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NOVEL PRODUCTS FROM BECKMANN FRAGMENTATION OF CAMPHOR OXIME IN POLYPHOSPHORIC ACID

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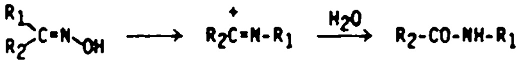
Abstract.- Heating camphor oxime with PPA affords, besides the known fragmentation products isoaminocamphor (4) and β-campholenonitrile (13), four isomeric ketones $C_{10}H_{14}O$ resulting from intramolecular acylation of the intermediate α-campholenonitrile (3). The ketones have been identified as 5-ketocamphene (6), 6-ketocamphene (8), tricyclenone (9), and endo-2,4-dimethylbicyclo[3.2.1]oct-2-ene-7-one (14). The latter results from a novel ring expansion, probably by way of a protonated cyclopropane.

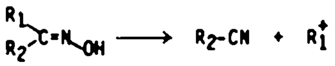
The Beckmann rearrangement of ketoximes (eq. 1) is frequently complicated by the incursion of "abnormal" Beckmann reactions.[1] In particular, when one of the alkyl groups attached to the oxime carbon is capable of stabilizing a positive charge, a fragmentation reaction leading to a carbonium ion and a nitrile (eq. 2) competes effectively with normal rearrangement. The choice between these competing pathways in such cases depends especially on the reagent and experimental conditions. Fragmentation is favored by reagents such as PCl_5, $SOCl_2$, and strong acids, while arylsulfonyl chlorides in pyridine or aqueous alkali often encourage rearrangement over fragmentation.[2]

Eq. 1. Beckmann rearrangement:



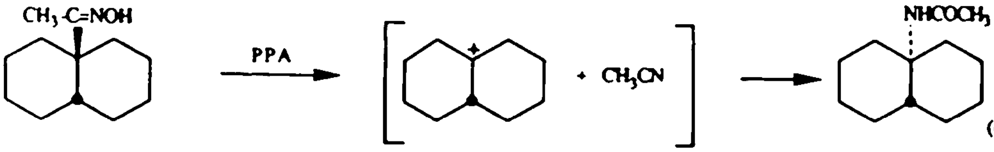
$$\begin{matrix}R_1\\R_2\end{matrix}\!\!>C{=}N\!\diagdown_{OH} \longrightarrow R_2\overset{+}{C}{=}N{-}R_1 \xrightarrow{H_2O} R_2{-}CO{-}NH{-}R_1$$

Eq. 2. Beckmann fragmentation:

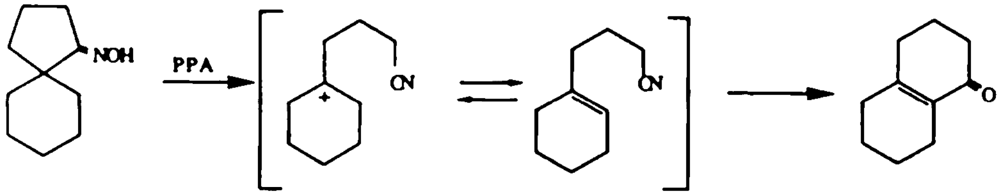


$$\begin{matrix}R_1\\R_2\end{matrix}\!\!>C{=}N\!\diagdown_{OH} \longrightarrow R_2{-}CN \;+\; R_1^{+}$$

Of particular interest to us are those cases in which a carbonium ion generated by oxime fragmentation in a medium in which it has an appreciable lifetime, such as concentrated sulfuric acid or polyphosphoric acid (PPA), interacts with its nitrile partner to form secondary recombination products. Recombination may take the form of capture of the carbocation by the unshared electrons of the nitrile (Ritter reaction), as exemplified in the rearrangement[3] of cis-9-acetyldecalin oxime (eq. 3), or alternatively the alkene formed by proton loss from the carbonium ion may be acylated by the nitrile, as has been observed[4] in the rearrangement of various spiro-oximes (eq. 4).

