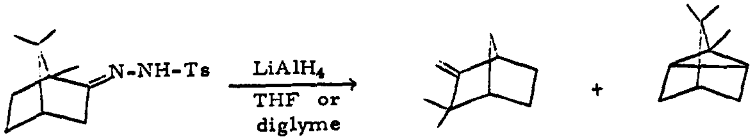
**Tetrahedron Letters No.29, pp. 3401-3407, 1966. Pergamon Press Ltd.
Printed in Great Britain.**

THE MECHANISM OF DECOMPOSITION OF SOME TRIVALENT METAL SALTS OF CAMPHOR TOSYLHYDRAZONE IN APROTIC SOLVENTS

Robert H. Shapiro
Department of Chemistry, University of Colorado, Boulder, Colorado

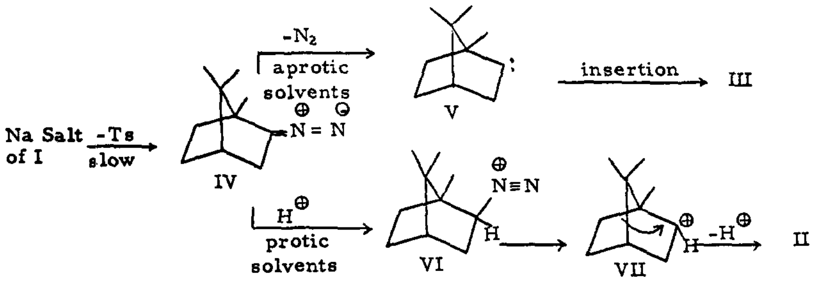
(Received 15 January 1966)

Camphor tosylhydrazone (I) decomposes to camphene (II) and tricyclene (III) upon treatment with one equivalent of lithium aluminum hydride in ethereal solvents. The camphene-tricyclene ratio, 60:40 (see TABLE), is unaffected by changes in reaction temperature or solvent.



I II III

This result is unexpected since the sodium salt of I decomposes almost exclusively to tricyclene (III) by heating in weakly proton donating solvents (1, 2), whereas camphene (II) formation is favored in strongly proton donating solvents. Powell and Whiting (1) concluded that III was generated from a carbenoid species (V) which resulted from the loss of nitrogen from diazocamphane (IV), an intermediate produced in the rate determining step. They also concluded that if a proton were available, the diazocamphane intermediate would lose nitrogen giving carbonium ion VII. This species then rearranges, with the expulsion of a proton, to camphene (II).



Further evidence in support of this mechanism was the observation that diazocamphane (IV) decomposes spontaneously to tricyclene in ethereal solutions (2, 4), whereas camphene (II) is the preponderant product in strongly proton donating solvents (2).

The results of this investigation demonstrate that the presence of a Lewis acid, namely salts of aluminum or boron, in the reaction medium will lead to mixtures highly enriched in camphene (II), regardless of the nature of the solvent. These results are summarized in the TABLE.

TABLE

Reaction of Camphor Tosylhydrazone with One Equivalent of Base

Solvent	Base	Temp.	Time	Yield Hydrocarbons(a)	% Camphene	% Tricyclene
THF	$LiAlH_4$	60°	1 hr.	*ca.* 0.5%	59	41
"	"	60°	2 hr.	*ca.* 1	59	41
"	"	60°	6 hr.	*ca.* 2	59	41
diglyme	"	70°	1 hr.	20	61	39
"	"	70°	2 hr.	20	60	40
"	"	70°	13 hr.	21	61	39
"	"	150°	1 hr.	60	59	41
"	$NaBH_4$	70°	1 hr.	0	--	--
"	"	150°	1 hr.	20	47	53
"	"	150°	2 hr.	21	48	52
"	"	150°	12 hr.	17	48	52
"	NaH	150°	7 min.	96	*ca.* 0.1	99.9
"	$NaH + Al(OEt)_3$	150°	4.5 min.	100	45	55
"	$NaH + B(OMe)_3$	150°	17 min.	100	42	58
"	$Al(OEt)_3$	150°	2 hr.	26	80	20

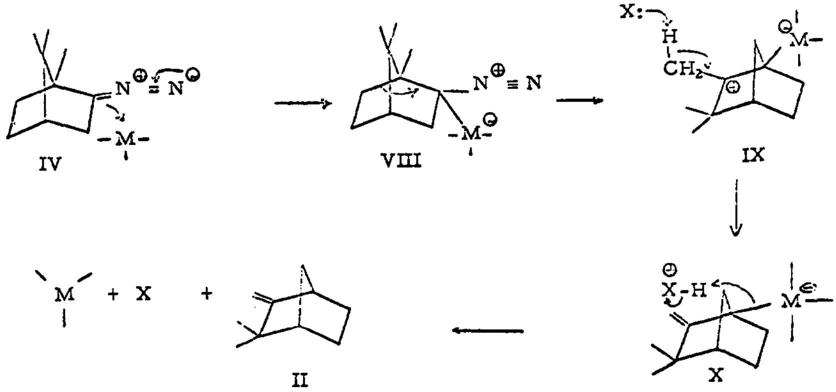
(a) o-xylene used as internal standard and appropriate correction made for its different mode of response in the gas chromatograph.

