

*Anal.* Calcd for  $C_{37}H_{21}N_3O_7S$ : C, 68.19; H, 3.25; N, 6.45; S, 4.92. Found: C, 68.16; H, 3.27; N, 6.47; S, 4.93.

Chromatography of a benzene solution of the above-described complex on basic alumina (grade II), followed by crystallization from ether, afforded the free thiophene 10 as deep red needles, mp 198–202°,  $\lambda_{max}^{benzene}$  513 m $\mu$  ( $\log \epsilon$  8700).

*Anal.* Calcd for  $C_{24}H_{16}S$ : C, 85.67; H, 4.80; S, 9.53. Found: C, 85.61; H, 4.88; S, 9.48.

Adduct of 10 with Tetracyanoethylene. 1,4-Diphenyl-1,4-epithio-2,2,3,3-tetracyano-1,2,3,4-tetrahydroanthracene (48).—A solution of thiophene 10 in benzene was prepared by alumina chromatography of its 2,4,7-trinitrofluorenone complex (0.929 g). To this red solution, tetracyanoethylene was added until the color vanished. Removal of the solvent *in vacuo*, followed by crystallization from methylene chloride–petroleum ether (Skelly F), afforded adduct 48 (0.548 g, 83%) as colorless plates, mp 268–280° dec.

*Anal.* Calcd for  $C_{30}H_{16}N_4S$ : C, 77.57; H, 3.47; N, 12.06; S, 6.90. Found: C, 77.40; H, 3.65; N, 11.78; S, 6.84.

A solution of thiophene 10 and N-phenylmaleimide in benzene

gave no indication of the formation of an adduct (tlc) after standing at room temperature for 22 hr.

Registry No.—9, 18929-57-2; 10, 18929-58-3; 10, (2,4,7-trinitrofluorenone complex), 18929-59-4; 15, 18929-60-7; 16, 18929-61-8; 17, 18929-62-9; 18, 18944-83-7; 19, 18927-54-3; 20, 18927-55-4; 21, 18927-56-5; 22, 18927-57-6; 23, 18927-58-7; 24, 18927-59-8; 25, 18927-60-1; 26, 18927-61-2; 27, 18927-62-3; 28, 18927-63-4; 34, 18927-64-5; 35, 18927-65-6; 36, 18927-66-7; 37, 18927-67-8; 40, 18927-68-9; 42, 18927-69-0; 43, 18944-84-8; 45, 18927-70-3; 46, 18944-85-9; 47, 18927-71-4; 48, 18944-86-0.

**Acknowledgment.**—We are grateful to the National Science Foundation for a grant in support of this work.

## Bicyclic Ketones. I. Decomposition of Terpene Ketone Tosylhydrazones

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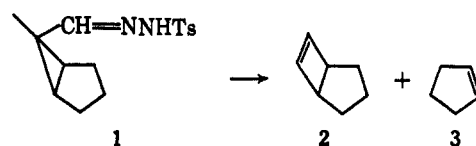
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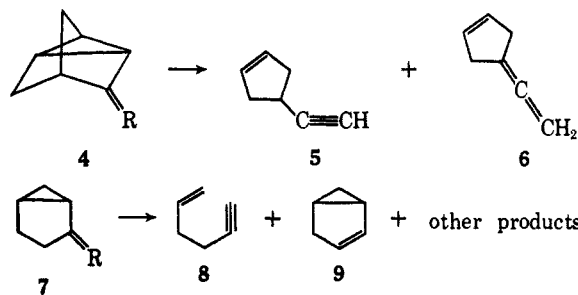
Bicyclic ketone tosylhydrazone sodium salts of the 3.1.0 and 4.1.0 systems decompose to hydrocarbons isomeric with the generated carbene. The structure of these hydrocarbons is related to the position of the cyclopropyl ring relative to the carbenoid carbon.  $\alpha$ -Ketocyclopropanes give acetylenic alkenes as major products while  $\beta$ -ketocyclopropanes hydrogen abstract giving bicyclic alkenes. No evidence has been found for the formation of insertion or ring-expansion products.

The preparation of bi- and tricyclic systems from carbenoid precursors is an established preparative reaction.<sup>2</sup> The decomposition of sodium salts of tosylhydrazones (the Bamford–Stevens reaction<sup>3</sup>) has led to a large variety of ring-expanded,<sup>4</sup> ring-contracted,<sup>5</sup> or insertion<sup>6</sup> products depending upon the structure of the starting material, and, as recently found, both the solvent<sup>7</sup> and the base concentration.<sup>8</sup> Evidence has been presented<sup>7,8</sup> that these products are produced as a result of either a carbenoid or cationic precursor.

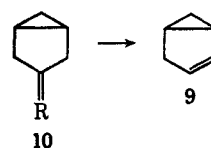
Simple cyclopropylcarbinyl systems have been examined in some detail.<sup>5a,6,7</sup> The nature of the products appears to depend more on the position of the cyclopropane ring relative to the carbenoid carbon than on any other factor. Thus although bicyclo[3.1.0]hexane-6-endo-carboxaldehyde tosylhydrazone (1) gives *cis*-bicyclo[3.2.0]hept-6-ene (2) and cyclopentene (3),<sup>9a</sup> incorporation of the carbenoid carbon into a bicyclic system gives no ring-expansion products.<sup>9</sup>



The primary products from such bicyclic  $\alpha$ -cyclopropylcarbenes are formed by a fragmentation reaction as observed by Cristol and Harrington<sup>9b</sup> and Lemal and Fry<sup>9c</sup> for nortricyclanone (4) (R = O) and by Freeman and Kuper<sup>9a</sup> for bicyclo[3.1.0]hexan-2-one (7) (R = O).