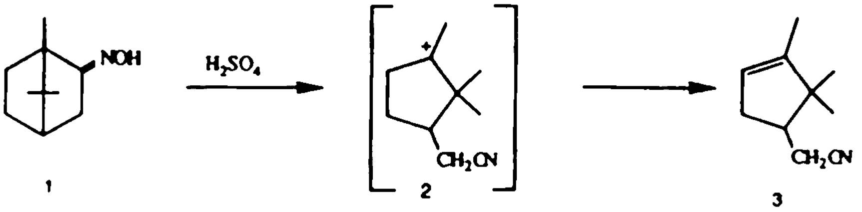


(eq 3)



(eq 4)

Camphor oxime (1) is representative of the structural type which fragments easily to a tertiary carbocation, and its fragmentation to α-campholenonitrile (3) with a variety of reagents was reported in the last century.[5] Even with p-toluenesulfonyl chloride in aqueous NaOH, camphor oxime gives only fragmentation products,[6] and Schmidt rearrangement of camphor affords less than 1% of lactam.[7] The only other reported case of formation of a lactam from camphor under Beckmann- like conditions is the synthesis of α-camphidone by treatment with hydroxylamine O-sulfonic acid.[8] We now report that when camphor oxime is heated in PPA, secondary reactions of carbocation 2 lead to an array of novel products, including four isomeric ketones containing two hydrogens less than camphor.



Results. Heating camphor oxime in PPA[9] at 125-130° for periods of 10-30 minutes gave a mixture of products, separable by chromatography. Column chromatography over alumina furnished, in 45% yield, a solid base, mp 38.5-40°, identified as isoaminocamphor (4) by hydrolysis to dihydrocampholenolactone (5) and by direct comparison with an authentic sample synthesized by acid cyclization of α-campholenamide (12). The iminolactone (4) has been previously observed as a product of treating camphor oxime with sulfuric acid.[5c,10]

Early fractions from column chromatography furnished ketonic material, shown by GLC to be a mixture. Consequently in subsequent runs the crude product was distilled and the distillate was separated into four volatile fractions by preparative GLC. In order of elution these four ketones were characterized as follows:

(a) Ketone 6 displayed a strong carbonyl band at 1750 cm^{-1}, along with bands at 1670 and 885 cm^{-1} suggestive of an exomethylene group. The proton NMR spectrum showed two methyl singlets and two one-proton singlets in the vinyl region, similar in appearance to the spectrum of camphene. The ^{13}C-NMR spectrum confirmed the presence of two methyls, the carbonyl function, and the $R_1R_2C=CH_2$ moiety. These spectra, along with the mass spectrum, were consistent with the formula $C_{10}H_{14}O$, and indicated that one of the methyl groups of camphor had been converted to an exomethylene group in 6. Wolff-Kishner reduction of 6 afforded camphene (7). Assuming that this reduction occurs without skeletal rearrangement, only two structures are in agreement with the carbonyl stretching frequency: 5-ketocamphene (6) or 6-ketocamphene (8). An authentic sample of 8 was prepared by the procedure of Nametkin and Zabrodin.[11] Its IR spectrum was distinctly different from that of 6, and consequently ketone 6 is assigned the structure of 5-ketocamphene. Its IR, ^1H-NMR, and ^{13}C-NMR spectra are in good agreement with those reported for this ketone by Werstiuk et al.[12]

(b) Ketone 9 was a solid, purified by sublimation to give a camphor- like substance, mp 100-103°, with strong IR absorption at 1755 cm^{-1}. The NMR spectrum showed three distinct methyl singlets and integrated for 14 protons, while the ^{13}C-NMR spectrum exhibited ten signals, so ketone 9 shares the formula $C_{10}H_{14}O$, confirmed by the mass spectral parent peak at 150. The absence of vinyl hydrogens and olefinic carbons in the ^1H and ^{13}C-NMR spectra showed it to be a saturated, and thus tricyclic, ketone. It was not identical with the well-known[13] cyclocamphanone (11).

