The Effect of Base Concentration and Solvent Polarity on the Base-Catalyzed Decomposition of Camphor Tosylhydrazone under Aprotic Conditions[1]

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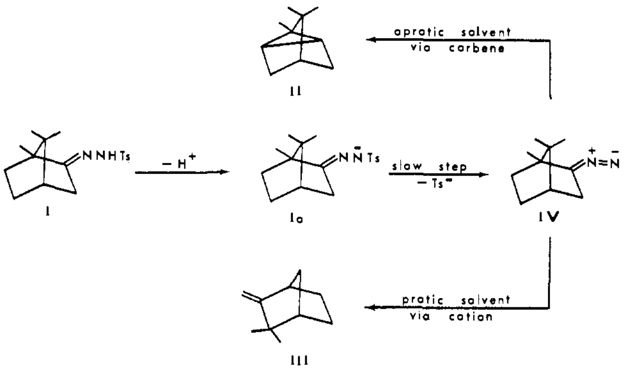
Abstract: Camphor tosylhydrazone decomposes to a mixture of camphene and tricyclene when heated with sodium methoxide or sodium hydride in aprotic solvents such as N,N-dimethylformamide, diglyme, and decalin. The ratio of camphene to tricyclene decreases with increasing base concentration and decreasing solvent polarity. In addition to solvent polarity and base concentration dependence, the effect of bases containing metal ions other than sodium was investigated; these ions include lithium, aluminum, and silver. The aluminum bases gave high proportions of camphene regardless of the base concentration or solvent polarity; the lithium ion behaved in the same manner but less strongly, and the bases containing silver behaved like sodium bases. The results of this investigation strongly indicate that each of the two hydrocarbon products can be generated from two distinct intermediates depending upon the conditions of the reaction.

Camphor tosylhydrazone (I) decomposes to tricyclene (II) and/or camphene (III) when heated with base in various solvents. It had been thought that the only factor which determines the relative amounts of the two hydrocarbons produced in the reaction is the proton-donating ability of the solvent. In the initial investigation of the base-catalyzed decomposition of camphor tosylhydrazone (*inter alia*), Bamford and Stevens reported the exclusive formation of camphene (III) in 94% yield when the reaction was run in ethylene glycol containing previously dissolved sodium.[3] Powell and Whiting later reinvestigated the Bamford–Stevens reaction of camphor tosylhydrazone and detected about 20% of tricyclene (II) in the camphene (III) by gas chromatography,[4] a tool not available to Bamford and Stevens. This later investigation was the first to show that the proton-donating ability (proticity) of the solvent governs the product distribution. It was found by Powell and Whiting that when camphor tosylhydrazone (I) is decomposed with sodium previously dissolved in acetamide, camphene (III) constitutes only about 1% of the hydrocarbon mixture, the remainder being tricyclene (II).[4] Since it was assumed that diazocamphane (IV) is an intermediate in the reaction,[4] this compound was allowed to decompose in 2-ethoxyethanol and at the usual reaction temperature (135°) the tricyclene–camphene ratio was 65:35. It was, therefore, concluded that the intermediate diazocamphane (IV) could be protonated by some solvents to give a diazonium and/or carbonium ion which collapses to yield camphene (III), whereas solvents of low proticity do not relinquish a proton and IV simply loses nitrogen to give a carbene intermediate which undergoes an intramolecular carbon–hydrogen insertion reaction to form tricyclene (II). It is interesting to note that even solvents like acetamide and 2-ethoxyethanol[5] which unquestionably have acidic hydrogens must be considered aprotic in the base-catalyzed decomposition of camphor tosylhydrazone (I). Diazocamphane (IV) has been reported to decompose spontaneously to tricyclene in ether solution,[6] whereas camphene (III) is the major product in strongly protic solvents such as 2,2,2-trifluoroethanol.[7]