Thus, camphor tosylhydrazone decomposes with lithium aluminum hydride in refluxing THF (b. p. 60°, 630 mm.) or in diglyme at 70° and 150° to give the same (within experimental error) camphene-tricyclene ratio. The overall yield of hydrocarbon product increases at higher reaction temperatures (5). Replacing lithium aluminum hydride with sodium borohydride led to the altered camphene-tricyclene ratio of 48:52, indicating strongly that the nature of the salt of camphor tosylhydrazone determines the amount of each product formed. Sodium borohydride was far less effective in the reaction than lithium aluminum hydride as evidenced by the lower yield at 150° and the complete lack of reaction at 70°. An excellent yield of tricyclene (III) was obtained, as expected (1,2) when the sodium salt, prepared with sodium hydride, was decomposed at 150° but when an aluminum or boron source was added after the formation of the sodium salt (evidenced by the cessation of hydrogen evolution), mixtures highly enriched in camphene (II) were obtained.

The aluminum salt of camphor tosylhydrazone can be calculated from the experimental data to decompose to a mixture of II and III in the ratio of 4:1, if it is assumed that the lithium salt decomposes exclusively to III as the sodium salt does. Since an aluminum ion will complex with three times as many tosylhydrazone anions as a lithium ion will, a ratio of 75:25 would be observed provided the aluminum salt gave only camphene (II). The observed ratio of 60:40 indicates that the aluminum salt decomposes to a mixture of camphene (II) and tricyclene (III) in a 60:15 ratio. This hypothesis was tested by treating camphor tosylhydrazone (I) with one equivalent of aluminum ethoxide and, indeed, the 4:1 ratio was observed (see TABLE).

Finally, decomposition of the reaction mixture with deuterium oxide in place of water in any of the camphene producing reactions gives only unlabeled camphene (II), as demonstrated by mass spectrometry.

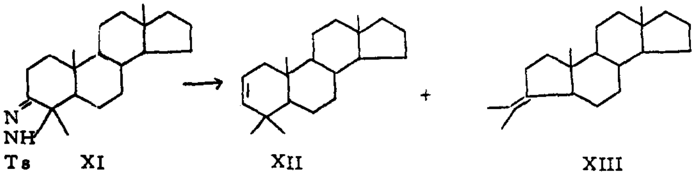
In summary, the following mechanism is proposed for the formation of camphene (II) in the presence of Lewis acids such as aluminum or boron containing species:



M = Al or B, X = solvent or tosylhydrazone anion.

The aluminum or boron species, which act as Lewis acids, are probably in the form of a tosylhydrazone salt at the beginning of the reaction, a *p*-toluenesulfinate salt near the end and mixed salts at intermediate stages. From the experimental data it appears that a boron species is not as effective as an aluminum species in the rearrangement process. Possibly this is due to increased solvation of the former Lewis acid source, thereby increasing its bulk.

In a recent communication (6), Fischer, Pelah, Williams and Djerassi reported that 4, 4-dimethyl-5α-androstan-3-one tosylhydrazone (XI) decomposes to 4, 4-dimethyl-Δ^2-5α-androstene (XII) under similar conditions. If the Lewis acid mechanism were operative in this system 3-isopropyldene-A-nor-5α-androstane (XIII), the normal Bamford-Stevens product (7) would have been expected as the major product. Since the Stanford group had no reason to expect a rearrangement product, no structural work was performed on their olefinic product (8). We repeated their experiment (9) and found a mixture of the two olefins XII and XIII in the ratio of 3:7 (10) as well as some of the saturated analog of XII (6). The nmr spectrum of the mixed hydrocarbon fraction (3. 3 mg.) clearly showed that the rearranged product XIII was the more abundant of the two olefins by the area under the two singlets at 1. 59 and 1. 72 ppm. (isopropylidene group). The olefinic protons in XII were of extremely low intensity, appearing between 5 and 6 ppm.



XI XII XIII

It therefore appears that the Lewis acid mechanism may have general significance and we are presently studying the effect of potential Lewis acids on other systems which can give different products from carbenoid and cationoid mechanisms.

Acknowledgements The author wishes to express his gratitude to the Council On Research And Creative Work, University of Colorado for the purchase of a gas chromatograph.

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8. Personal communication from Professor C. Djerassi.
9. We thank Professor C. Djerassi for a sample of XI.
10. Carbowax 20M column, 200°, Helium flow 40 ml. /min. It was assumed that the isomers had the same mode of response.