756 (1931).