During a recent investigation of the base-catalyzed decomposition of cyclopropanecarboxaldehyde tosylhydrazone (V), Smith, Shechter, Bayless, and Friedman made two very important observations;[8] first, that bicyclobutane (VI) is the predominant product when the reaction is carried out in ethylene glycol (protic) and that cyclobutene (VII) predominates in diethyl Carbitol or triethylcarbinol; second, that when a deficiency of base is used with one of the aprotic solvents, bicyclobutane (VI) is again the major product. These results were coupled with those from earlier investigations[4] and a deuterium-labeling experiment[8] and it was concluded that VI was generated from a diazonium and/or carbonium ion. Wiberg and Lavanish studied the stereochemistry of this reaction in ethylene glycol and found that if a deuterium atom is attached to the imino

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[2] (a) National Science Foundation Trainee Fellow 1965–1966; (b) National Science Foundation Undergraduate Research Participant 1966–1967.

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

[4] J. W. Powell and M. C. Whiting, *Tetrahedron*, 7, 305 (1959).

[5] Decomposition of camphor tosylhydrazone with sodium previously dissolved in 2-ethoxyethanol led to a tricyclene–camphene ratio of 92:8 (ref 4).

[6] V. Heubaum and W. A. Noyes, *J. Am. Chem. Soc.*, **52**, 5070 (1930).

[7] P. Clarke, M. C. Whiting, G. Papenmeier, and W. Reusch, *J. Org. Chem.*, 27, 3356 (1962).

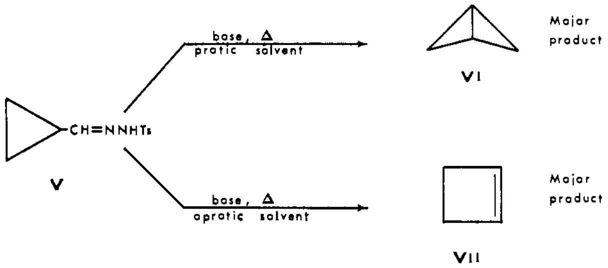
[8] J. A. Smith, H. Shechter, J. Bayless, and L. Friedman, *J. Am. Chem. Soc.*, **87**, 659 (1965).

Table I. Effect of Base Concentration and Solvent Polarity on Per Cent of Tricyclene Formed

	Tricyclene formed, %											
	Sodium hydride, equiv[a]						Sodium methoxide, equiv[a]					
Solvent	0.25	0.50	0.75	1.00	1.25	1.50	0.25	0.50	0.75	1.00	1.25	1.50
Dimethylformamide	25	25	25	33	95	100	23	24	24	36	45	84
Diglyme	37	43	47	61	100	100	40	41	43	60	84	97
Decalin	54	58	66	88	90	93	52	52	53	72	100	100

[a] Equivalents of base per millimole of camphor tosylhydrazone, decomposed at 140 ± 5°.

carbon of the tosylhydrazone V, the resulting bicyclobutane contains a deuterium atom in its *exo* position.[9] If, however, unlabeled V is decomposed in ethylene glycol-d_2, then the heavy isotope will be found in the *endo* position of VI.[10]



This investigation is concerned with the effect of polarity of aprotic solvents, such as N,N-dimethylformamide (DMF), diglyme, and decalin, on the tricyclene–camphene ratio resulting from the base-catalyzed decomposition of camphor tosylhydrazone (I). In addition, the dependence of the product distribution on the relative amount of base used, as well as the effect of ions other than sodium, was studied. The most important data obtained in this investigation are: (1) at low concentrations of sodium bases in aprotic solvents tricyclene (II) appears to be generated predominantly from a cationic intermediate; (2) camphene (III) formation is favored at lower sodium base concentration in aprotic solvents, and tricyclene (II) formation is favored in protic solvents at high base concentration; (3) camphene (III) formation is favored in aprotic solvents of higher polarity, other factors being equal; and (4) aluminum and, to a lesser extent, lithium bases lead to camphene (III) formation in aprotic solvents and this effect appears to be independent of solvent polarity.