Freeman and Kuper<sup>9a</sup> have also examined bicyclo[3.1.0]hexan-3-one (10) (R = O). In this instance, where the cyclopropyl is  $\beta$  to the generated carbene, the only product is formed as a result of hydrogen abstraction (9).



(1) Abstracted from the M.S. Theses of R. H. Chung and Y. N. Vaishnav and the Ph.D. Thesis of C. C. Shroff, Howard University, 1968.

(2) See, for example, W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964; E. Chinopoulos, *Chem. Rev.*, **63**, 235 (1963).

(3) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952); J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959).

(4) J. W. Wilt, J. M. Kosturik, and R. C. Orowski, *J. Org. Chem.*, **30**, 1052 (1965).

(5) (a) L. Friedman and H. Schechter, *J. Amer. Chem. Soc.*, **82**, 1002 (1960); (b) J. Meinwald, J. W. Wheeler, A. A. Nimetz, and J. S. Liu, *J. Org. Chem.*, **30**, 1040 (1965).

(6) H. M. Frey and I. D. R. Stevens, *Proc. Chem. Soc.*, 144 (1964).

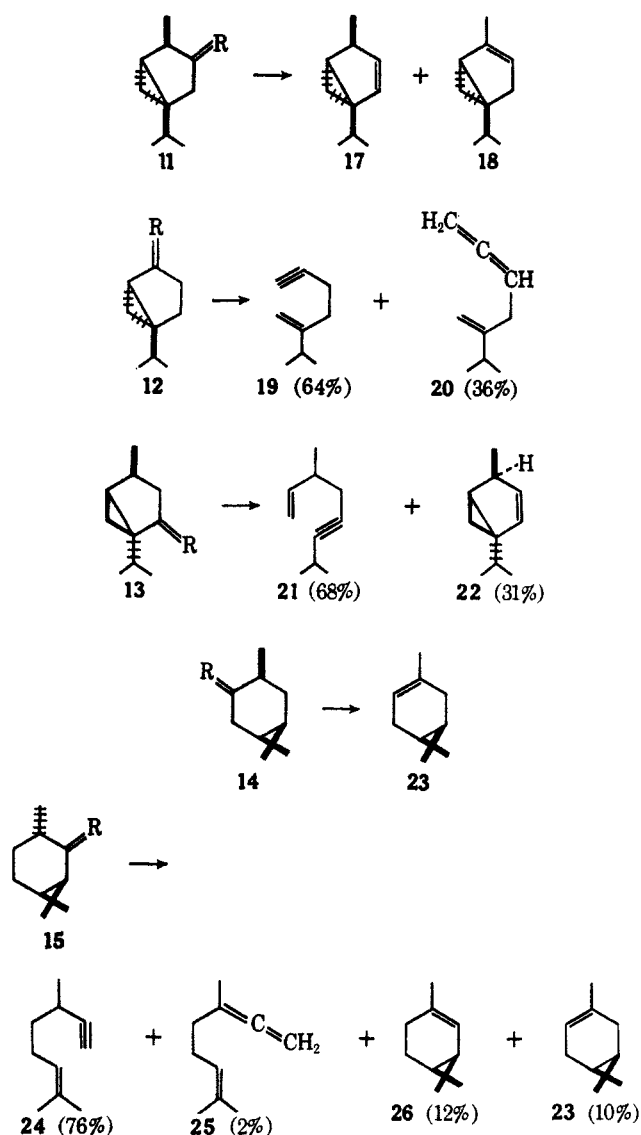
(7) J. A. Smith, H. Schechter, J. Bayless, and L. Friedman, *J. Amer. Chem. Soc.*, **87**, 659 (1965); K. B. Wiberg and J. M. Lavanish, *ibid.*, **88**, 365 (1966).

(8) R. H. Shapiro, J. H. Duncan, and J. C. Clopton, *ibid.*, **89**, 471, 1442 (1967).

(9) (a) P. K. Freeman and D. G. Kuper, *J. Org. Chem.*, **30**, 1047 (1965); (b) S. J. Cristol and J. K. Harrington, *ibid.*, **28**, 1413 (1963); (c) D. M. Lemal and A. J. Fry, *ibid.*, **29**, 1673 (1964).

We have examined a series of cyclopropyl ketones in which the cyclopropyl ring is either  $\alpha$  or  $\beta$  to the generated carbenoid center with other alkyl substituents attached to the rings. These include the more complicated bicyclo[3.1.0]hexane system and the bicyclo[4.1.0]heptane system. Specifically, we have examined the thermal decomposition of the sodium salts ( $R = \text{NN-SO}_2\text{C}_6\text{H}_4\text{CH}_3\text{-}p \text{ Na}^+$ ) of the tosylhydrazones of thujone (*cis*-4-methyl-1-isopropylbicyclo[3.1.0]hexan-3-one) (**11**,  $R = \text{O}$ ), sabina ketone (5-isopropylbicyclo[3.1.0]hexan-2-one) (**12**,  $R = \text{O}$ ), dihydroumbellulone (*trans*-4-methyl-1-isopropylbicyclo[3.1.0]hexan-2-one) (**13**,  $R = \text{O}$ ), 4-isocaranone (*cis*-4,7,7-trimethylbicyclo[4.1.0]heptan-3-one) (**14**,  $R = \text{O}$ ), and 2-caranone (carone) (*trans*-3,7,7-trimethylbicyclo[4.1.0]heptan-2-one) (**15**,  $R = \text{O}$ ) (Scheme I).