Wolff-Kishner reduction of 9 gave a solid hydrocarbon with only seven signals in its ^{13}C-NMR spectrum, evidencing a structure possessing some symmetry element. The hydrocarbon was quickly identified as tricyclene (10) by comparison with an authentic sample, thus demonstrating that ketone 9 must be tricyclenone.[14]

(c) Ketone 8 had carbonyl absorption at 1750 cm^{-1}, with bands at 1655, 1670, and 890 cm^{-1} characteristic of an exomethylene double bond. The proton NMR spectrum showed two methyl singlets as well as two sharp singlets in the vinyl region. The general similarity of the spectra of 8 and 6 suggested that 8 was 6-ketocamphene (α-camphenone),[15] and this was confirmed by spectroscopic comparison with a synthetic sample.

(d) A fourth ketone isomer of $C_{10}H_{14}O$ was isolated in low yield. Further experimentation showed that the amount of this compound increased with longer reaction times; after one hour in PPA at 130°, this isomer (14) constituted 24% of the volatile material, and could be isolated in quantity via the semicarbazone. Ketone 14 obtained in this way was still only 90-95% pure, but could be further purified by preparative GLC, column chromatography, and distillation.

Ketone 14 showed strong infrared absorption at 1747 cm^{-1}, characteristic of a cyclopentanone carbonyl. A weak band at 1660 cm^{-1} suggested the presence of a double bond, not conjugated with the carbonyl group. The mass spectrum showed the molecular ion at m/z 150, consistent with the formula $C_{10}H_{14}O$.

The proton NMR spectrum showed only two methyl groups; one of these (d, δ 0.97) is attached to a saturated tertiary carbon, while the other (t, δ 1.71) is attached to an olefinic carbon and shows long- range coupling with two protons. A single proton appeared in the vinyl region (q, δ 5.21). The remaining seven protons appeared as complex overlapping multiplets between 1.8 and 2.7 ppm. The ^{13}C-NMR spectrum confirmed the presence of two methyls and a trisubstituted double bond; off-resonance decoupling as well as a DEPT spectrum showed, in addition, two methylene and three methine groups. One of the methines, from its chemical shift of 51.5, is likely to be a bridgehead carbon adjacent to the ketone (cf. C-1 in norcamphor at 50.1 ppm).[16]

These data are already sufficient to show that ketone 14 is an unusual rearrangement product. Unlike its isomers, which contain either three methyls or two methyls plus an exocyclic methylene group, 14 has only two methyls; one of the three original methyl groups of camphor has been converted into a saturated methylene or methine. Moreover, with only two methyls, the remaining eight carbons of 14 must be incorporated into a bicyclic skeleton, and consequently 14 cannot contain the bicyclo[2.2.1]heptane framework of 6, 8, and 9.

Only four eight-carbon bicyclic skeletons which possess at least one five-membered ring are possible: cyclopropylcyclopentane, bicyclo[3.2.1]octane, bicyclo[3.3.0]octane, and spiro(4,3)octane. The latter is ruled out by the absence of saturated quaternary carbons in the ^{13}C-NMR spectrum, and the first seems a highly unlikely strained reaction product, but consideration of possible structures containing the remaining two skeletons still left at least twenty plausible candidates.

Additional elements of connectivity were established by [^1H, ^1H] and [^{13}C, ^1H] correlation NMR spectra. The ^{13}C methine signal at 35.3 ppm is coupled to the one- proton multiplet at 2.67 ppm, which is in turn coupled with the upfield methyl group, indicating that this methyl occupies a position either allylic to the double bond or adjacent to the ketone. The methylene carbon at 34.5 ppm is coupled to upfield protons at 1.93 and 2.05 ppm, while the other methylene (37.7 ppm) is coupled to downfield protons at 2.14 and 2.41 ppm, suggesting that this methylene may be next to the ketone function.