Effect of Solvent Polarity and Base Concentration

During our initial investigation on the base-catalyzed decomposition of camphor tosylhydrazone (I) in aprotic solvents[11] we observed a lack of reproducibility in the tricyclene–camphene ratio when 1 equiv (±5%) of a nonaluminum-containing base was used. Considering the earlier observation,[8] an increase in the relative amount of carbonium ion product (camphene) was expected in the presence of less than 1 equiv of base. This hypothesis was tested by treating camphor tosylhydrazone (I) with increasing amounts of sodium hydride in diglyme. At low sodium hydride concentration (0.25, 0.50, and 0.75 equiv) camphene (III) was found in abundance. However with 1.00 equiv of base, tricyclene (II) becomes the major product, and with 1.25 or more equiv, II is the only hydrocarbon formed. Essentially the same results were obtained using sodium methoxide as the base even though the reaction of this with the tosylhydrazone I yields 1 equiv of methanol. These results and the ones which follow are summarized in Table I.

From the results obtained using sodium hydride and methoxide in diglyme it is clear that higher concentrations of base lead to increased amounts of II relative to III.[12] The total yield of hydrocarbon products was determined by the limiting reagent and in all cases shown in Table I the combined yield of camphene and tricyclene amounted to 90–95%. In several experiments aliquots were taken at regular intervals and although the total yield increased with time, the ratio of tricyclene to camphene remained constant within experimental error (±3%). This constancy of product ratio is in complete accord with the proposed mechanism of the reaction,[4] for which *p*-toluenesulfinate is believed to be lost from the conjugate base Ia of the tosylhydrazone in the rate-determining step; the resulting diazo compound decomposes rapidly with or without the aid of a proton.

The effect of polarity of aprotic solvents was then investigated in the same type of experiment, *i.e.*, varying the amount of base in an orderly fashion. The results from these experiments are shown in Table I. It can be seen that, all other factors being equal, camphene (III) formation is favored in the more polar DMF and tricyclene (II) formation is favored in the less polar decalin. Moreover, the experiments in which sodium methoxide and DMF were used led to a lower tricyclene–camphene ratio than those using sodium hydride in the same solvent. The effect of the equivalent of methanol in the more polar solvent was apparent.

Although solvent polarity is a major factor in determining the tricyclene–camphene ratio, the relative amount of base present is even more important. The results of three additional experiments proved this point. First, camphor tosylhydrazone (I) was decomposed with 5 equiv of sodium hydroxide in diglyme and tricyclene (II) was produced exclusively and quantitatively. The 1 equiv of liberated water with its unequivocal high proticity seemingly did not contribute a proton to the formation of a cation. Second and similar to the first experiment, decomposition of I with 10 equiv of sodium methoxide in diglyme containing 40 equiv of water gave only a trace (*ca.* 0.3%) of camphene (III), the remainder being II. The water (20 mmoles; 360 mg) constituted about 8% of the solvent by volume. Therefore this last result differs

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[9] K. B. Wiberg and J. M. Lavanish, *J. Am. Chem. Soc.*, **88**, 365 (1966).

[10] Personal communication from Professor Wiberg. See also K. B. Wiberg and J. M. Lavanish, *ibid.*, **88**, 5272 (1966); F. Cook, H. Shechter, J. Bayless, L. Friedman, R. L. Foltz, and R. Randall, *ibid.*, **88**, 3870 (1960).

[11] R. H. Shapiro, *Tetrahedron Letters*, 3401 (1966).

[12] Camphene and tricyclene are not interconverted under the reaction conditions, *i.e.*, with added sodium *p*-toluenesulfinate and base.

considerably from the earlier report that 1.25% added water is enough to cause a reversal of the predominant product.[8] Finally, I was decomposed with sodium methoxide in 2-methoxyethanol, which by analogy should be considered aprotic.[5] The tricyclene–camphene ratio obtained with 1.00 equiv of base was 20:80, whereas with 5.00 equiv, the ratio became 60:40, a result which demonstrates not only the severe influence of the base concentration, but also that *2-methoxyethanol is a protic solvent.*[4]

The most serious problem connected with the interpretation of some of the earlier results obtained in this field is the lack of consideration of the effect of base concentration. Bamford and Stevens[3] used an average of about 2 equiv of base in their reactions, whereas Powell and Whiting[4] used an average of more than 4 equiv of base. Considering our results and the one referred to earlier[8] it is clear that Whiting's experiments[4] would favor the formation of tricyclene.