SCHEME I



The bicyclic ketones investigated have all been prepared previously. Details are included in the Experimental Section. Most of the nuclear magnetic resonance spectra have not been reported. They will be examined in detail in a subsequent paper. Pyrolysis of the sodium salts of the tosylhydrazones followed the general procedure of Friedman and Schechter,<sup>5</sup> all

volatile components being collected in a series of cold traps. Analysis of the products was then accomplished by gas chromatography and separation was accomplished using the same procedure. Thujone tosylhydrazone sodium salt (**11**,  $R = \text{NN-Ts}$ ) gave a 1:1 mixture of two major components plus a small amount of another component. Component A was identified as  $\beta$ -thujene (**17**) by gas chromatographic comparison with an authentic sample.<sup>10</sup> Component B was identified as  $\alpha$ -thujene (**18**) by gas chromatographic comparison with an authentic sample.<sup>10</sup> Although the similar retention times of the two components precluded separation, the infrared spectra and nmr spectra of the mixture are consistent with a 1:1 mixture of  $\alpha$ - and  $\beta$ -thujene. Reduction of the mixture with a platinum oxide catalyst gave predominantly one material which was identical with thujane (**16**).<sup>10</sup>

Sabina ketone tosylhydrazone sodium salt (**12**,  $R = \text{NN-Ts}$ ) gave a two-component mixture in a ratio of 64:36. Separation of these components by gas chromatography gave 5-isopropylhex-5-en-1-yne (**19**) and 5-isopropylhexa-5,2,1-triene (**20**). The assigned structure is based upon the infrared spectra and the nmr spectra of these components plus the fact that no skeletal isomerization had occurred. This was established by catalytic reduction of the mixture to a single component, 2,3-dimethylheptane. Dihydroumbellulone tosylhydrazone sodium salt (**13**,  $R = \text{NN-Ts}$ ) gave two components, 2,6-dimethyloct-7-en-3-yne (**21**) and *trans*-1-isopropyl-4-methylbicyclo[3.1.0]hex-2-ene (umbellulene) (**22**). The first component was identified on the basis of its infrared and nmr spectra as well as by its reduction to 2,6-dimethyloctane. The position of the acetylene was established by ozonolysis which gave isobutyric acid. The second component was identified on the basis of its infrared and nmr spectra and by direct comparison to an authentic sample.<sup>10</sup>

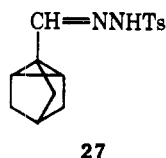
4-Isocaranone tosylhydrazone sodium salt (**14**,  $R = \text{NN-Ts}$ ) gave a single component identified as 3,7,7-trimethylbicyclo[4.1.0]hept-3-ene ( $\Delta$ -3-carene) (**23**) on the basis of a comparison with an authentic sample. 2-Caranone tosylhydrazone sodium salt (**15**,  $R = \text{NN-Ts}$ ) gave a four-component mixture. Component 1 was isolated and identified as 3,7-dimethyloct-6-en-1-yne (**24**) on the basis of infrared and nmr spectra, carbon-hydrogen analysis and reduction to 3,7-dimethyloctane. The structure of the other components was determined as follows. Treatment of **24** with sodium methoxide gives a partial isomerization to an allene contained in the original mixture. This is presumed to be **25**. The other two components had retention times identical with the mixture obtained from treatment of  $\Delta$ -3-carene (**23**) with potassium

(10) We thank Professor R. H. Eastman of Stanford University for providing authentic samples of  $\alpha$ -thujene,  $\beta$ -thujene, thujane and umbellulene.

*t*-butoxide. Brown and Suzuki<sup>11</sup> have established this mixture to consist of  $\Delta$ -3-carene (**23**) and  $\Delta$ -2-carene (3,7,7-trimethylbicyclo[4.1.0]hept-2-ene) (**26**). Treatment of the tosylhydrazone of 2-caranone with more than 1 equiv of sodium methoxide followed by pyrolysis gave a mixture richer in **23** and **25** consistent with the previous observation by Freeman and Kuper<sup>9a</sup> and Cristol and Harrington<sup>9b</sup> that such acetylenes isomerize to allenes in the presence of excess base.

These products reveal that the original finding of Freeman and Kuper,<sup>9a</sup> Cristol and Harrington,<sup>9b</sup> and Lemal and Fry<sup>9c</sup> is a general phenomenon. Cyclopropyl ketones which possess the carbonyl group  $\alpha$  to the cyclopropane ring lead predominantly to fragmented acetylenic products while cyclopropyl ketones which do not have a conjugated carbonyl group do not fragment (or ring expand) but form products originating from hydrogen abstraction. No insertion products have been found in any of these reactions.