Even with this spectroscopic information, half a dozen possible structures remained in consideration, and consequently chemical information was sought. Reduction of the ketone was effected by treatment of the p-toluenesulfonylhydrazone with n-butyllithium. The bicyclic diene 15 which was formed showed three distinct signals in the vinyl region of the proton NMR spectrum: a broad singlet at δ 4.65, corresponding to the vinyl proton present in ketone (14), and two new one-proton signals at δ 5.55 and 6.25, each a doublet of doublets. These data strongly suggest that the new double bond in 15 is located on the two-carbon bridge of a bicyclo-[3.2.1]octane, and that ketone (14) consequently has the unit $-CH_2CO-$ as the two-carbon bridge of a bicyclo[3.2.1]octane.

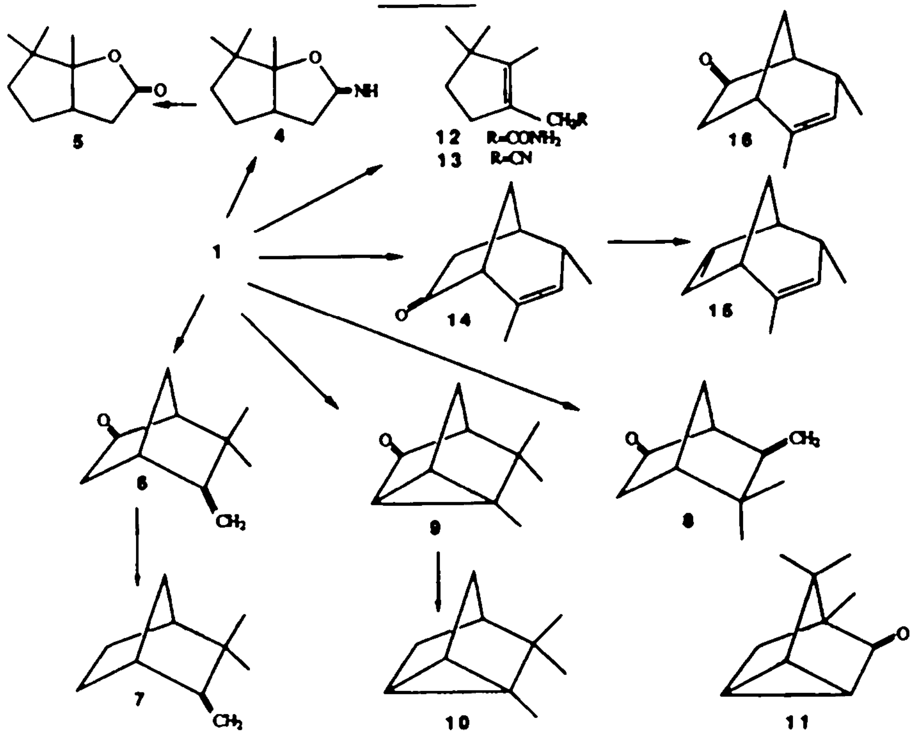
Examination of the literature revealed that several isomers of a dimethylbicyclo[3.2.1]octadiene structure are known, and indeed, the NMR spectrum of the Shapiro product 15 proved to be identical with that reported[17] for endo-2,4-dimethylbicyclo[3.2.1]octa-2,6-diene. Consequently the structure of ketone 14 is narrowed to two possiblities: 14 or 16.

Final proof of structure was realized by a single-crystal X-ray analysis of the p-toluenesulfonylhydrazone 17. The structure, refined to an R-value of 6.3%, showed that the ketone has the structure endo-2,4- dimethylbicyclo[3.2.1]oct-2-ene-7-one (14); the ORTEP drawing of the p-toluenesulfonylhydrazone is shown in Figure I. The X-ray analysis shows clearly that both methyls are attached to the three-carbon bridge, the methyl group at C-4 being endo. Details of bond lengths and angles, dihedral angles, and thermal parameters may be found in the Supplemental Material. With the structure securely determined, the proton and ^{13}C-NMR spectra could be fully assigned (see Experimental Section) and are in full agreement with structure 14.