Since less than 1 equiv of base in an aprotic solvent leads to larger relative amounts of camphene (III), presumably *via* a cationic intermediate, a proton must originate from the unreacted tosylhydrazone as has been postulated previously.[8] We tested this hypothesis in two ways. The first method was to decompose I with varying amounts of sodium methoxide in diglyme containing 40 equiv of deuterium oxide (99.7% isotopic purity).[13] If the hypothesis were correct then the camphene (III) generated in the reaction would be monodeuterated. The results of these experiments are shown in Table II and it can be seen that III produced under these conditions is 80 ± 2% d_1 species. The theoretical deuterium atom incorporation is about 97.5%. Two explanations can be offered for the low deuterium incorporation: (1) not all of the camphene (III) is generated from a cationic intermediate which is dependent on a proton for its formation, and (2) the selectivity of the diazocamphane (IV) for hydrogen is seven times that for deuterium. An isotope effect of about this magnitude was also noted by Wiberg in a similar investigation[10] and because the amount of deuterium incorporation does not appear to be dependent on base concentration, explanation 2 is more reasonable.

Table II. Reaction of Camphor Tosylhydrazone with Sodium Methoxide in the Presence of Deuterium Oxide (40 equiv)

NaOMe equiv	Amount of monodeuterated tricyclene, %	Amount of monodeuterated camphene, %	II:III ratio,[b]
0.75	64	79	35:65
2.00	25	81	57:43
4.00	8	82	92:8
10.00	6	*a*	99.7:0.3

[a] Low yield of camphene precluded collection. [b] Total yield of hydrocarbons was >95% based on limiting reagent.

The second method was to label the tosylhydrazone I with deuterium on the nitrogen attached to the sulfonyl group and decompose the labeled compound with less than 1 equiv of sodium hydride in diglyme. The results from this experiment agreed qualitatively with those discussed above, but quantitative correlations were not possible because several attempts to prepare the labeled tosylhydrazone led to products of poor isotopic purity (see Experimental Section). For example, tosylhydrazone which analyzed as 20% d_1 gave camphene containing 14% of the monodeuterated species, *i.e.*, 70% incorporation. Since the reaction of tosylhydrazone with less than 1 equiv of sodium hydride may also show a large primary isotope effect, *i.e.*, H_2 is formed in preference to HD, no quantitative correlation could be made at this time.[14]

The results from these deuterium labeling experiments (Table II) shed some light on the nature of the intermediate leading to tricyclene (II).[13] The tricyclene (II) was collected from the experiments employing deuterium oxide and increasing amounts of sodium methoxide. In the reaction for which 0.75 equiv of base was used, 64% of the tricyclene contained one deuterium atom. At higher concentrations of base the amount of deuterium incorporation decreased dramatically. The reaction of I containing 20% d_1 with sodium hydride (0.75 equiv) gave tricyclene containing 11% d_1, or a 55% incorporation of deuterium.

The effect of the sodium ion was tested by decomposing I with 0.5 equiv of sodium methoxide in diglyme with added sodium acetate. Two experiments, one using 0.5 equiv of sodium acetate and the other using 2.00 equiv, were performed. The per cent of tricyclene (II) was 42 and 40%, respectively, compared to 41% with no added sodium source. Therefore the anionic portion of the base is responsible for the high tricyclene–camphene ratio at high base concentrations.

These results strongly indicate that tricyclene is generated from two different intermediates depending on the base concentration. At low concentration (less than 1 equiv) a cationic species intervenes, whereas at high concentrations II results from a transannular carbon–hydrogen insertion reaction of an intermediate carbene. We propose the mechanism shown in Figure 1 to explain this behavior.