The wide variety of substituted alkyl groups available in these bicyclic ketones (bridgehead isopropyl in sabina ketone (**12**, R = O),  $\alpha$ -isopropyl in dihydroumbellulone (**13**, R = O) and  $\beta,\beta$ -dimethyl in carone (**15**, R = O) indicates that the alkyl substitution on the cyclopropane ring is of very little importance in determining the mode of decomposition. Also, since carone (**15**, R = O) is a 4.1.0 bicyclic system while sabina ketone (**12**, R = O) and dihydroumbellulone (**13**, R = O) are 3.1.0 bicyclic systems, the change from a 5,3 fused system to a 6,3 fused system makes little difference. In fact, since simpler cyclopropyl carbonyl systems ring expand<sup>4,5a,9a</sup> and cyclopropyl which is a part of a bridgehead position (**27**) gives no cleavage products,<sup>12</sup> the major factor is the position of the cyclopropane ring relative to the carbenoid carbon being generated.



Our results parallel those of Freeman and Kuper<sup>9a</sup> and Cristol and Harrington<sup>9b</sup> even though their diazo compounds are generated in a different manner. Their diazo compounds were obtained from the tosylhydrazone and sodium methoxide in an aprotic solvent whereas we performed the sodium salt and pyrolyzed it in a Celite diluent.<sup>5,7a</sup> This method of preparation, the transient color, the transient infrared absorption band of the diazo compound, and the absence of any products containing a rearranged carbon skeleton indicates that cationic intermediates are not an important factor in this system.

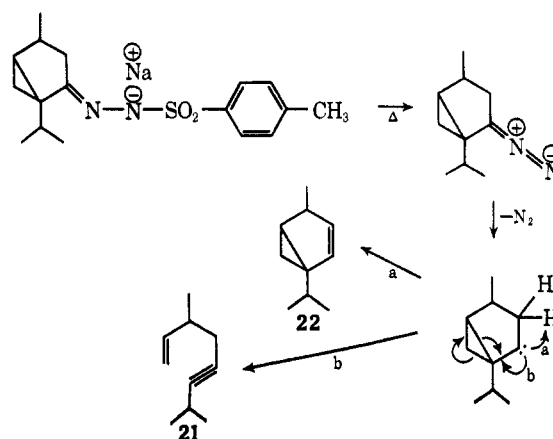
Allenes **20** and **25** presumably arise from isomerization of acetylenes **19** and **24**. The small amount of isomerization of **24** to **25** relative to the results of Freeman and Kuper<sup>9a</sup> and Cristol and Harrington<sup>9b</sup> might be attributed to the difference in decomposition procedures.

This, however, is not the case since a large amount of allene **20** is formed from the decomposition of the sodium salt of sabina ketone tosylhydrazone. No allene is formed from the more stable disubstituted acetylene **21**. This large variation in allene formation cannot be attributed to base concentration since variation of base concentration had only a small effect on the acetylene–allene ratio and this ratio was reproducible. The relative abundance of allene appears to be related to the acetylene–allene stability.

It is surprising that no  $\alpha$ -hydrogen abstraction occurs with sabina ketone since it is a major mode of decomposition in both dihydroumbellulone and 2-caranone both of which are also  $\alpha$ -cyclopropyl ketones. It is also surprising that hydrogen abstraction is so specific for 4-isocarane (>99%  $\Delta$ -3-carene) since it is not specific for thujone.

The formation of the primary products can be rationalized in the manner given in Scheme II. The

SCHEME II



absence of any appreciable insertion or ring-expansion products indicates that conjugation with the cyclopropyl ring in a bicyclic system provides an easier pathway for decomposition to olefinic products. This pathway plus  $\alpha$ -hydrogen abstraction prevails over all alternate processes.

### Experimental Section

Melting points were taken on a Thomas–Hoover melting point apparatus in open capillaries and are uncorrected. Infrared spectra were taken on a Perkin–Elmer Model 137B Infracord with sodium chloride optics using polystyrene as a calibration. Nuclear magnetic resonance spectra were taken on a Varian A-60 spectrometer in carbon tetrachloride or deuteriochloroform with tetramethylsilane as an internal reference. Gas chromatography (including separations) was done on an Aerograph Model 661 flame ionization instrument using  $\frac{1}{8}$ -in. stainless steel columns. Elemental analysis were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

**Thujone (11, R = O).**—Thujone was obtained by fractional distillation of oil of cedar leaf American according to the procedure of Eastman and Winn.<sup>13</sup> Our material had bp 82.5–83° (16.5 mm) [lit.<sup>13</sup> bp 83.3–84.1° (17 mm)] and gave a single peak on gas chromatography (Butanediol succinate and Carbowax 1000): infrared 5.75  $\mu$  (C=O); the nmr spectrum showed no absorptions below  $\delta$  2.6.

**Sabina Ketone (12, R = O).**—Sabinene, obtained from oil of savin (Fritzsche) by distillation, was ozonized in pentane and decomposed with 30% hydrogen peroxide and 10% sodium hy-

(11) H. C. Brown and A. Suzuki, *J. Amer. Chem. Soc.*, **89**, 1933 (1967).

(12) J. W. Wilt, C. A. Schneider, H. F. Dabek, Jr., J. F. Kraemer, and W. J. Wagner, *J. Org. Chem.*, **31**, 1543 (1966).