Finally, several fractions from chromatography of the Beckmann mixture showed nitrile absorption at 2260 cm^{-1}, and it was possible to isolate a small amount of a liquid nitrile by distillation and preparative GLC. Its spectra were different from those of 3, but the six-proton singlet and lack of vinyl protons in the NMR allowed its identification as β-campholenonitrile (13), confirmed by comparison with an authentic sample. This nitrile has previously been obtained from camphor oxime by treatment with hydriodic acid.[18]

Discussion. A mechanism which accounts for the novel array of products from camphor oxime is presented in Scheme 2. Fragmentation of the protonated oxime leads to cation 2, the intermediate to previously observed fragmentation products. In PPA, this cation has sufficient lifetime to equilibrate with α-campholenonitrile (3) and also to rearrange, by methyl migration, leading to β-campholenonitrile (13). Partial hydrolysis of 13 to the amide 12, followed by acid-catalyzed cyclization, leads to isoaminocamphor (4), as could be confirmed by heating 13 with PPA.

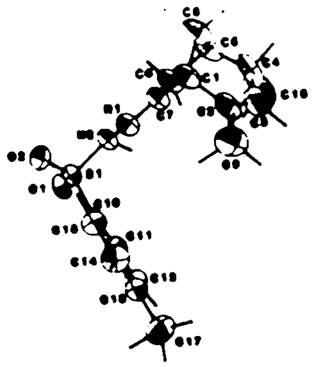
Scheme 1



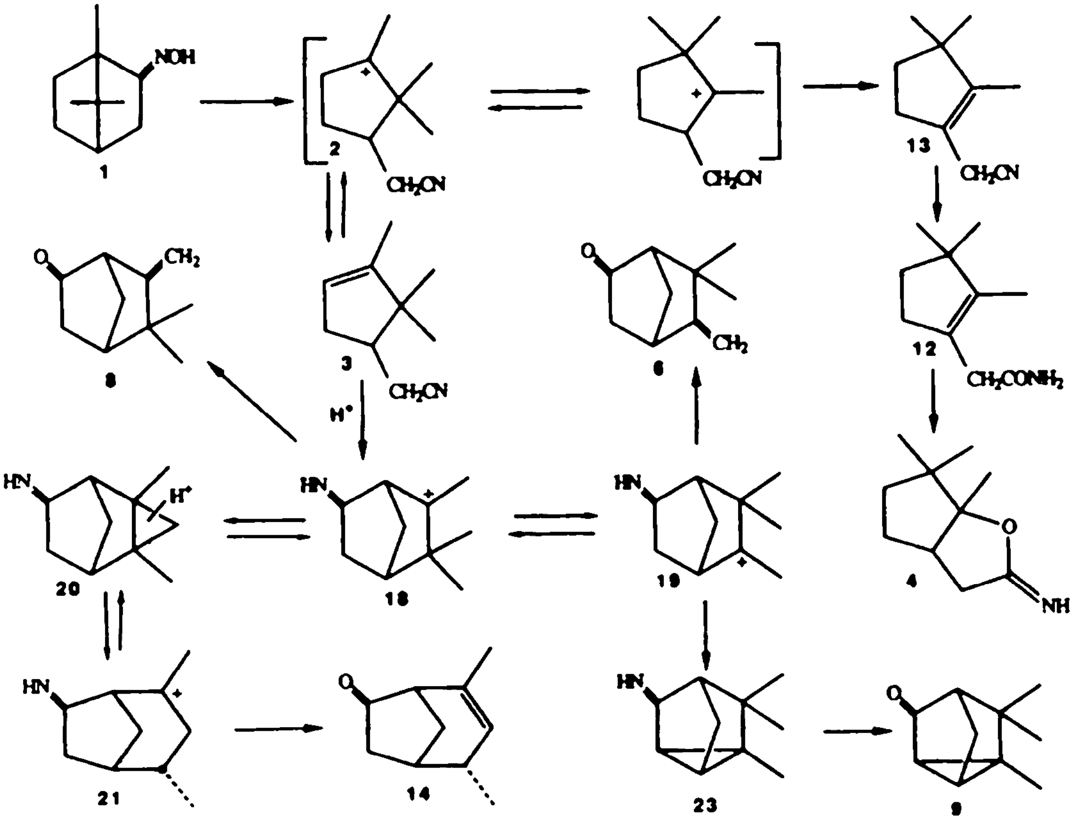
The double bond in α-campholenonitrile (3) is suitably situated to permit intramolecular acylation by the protonated nitrile, a reaction type we have observed[4] in reactions of other oximes in PPA. The bicyclic carbocation 18 so produced can lead directly to 6-ketocamphene (8) by elimination of a proton and hydrolytic workup. Cation 18 can also undergo rapid methyl migration leading to a comparably stable tertiary carbocation 19, the precursor of 5-ketocamphene (6). Alternatively, cation 19 may cyclize to 22, the immediate precursor of tricyclenone (9), either via a protonated cyclopropane intermediate or by intramolecular capture of the carbonium ion by the double bond of the tautomeric enamine. The acid-catalyzed equilibration of camphene (7) and tricyclene (10) is well-recognized.[19]