The key step in the proposed mechanism is the equilibrium between diazocamphane and its corresponding diazonium ion. When less than 1 equiv of base is used there will be an excess of methanol pushing the reaction in the direction of the diazonium ion, following the law of mass action. Conversely, in the presence of excess base the equilibrium will favor the diazo compound. Moreover, more polar solvents would favor the ion in the equilibrium. Under the relatively severe reaction conditions both the diazo and diazonium intermediates can lose nitrogen to give a carbene or carbonium ion, which go to products; the diazonium intermediate could also go directly to products.[13] The tricyclene formation from a cation is analogous to the formation of bicyclobutane from a cation,[8,9] but the rearrangement of a carbonium ion to camphene (III) is not consistent with the results from the recent investigations on poorly solvated carbonium ions, for which rearrangement is reported to be minimized.[15]

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[13] For a preliminary communication describing this aspect of the investigation see R. H. Shapiro, J. H. Duncan, and J. C. Clopton, *J. Am. Chem. Soc.*, **89**, 471 (1967).

[14] If the isotope effect of conjugate base formation is of the same order of magnitude as the diazo–diazonium reaction, the value of 70% deuterium incorporation is meaningful. We are presently conducting experiments to measure the isotope effect, if any, of this reaction.

[15] (a) A. T. Jurewicz, J. H. Bayless, and L. Friedman, *J. Am. Chem. Soc.*, 87, 5788 (1965); (b) J. H. Bayless, F. D. Mendicino, and L. Friedman, *ibid.*, **87**, 5791 (1965).

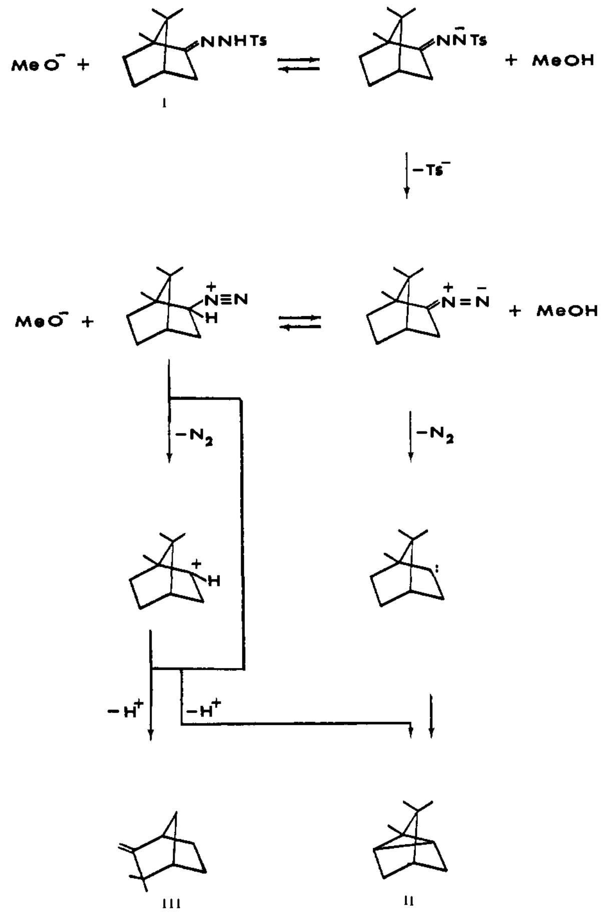

Figure 1.

For reactions run with sodium hydride in decalin, Kirmse, von Bülow, and Schepp recently proposed that a vinyl anion is the intermediate in the decomposition of various tosylhydrazones to olefins.[16] A similar proposal had been previously invoked by Fischer, Pelah, Williams, and Djerassi for the olefin formation resulting from the reaction of some steroidal tosylhydrazones with excess lithium aluminum hydride.[17] The latter group showed that a deuterium atom was incorporated when the reaction mixture is decomposed with deuterium oxide whereas the former workers performed no corresponding experiment. Kirmse's group did, however, decompose both N-d_1-acetone and 1,1,1,3,3,3-d_6-acetone tosylhydrazone with sodium hydride in decalin. They reported 2-d_1-propene and 1,1,1,3,3-d_5-propene as the products, but these products are also in complete accord with a cationic mechanism. Since these workers used a sevenfold excess of base which according to our results should give a carbene intermediate, these results are not consistent with ours. When our reaction mixtures are decomposed with deuterium oxide, no deuterium is incorporated.