(13) R. H. Eastman and A. V. Winn, *J. Amer. Chem. Soc.*, **82**, 5909 (1960).

dioxide. The alternate ozonolysis procedure of Criegee and Gunther<sup>14</sup> which uses tetracyanoethylene as an acceptor gave much poorer yields and a large amount of polymerized material. Our sabina ketone (9.4 g from 10 g of sabinene, 87%) had bp 87–89° (10 mm) [lit.<sup>14</sup> bp 89° (10.5 mm)]. Gas chromatography (15% Carbowax 1000, 5 ft ×  $\frac{1}{8}$  in.) indicated a purity of 98.5%: infrared 5.81 (C=O), 9.80  $\mu$  (cyclopropane); nmr  $\delta$  0.95 (doublet,  $J = 7$  cps), 1.00 (doublet,  $J = 7$  cps, area equal to eight protons), complex absorption at 1.1–1.8 (2 H) and an apparent singlet at 1.95 (4 H).

**Dihydroumbellulone (13, R = O).**—Umbellulone was extracted from oil of mountain laurel (Fritzsche) by the method of Wienhaus and Todenhöfer<sup>16</sup> and had bp 90–92° (10 mm) [lit.<sup>17</sup> bp 80° (5 mm)]: infrared 5.89 (C=O), 9.74  $\mu$  (cyclopropane); nmr  $\delta$  5.18 (1 H, C=CH, broad singlet), 2.09 (3 H, CH<sub>2</sub>C=, doublet), 2.00 (1 H, -CH(CH<sub>3</sub>)<sub>2</sub>, septet), complex absorption 0.8–1.4 (9 H). Catalytic reduction with a Rh–Al<sub>2</sub>O<sub>3</sub> (5%) catalyst gave dihydroumbellulone, bp 75–78° (9 mm) [lit.<sup>16</sup> bp 78° (8 mm)]. Analysis by gas chromatography (15% Carbowax 1000, 5 ft ×  $\frac{1}{8}$  in.) showed an impurity estimated to be less than 2%. Catalytic reduction with PtO<sub>2</sub> as a catalyst gave 18% saturated alcohol (dihydroumbellulol) as well as dihydroumbellulone. The yield with Rh–Al<sub>2</sub>O<sub>3</sub> was 90%: infrared 5.81 (C=O), 9.93  $\mu$  (cyclopropane); the nmr spectrum was very similar to umbellulone except for the absence of the signal at 5.18 and the upfield shift of the unsaturated methyl group.

*Anal.* Calcd for C<sub>10</sub>H<sub>16</sub>O: C, 78.90; H, 10.59. Found: C, 78.96; H, 10.61.

**4-Isocarane (14, R = O)** was prepared by a procedure analogous to that of Brown and Suzuki.<sup>11</sup> Our material had bp 71° (4 mm) [lit.<sup>11</sup> bp 80–81° (5.3 mm)] in a 95% yield from the alcohol: infrared 5.85  $\mu$ ; the nmr spectrum showed no vinyl hydrogens and no absorptions below  $\delta$  2.4.

*Anal.* Calcd for C<sub>10</sub>H<sub>16</sub>O: C, 78.90; H, 10.59. Found: C, 79.27; H, 10.83.

**2-Caranone (15, R = O).**—Dihydrocarvone was prepared from *d*-carvone (Fritzsche) by the method of Wallach.<sup>18</sup> Dihydrocarvone hydrochloride was prepared from dihydrocarvone by the method of Klotz<sup>19</sup> and converted directly into 2-caranone by his procedure. Our material had bp 52–54° (0.5 mm) [lit.<sup>19</sup> bp 115–116° (15 mm)]; infrared 5.95  $\mu$  (C=O); the nmr spectrum showed no absorptions below  $\delta$  2.2.

**Thujone Tosylhydrazone (11, R = NNHTs).**—To a solution of thujone (1.52 g, 10 mmol) in methanol (5 ml) was added *p*-toluenesulfonylhydrazine (1.96 g, 10 mmol) in tetrahydrofuran (12 ml). The reaction mixture was stirred at room temperature for 48 hr under a static pressure of nitrogen.<sup>20</sup> The excess solvent was evaporated and the crude tosylhydrazone dried overnight in a vacuum desiccator. The crude solid so obtained was recrystallized from 3:2 ethanol–water giving thujone tosylhydrazone (2.36 g, 74%): mp 109.5–110.5°; infrared 6.05, 6.25  $\mu$ ; nmr similar to ketone with exception of 5 H at  $\delta$  7.3–8.3 (phenyl plus NH) and a singlet at  $\delta$  2.4 (3 H, CH<sub>3</sub>C=C).

*Anal.* Calcd for C<sub>17</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>S: C, 63.73; H, 7.54; N, 8.74; S, 10.00. Found: C, 64.09; H, 7.82; N, 8.69; S, 10.22.