The rapid equilibrium between the isomeric campholenonitriles 3 and 13 under the reaction conditions can be verified by showing that the same set of fragmentation products obtained from camphor oxime is obtained when either 3 or 13 is heated with PPA. Moreover, all the products obtained from d-camphor are racemic, apparently a consequence of the rapid equilibration of 3 with 13.

Figure 1.



Scheme 2



The most economical mechanism to account for the novel ring-expanded product **14** is an intramolecular insertion reaction of either carbocation **18** or **19** to form protonated cyclopropane **20**; indeed, **20** may be an intermediate[20] in the interconversion of **18** and **19**. Opening of the strained bond between the quaternary carbons in **20** can now lead to ion **21**, which is converted by deprotonation and hydrolysis to **14**. The increase in yield of **14** with time probably reflects the relief of strain in opening **20** to **21**, although the formation of a bicyclo[3.2.1]octane as the apparently more stable product of acid-catalyzed equilibrium contrasts with the isomerization of a variety of bicyclic C_8 substrates to the bicyclo[3.3.0]octyl cation under long-lived ion conditions in superacid media.[21] Schleyer et al.[22] have shown, on the other hand, that bicyclo[3.2.1]octane is the most stable of the bicyclooctanes, due primarily to more favorable entropy. The only precedent for the novel rearrangement of **20** to **21** of which we are aware is the $AlCl_3$-catalyzed isomerization of 2-methylnorbornane to bicyclo[3.2.1]octane.[23]

These results provide an additional, and particularly interesting, example of the dependency of the course of Beckmann rearrangement and fragmentation on the reagent employed, especially in those cases where the primary fragmentation products may undergo an array of subsequent acid-catalyzed cyclizations and rearrangements.

Experimental Section

General. Boiling points and melting points (Pyrex capillary) are uncorrected. Preparative gas-liquid partition chromatography (GLC) was performed on a Varian Aerograph 90-P3 gas chromatograph. IR spectra were obtained on Perkin-Elmer Model 257 and 297 recording spectrophotometers. ^1H-NMR spectra were obtained on the following spectrometers: Varian T-60, Varian EM-390, JEOL FX-270, and Bruker AM-500. ^{13}C-NMR spectra were run on JEOL FX-270 and PFT-100 spectrometers. 2D [^1H, ^1H] and [^{13}C, ^1H] correlated spectra were obtained on the Bruker AM-500 instrument. Chemical shifts are expressed in ppm downfield from tetramethylsilane, and coupling constants (J) are given in Hz. Mass spectra were acquired on a Finnigan 4000 GCMS instrument.

Substrates. *Camphor oxime*. d-Camphor was purified by subliming twice at 17 mm. A solution of 15 g camphor and 15 g of hydroxylamine hydrochloride in 75 mL of absolute ethanol and 75 mL of pyridine was heated under reflux for 1 h and concentrated at reduced pressure. The residue was triturated with water, air-dried, and recrystallized twice from CCl_4 or petroleum ether (bp 60-70°), affording 16 g of oxime, mp 119.5-120°, $[\alpha]_D^{20}$ -41.1° (c 2.90, abs. ethanol); lit.[5] mp 120°, $[\alpha]_D^{20}$ -42.4° (ethanol). The infrared spectrum showed no trace of carbonyl absorption.