Effect of Ions Other Than Sodium

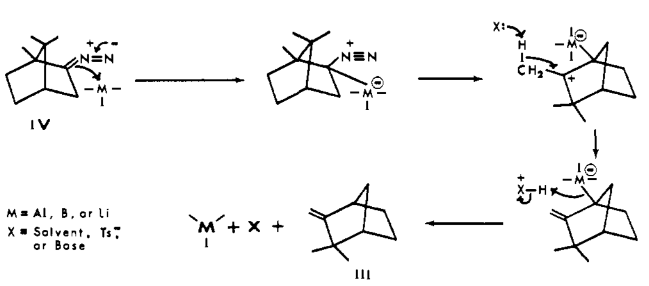

Figure 2.

We have previously reported, in a preliminary communication, the effect of trivalent metal cations on the decomposition of camphor tosylhydrazone (I).[11] We have now compared the effect of aluminum-containing bases with those containing lithium and silver. The results of these experiments are summarized in Tables III, IV, and V.

Table III. Decomposition of Camphor Tosylhydrazone with Aluminum Isopropoxide—Per Cent of Tricyclene Formed

	Tricyclene formed, %		
	Aluminum isopropoxide, equiv[a]		
Solvent	1.0	3.0	15.0
Diglyme	50	54	50
Decalin	50	50	53

[a] Equivalents of aluminum isopropoxide per millimole of camphor tosylhydrazone.

Table IV. Decomposition of Camphor Tosylhydrazone with Lithium Hydride in Diglyme

Base, equiv	1.0	2.0	10.0
Tricyclene,[a] %	40	45	83

[a] Values are ±3% and are the averages of at least five experiments.

Table V. Decomposition of Camphor Tosylhydrazone with Silver Carbonate in Diglyme

Base, equiv	0.5	1.0	5.0
Tricyclene, %	63	76	99

Camphor tosylhydrazone (I) decomposes in the presence of freshly distilled aluminum isopropoxide in diglyme or decalin to yield about equal amounts of tricyclene (II) and camphene (III), and this ratio is unaffected by increasing the base concentration to a 15-fold excess (Table III). This result is in accord with the previous report that in the reaction of I with lithium aluminum hydride the II:III ratio is not changed by varying the concentration of base, the solvent, or the reaction temperature.[11] The explanation offered is that the trivalent metal cation can act as a Lewis acid and form an intermediate which resembles a carbonium ion in its behavior and give camphene (III) as a major product. The proposed mechanism is shown in Figure 2.[11]

In the earlier investigation concerned with metal species acting as Lewis acids, it was assumed that a lithium base would behave the same way as a sodium base.[11] It was found, however, during the present investigation that this was only partly true. Indeed, the tricyclene–camphene ratio increased dramatically with increasing base concentration (see Table IV), but even with 10 equiv of base the camphene (III) still

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(16) W. Kirmse, B.-G. von Bülow, and H. Schepp, *Ann.*, **691**, 41 (1966).

(17) M. Fischer, Z. Pelah, D. H. Williams, and C. Djerassi, *Ber.*, **98**, 3236 (1965).

constituted 17% of the hydrocarbon mixture. Thus the lithium ion (or its equivalent) with its high charge density may also act as a Lewis acid in this system, but not as strongly as an aluminum species.

Table V shows the per cent of tricyclene obtained from the reaction of I with silver carbonate in diglyme. The yields from this reaction were only fair (20–30%), unreacted starting material being recovered. It can readily be seen in the table that the silver base behaves very much like the sodium bases, and it apparently cannot participate as a Lewis acid presumably because of its size.

In conclusion, the products (and intermediates) from the base-catalyzed decomposition of camphor tosylhydrazone (I) are completely dependent on: (1) the concentration of base, (2) the polarity of the aprotic solvent, and (3) the nature of the metal ion on the base. Tricyclene (II) can apparently arise by way of a cation or carbene and camphene (III) can be generated from a cation or the Lewis acid complex, which can be viewed as a metal ion coordinated to a carbene.