**Sabina Ketone Tosylhydrazone (12, R = NNHTs).**—A mixture of *p*-toluenesulfonylhydrazine (12.6 g, 0.068 mol), sabina ketone (9.4 g, 0.068 mol) and *p*-toluenesulfonic acid (0.2 g, 0.0007 mol) in methanol was heated on a water bath at 45° for 10 min. After the flask was cooled to room temperature, the crystalline product was filtered and washed with cold petroleum ether. The yield was 23 g (80%). Recrystallization from 95% ethanol gave 20.5 g of mp 120–122° dec; infrared 6.09, 6.24  $\mu$ ; nmr similar to ketone with the exception of a new signal at  $\delta$  7.1–7.8 (5 H, quartet plus, phenyl and NH), singlet at 2.4 (3 H, CH<sub>3</sub>C=) and broadening of the original singlet at 1.95.

*Anal.* Calcd for C<sub>16</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>S: C, 62.73; H, 7.24; N, 9.14; S, 10.45. Found: C, 62.65; H, 7.27; N, 9.23; S, 10.66.

**Dihydroumbellulone Tosylhydrazone (13, R = NNHTs).**—To

a solution of *p*-toluenesulfonylhydrazine (6.00 g, 0.322 mol) in 55 ml of methanol, dihydroumbellulone (4.99 g, 0.325 mol) and *p*-toluenesulfonic acid (0.44 g, 0.0026 mol) were added all at once. The mixture was heated to 45° for 10 min. After the flask was cooled to room temperature, the crystalline product was filtered and washed with cold petroleum ether (bp 30–60°). The product [8.97 g (80%), mp 125–129° dec] was recrystallized from 95% ethanol giving 6.97 g: mp 128.5–130° dec; infrared 3.14, 6.04, 6.29  $\mu$ ; nmr similar to original ketone except for a new signal at  $\delta$  7.3–8.3 (5 H, quartet plus, phenyl and NH), and a singlet at 2.45 (3 H, CH<sub>3</sub>C=C).

*Anal.* Calcd for C<sub>17</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>S: C, 63.73; H, 7.55; N, 8.74; S, 10.00. Found: C, 63.77; H, 7.36; N, 8.70; S, 10.25.

**4-Isocarane Tosylhydrazone (14, R = NNHTs).**—To a solution of 18.6 g (0.1 mol) of *p*-toluenesulfonylhydrazine in methanol (40 ml) was added 4-isocarane (15.2 g, 0.1 mol). The solution was warmed a little and allowed to stand. The crystalline material which separated in 2 hr was filtered, dried and recrystallized from ethanol: yield, 24.0 g, 75%, mp 132–133°; infrared 6.16, 6.24  $\mu$ ; nmr similar to ketone except for the signals attributable to the tosyl and NH groups.

*Anal.* Calcd for C<sub>17</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>S: C, 63.73; H, 7.55; N, 8.74; S, 10.00. Found: C, 63.83; H, 7.73; N, 8.77; S, 10.16.

**2-Caranone Tosylhydrazone (15, R = NNHTs).**—To a solution of *p*-toluenesulfonylhydrazine (1.82 g, 10 mmol) in methanol (5 ml) was added carane (1.52 g, 10 mmol). To this mixture 10 mg of *p*-toluenesulfonic acid was added, and the reaction mixture allowed to stand. The crystalline material which separated when the flask was cooled was filtered (1.92 g, 60%). A second crop gave 0.06 g (20%), total yield 80%. The combined material was recrystallized from methanol giving material of mp 117–118°; infrared 6.15, 6.25  $\mu$ ; nmr similar to the ketone except for the signals attributable to the tosyl and NH group. The difference between the 9-methyl and 8-methyl groups has been reported as 22 cps while that of 2-isocarane tosylhydrazone has been reported as 26 cps.<sup>20</sup> We find a difference of 29 cps. Tosylhydrazone prepared by Brown's procedure<sup>20</sup> had the same melting point, did not depress the melting point of the first tosylhydrazone, and exhibited the same nmr spectrum.

*Anal.* Calcd for C<sub>17</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>S: C, 63.73; H, 7.55; N, 8.74; S, 10.00. Found: C, 63.56; H, 7.62; N, 8.61; S, 10.31.

**Decomposition of Thujone Tosylhydrazone Sodium Salt.**—The tosylhydrazone (3.2 g, 10 mmol) was dissolved in a minimum quantity of methanol (5 ml) and to this solution was added sodium methoxide (0.54 g, 10 mmol). The contents were warmed on a water bath at 40–45°. Traces of methanol were then removed at reduced pressure overnight. The solid was scraped off the sides of the flask, diluted with an equal amount of dry Celite and the mixture heated to 160° in an oil bath at reduced pressure (5 mm). The distillate was collected in a Dry Ice–methanol trap followed by another trap of the same type. The distillate (70%) showed absorption in the infrared spectrum at 3.29, 6.29, 7.24, 7.34, 7.60, 9.75, 12.85 and 13.46  $\mu$ . Gas chromatographic analysis on a 5 ft ×  $\frac{1}{8}$  in. 15% UCON SHO 5100 column showed two peaks in a 1:1 ratio. Hydrogenation of the crude mixture (0.10 g) on Adam's catalyst (PtO<sub>2</sub>) gave an uptake of 16.1 ml (99% of 1 mol). The reduced material was analyzed by gas chromatography 5% SE 30, 10 ft ×  $\frac{1}{8}$  in., 110° and showed two peaks identical in retention time (by peak enhancement) to an authentic sample of thujane<sup>21</sup> (27 min) and *cis*-1-methyl-4-isopropylcyclohexane (30 min).

The nmr spectrum of  $\beta$ -thujene<sup>22</sup> shows a complex quartet centered at  $\delta$  5.55 (2 H), multiplet at 2.5 (1 H), two doublets centered at 1.0 and 0.92 plus additional absorption in the region 0.8–1.6, the whole region equivalent to 13 H.  $\alpha$ -Thujene<sup>22</sup> shows absorption at 4.9 (broad singlet, 1 H), 2.3 (broad absorption, 2 H), 1.75 (broad singlet plus underlying, 4 H), 1.4 (complex absorption, 7 H). All but one absorption (at 5.6) of the crude decomposition mixture could be assigned to absorptions of  $\alpha$ - and  $\beta$ -thujene.<sup>22</sup> This absorption was due to a third component present in a small amount. It was collected but the small amount precluded identification. The mixture of  $\alpha$ - and  $\beta$ -thujene was analyzed as their almost identical retention times on a number of columns precluded their separation.

(21) Thujane was obtained from Professor R. H. Eastman of Stanford University. Wolff–Kishner reduction of thujone also gave the same material. (22)  $\alpha$ -Thujene was prepared by D. L. Forbess.  $\beta$ -Thujene was prepared by J. N. Lowe. Courtesy of R. H. Eastman.

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*Anal.* Calcd for  $C_{10}H_{16}$ : C, 88.16; H, 11.84. Found: C, 88.18; H, 11.82.

**Decomposition of Sabina Ketone Tosylhydrazone.**—The same procedure was used to prepare the sodium salt and decompose it as with thujone. The distillate which contained some methanol was analyzed by gas chromatography (15% UCON SHO 5100 on Chromosorb W). It indicated two minor components in addition to the two major ones. Preparative gas chromatography using the same column at 25° tediously gave a separation of two components. Component A (retention time 5.5 min) (36% of the mixture, 93% pure after isolation) was assigned structure **20** on the basis of the following data: infrared 5.12 (allene), 5.76, 6.09 (isolated double bond), 11.18  $\mu$  (terminal methylene group); nmr triplet centered at 5.0 (1 H,  $CH_2=C=CHCH_2-$ ), multiplet centered at 4.65 (4 H,  $CH_2=C=CH-$  and  $CH_2=C$ ), broad singlet at 2.70 (2 H, doubly allylic,  $C=CCH_2C=C$ ), multiplet centered at 2.25 (1 H,  $(CH_3)_2CH-$ ,  $J = 7$  cps) and doublet centered at 1.05 [6 H,  $J = 7$  cps,  $(CH_3)_2CH-$ ]. Component B (retention time 7.25 min) (64% of the mixture, 98.5% pure after isolation) was assigned structure **19** on the basis of the following data: infrared, 3.06, 4.73 (terminal acetylene), 11.2  $\mu$  (terminal methylene); nmr doublet centered at 4.72 (2 H,  $J = 5$  cps, terminal  $CH_2$ ), singlet at 2.25 (4 H, two allylic methylene groups), multiplet centered at 2.17 (1 H,  $CH_2CH(CH_3)C=$ ), broad singlet at 1.77 (1 H,  $HC\equiv C-$ ) and a doublet centered at 1.05 [6 H,  $J = 7$  cps,  $(CH_3)_2CH$ ].

The crude decomposed product was reduced on a platinum oxide catalyst. Analysis by gas chromatography (5% SE-30 on Chromosorb W, 45°) indicated one peak with a retention time of 7.1 min identical (by peak enhancement) with 2,3-dimethylheptane. Its infrared spectrum was identical with that of an authentic sample. This reduced product along with the spectral data given above establishes the structures of **19** and **20**.

**Decomposition of Dihydroumbellulone Tosylhydrazone.**—The same general procedure was used to prepare the sodium salt and to decompose the salt. The distillate, which contained a small amount of methanol, was analyzed by gas chromatography. The two components were tediously separated by preparative gas chromatography (5% SE-30 on Chromosorb W, 5 ft  $\times$   $\frac{1}{8}$  in., 40°). Component A (retention time 11 min, 31% of the mixture) was assigned structure **22** on the basis of the following data: infrared 6.25 (double bond conjugated with cyclopropyl), 9.75  $\mu$  (cyclopropane); nmr pair of partially resolved doublets centered at  $\delta$  5.70 and 5.10 (2 H,  $J = 6$  cps,  $HC=CH$ ), multiplet centered at 3.15 (1 H,  $C=CCHCH_3$ ), multiplet centered at 2.0 [1 H,  $-CH(CH_3)_2$ ], multiplet centered at 1.0 (9 H, three  $CH_3$  groups), quartet centered at 0.4 (1 H, cyclopropyl H) and doublet centered at 0.1 (2 H, cyclopropyl H). This structure was confirmed by a comparison of the infrared and nmr spectra with those of umbellulene prepared from dihydroumbellulone *via* the Cope reaction.<sup>23</sup>