Experimental Section

Decomposition of Camphor Tosylhydrazone (I) with Sodium Methoxide. Camphor tosylhydrazone (I)[3] (320 mg; 1.0 mmole) was dissolved in 5 ml of diglyme (distilled from sodium hydride), decalin (distilled), or DMF (distilled), and the desired amount of sodium methoxide was added. The reaction vessel was protected from moisture, and the mixture was heated at 140° until the evolution of nitrogen subsided. The results were reproducible with respect to the II–III ratio and total yield whether or not the reaction was initiated under an atmosphere of nitrogen. Exactly the same procedure was followed using aluminum isopropoxide or silver carbonate as the base.

Decomposition of Camphor Tosylhydrazone (I) with Sodium Hydride. The same procedure as above was followed except the tosylhydrazone (I) was added to the hydride in solvent. When the evolution of hydrogen subsided, the vessel containing the reaction mixture was immersed in the preheated oil bath. Exactly the same procedure was followed using lithium hydride as the base. Hydrogen evolution was quantitative as measured by the water displacement method.

Control Experiments. Thermal Stability of Camphor Tosylhydrazone (I). I was heated in diglyme at 140° for 1 hr. No tricyclene or camphene could be detected by gas chromatography. The same results were obtained when camphor tosylhydrazone was heated in diglyme in the presence of sodium *p*-toluenesulfinate or sodium carbonate under the same conditions.

Stability of Tricyclene and Camphene. Mixtures of II and III were heated in diglyme alone, with excess base and/or sodium *p*-toluenesulfinate, and no change was noted in the composition before and after the treatment.

Attempted Preparation of N-d_1-Camphor Tosylhydrazone. Camphor tosylhydrazone (I) was dissolved in a dilute solution of sodium methoxide in methanol-*d* and D_2O was added to the cloud point at about 60°. The solution was heated at reflux for 2 hr and then cooled to room temperature whereupon crystals of I were deposited. These were collected by filtration, and the exchange process was repeated twice more. The final exchange product was dried at reduced pressure for 12 hr. Mass spectral analysis showed the tosylhydrazone to be about 80% d_0 and 20% d_1.[18] Since no d_2 species was present, it was assumed that no exchange of the ring hydrogens occurred. Several attempts employing longer reaction times led to similar results.

I was also allowed to react with 1 equiv of methyllithium at −78° for 2 hr, and then the reaction was quenched with D_2O. Isolating the tosylhydrazone with ether led to a product with about the same isotopic purity as above.

Isolation of Products. In the reactions employing diglyme or DMF as the solvent, the cooled reaction mixture was poured into water and petroleum ether was added. When less than 1 equiv of base was used, the mixture was filtered, and the unreacted tosylhydrazone was collected. The petroleum ether layer was washed at least six times with an equal volume of water to remove all of the reaction solvent, dried over sodium sulfate, and concentrated to a small volume on a rotary evaporator.

The reactions which were conducted in decalin were centrifuged and analyzed directly. A solution of camphor tosylhydrazone (I) in decalin does not analyze for tricyclene (II) or camphene (III).

Analysis of Products. The petroleum ether or decalin solution of products was analyzed by a Varian Aerograph Model 202-B gas chromatograph using helium as the carrier gas. For analytical purposes a 5 ft × $^1/_8$ in. FFAP (15%) on Chromosorb W column heated to 75° and a gas flow of 20 cc/min were used. For preparative purposes a 5 ft × 0.25 in. FFAP (15%) on Chromosorb W column heated to 100° and a gas flow of 25 cc/min were used. The retention times of tricyclene and camphene were 4.2 and 5.8 min, respectively, on the analytical column and 4.6 and 6.2 min, respectively, on the preparative column.

The deuterated tricyclene and camphene were analyzed for isotopic content with a CEC 21-103C mass spectrometer equipped with an all-glass inlet system.

The yields of products were determined by using *o*-xylene as an internal standard and correcting for the different mode of response in the gas chromatograph detectors. The areas under the peaks were measured with a Disc integrator.

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[18] We thank Dr. A. M. Duffield for determining the mass spectra using a direct inlet system of an Atlas CH-4 mass spectrometer.