Component B (retention time 14.5 min, 68% of the mixture) was assigned structure **21** on the basis of the following data: infrared 4.45 (central acetylene), 6.09 (isolated double bond), 5.45 (overtone of terminal methylene), 10.98 (terminal methylene group); nmr multiplet centered at  $\delta$  5.70 (1 H,  $CH_2=CH-$ ), triplet with additional splitting centered at 5.0 (2 H,  $CH_2=CH$ ), broad absorption centered at 2.25 (4 H, allylic H), four absorptions centered at 1.15 (9 H, three methyl groups). The position of the central double bond was confirmed by ozonolysis of the crude distillate. After an oxidative work-up ( $H_2O_2$ , NaOH) the residue was treated with diazomethane. Analysis by gas chromatography (15% Apiezon L on Chromosorb W) indicated the presence of methyl isobutyrate (retention time 4.1 min at 37°) confirmed by peak enhancement with an authentic sample. Reduction of component B over a platinum oxide catalyst gave a single component identical with 2,6-dimethyloctane established by gas chromatographic peak enhancement (5% SE-30, 5 ft  $\times$

$\frac{1}{8}$  in., 60°, retention time 12 min). Its infrared spectrum was identical with that of an authentic sample.

**Decomposition of 4-Isocarane Tosylhydrazone.**—The same general procedure was used to prepare the sodium salt and to decompose it. The distillate was identified as  $\Delta$ -3-carene by its infrared and nmr spectra and was shown to be >99%  $\Delta$ -3-carene by gas chromatographic analysis (8% DEGS, SE-30 and 15% Carbowax 1000 on Chromosorb W).

**Decomposition of 2-Carane Tosylhydrazone.**—The same general procedure was used to prepare the sodium salt and to decompose it. The distillate (50%) was analyzed by gas chromatography (5% SE-30, 10 ft  $\times$   $\frac{1}{8}$  in., 120°). Four components were observed with relative areas of 76, 12, 10 and 3 and retention times of 18, 20, 21 and 23 min, respectively. The infrared spectrum of the distillate showed absorptions at 3.01, 3.39, 3.49, 4.72, 5.10 (vw), 6.1, 6.95, 7.3, 9.05, 11.25 and 12.1  $\mu$ . An attempt was made to effect some separation by spinning band distillation (70 TP, reflux ratio 30:1) but the fractions were substantially of the same composition when analyzed by gas chromatography. The major component was separated by preparative gas chromatography (15% UCON SHO 5100 on Chromosorb W, 5 ft  $\times$   $\frac{1}{8}$  in.). It exhibited the following properties: infrared 3.01 (terminal acetylene), 3.34, 4.72 (acetylene), 6.1 (isolated double bond), 11.25  $\mu$  (terminal methylene group); nmr triplet plus centered at  $\delta$  5.0 attributed to (1 H,  $C=CH$ ), two absorptions at 1.7 with additional splittings (6 H,  $(CH_3)_2C=$ ), doublet at 1.2 (3 H,  $J = 7$ ,  $CH_3CH$ ) and complex absorption in the region  $\delta$  1.8–2.2 attributed to  $>C=C(CH_2)-$  and  $>C=C(CH)-$  (5 H) plus a singlet at 1.5 (1 H,  $HC\equiv$ ).

*Anal.* Calcd for  $C_{10}H_{16}$ : C, 88.16; H, 11.84. Found: C, 88.06; H, 11.96.

It is assigned structure **24** on the basis of these properties and its reduction to 2,6-dimethyloctane as established by peak enhancement on gas chromatography (5% SE-30, 10 ft  $\times$   $\frac{1}{8}$  in., 110°, 27 min) and comparison of infrared spectra. The presence of a terminal acetylene was confirmed by treatment of the distillate with ammoniacal silver nitrate. A precipitate formed immediately. Evaporation of the filtrate gave a residue with retention times identical with  $\Delta$ -3- and  $\Delta$ -2-carene on gas chromatography. The silver acetylide was decomposed with 50% nitric acid and after extraction with pentane gave a single peak identical with the major component of the decomposition. The structures of the minor products are assigned on the basis of the following experiments.

$\Delta$ -3-Carene<sup>24</sup> was isomerized to a 60:40 mixture of  $\Delta$ -3- and  $\Delta$ -2-carene by the method of Acharya and Brown.<sup>20</sup> Comparison of retention times and peak enhancement (15% UCON SHO 5100) indicated that two of the minor components of the pyrolysis were  $\Delta$ -3- and  $\Delta$ -2-carene.

The acetylene **24** was isomerized to allene **25** by treatment of the crude product (0.100 g) with sodium methoxide (0.150 g) and methanol (1 ml) in a sealed tube. The reaction mixture was heated at 170° for 3 hr, then extracted with water and petroleum ether after cooling. The petroleum ether extract was dried over anhydrous sodium sulfate and the petroleum ether removed. The infrared spectrum of the residue showed a much more pronounced band at 5.09  $\mu$  as well as those at 3.01 and 4.72  $\mu$ . Gas chromatography (15% UCON SHO 5100, 25°) indicated that the remaining unidentified peak had increased in intensity at the expense of the acetylene (1:1 *vs.* 76:2 in the decomposition mixture).

**Registry No.**—**11** (R = NNHTs), 18791-12-3; **12** (R = NNHTs), 18767-53-8; **13** (R = NNHTs), 18791-13-4; **14** (R = NNHTs), 18767-54-9; **15** (R = NNHTs), 18767-55-0; **17**, 18767-59-4; **18**, 3917-48-4; **19**, 18767-56-1; **20**, 18767-57-2; **21**, 18791-14-5; **22**, 18767-58-3; **24**, 18791-15-6.

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