α-Campholenonitrile[5c] and *β-campholenonitrile*[5c,18] were prepared by published procedures by treatment of camphor oxime with 25% sulfuric acid and hydriodic acid, respectively.

Rearrangement of camphor oxime in PPA.- The oxime (15 g) was stirred with 150 g of PPA and heated. An exothermic reaction occurred at 105°; the mixture was maintained at 125-130° for 10 min, then cooled below 100° and slowly poured into 1 L of 4N NaOH and crushed ice. A strong odor of ammonia was observed. The mixture was stirred until homogeneous and extracted with five 200-mL portions of chloroform. The extracts were dried over magnesium sulfate and concentrated, leaving 12.5 g of a yellow semi-solid residue with IR absorption at 2257, 1750, and 1680 cm^{-1}. This crude mixture was worked up by one of the following procedures:

Procedure A: The residue was chromatographed on alumina, eluting initially with pentane and gradually changing to ether, taking 50-mL fractions. Fractions 1-26, eluted with pentane, were concentrated to yield 4.55 g of a pale yellow oily solid, shown by IR and reaction with 2,4-dinitrophenylhydrazine to be a mixture of ketones. Fractions 26-32, eluted with pentane-ether, gave no material. Fractions 32-150, eluted with ether, afforded 6.75 g of a colorless, low-melting solid. Two distillations through a small Vigreux column gave pure isoaminocamphor (**4**), mp 38.5-40° (lit[24] mp 39°).

Anal. Calc for $C_{10}H_{17}NO$: C, 71.81; H, 10.25; N, 8.38. Found: C, 71.97; H, 10.49; N, 8.40.

Procedure B: The crude product from rearrangement of 40 g of camphor oxime for 30 min at 125° was distilled at reduced pressure to give 21.3 g of a liquid mixture, bp 113-120° (50 mm). The distillate was separated into two rough fractions by chromatography on alumina with hexane-benzene. Fraction 1 was shown by GLC analysis (10' x ¼" column of 10% Carbowax 20M, 160°, 40 mL/min helium flow) to consist of four components with retention times of 5.3 min (5-ketocamphene, **6**), 6.2 min (tricyclenone, **9**), 7.0 min (6-ketocamphene, **8**), and 8.1 min (*endo*-2,4-dimethylbicyclo[3.2.1]oct-2-en-7-one, **14**). Fraction 2 was a solid ketone, which was sublimed twice to give pure tricyclenone (**9**), mp 100-103° (lit[14b] mp 97.5-100°).

Isoaminocamphor (**4**).- The oxalate, mp 149-150° d (lit[24] mp 148°), and the hydrochloride, mp 88-89° (lit[24] mp 89°) did not depress the melting points of authentic samples. A sample of **4** was hydrolyzed as reported[10] to dihydrocampholenolactone (**5**), mp 35-37° (lit[10,18] mp 35°; 37-38°). Its hydrazide, mp 154.5-156°, did not depress the melting point of an authentic sample,[18] mp 155-156°.

An authentic sample of **4** was prepared by acid cyclization[24] of β-campholenamide (**12**), while authentic **5** was prepared by acid cyclization of β-campholenic acid.[18]

6-Ketocamphene (**8**).- The ketone showed IR (CCl_4) 1750, 1670, 1655, 890 cm^{-1}; NMR ($CDCl_3$): δ 1.15 (s, 3H), 1.22 (s, 3H), 1.6-2.5 (m, 5H), 3.20 (m, 1H), 5.00 (s, 1H), 5.24 (s, 1H). The spectra were identical with those of an authentic sample prepared by the method of Nametkin and Zabrodin.[11]

Tricyclenone (9).- The solid ketone, mp 100-103°, had strong IR absorption at 1755 cm^{-1} ((CCl_4); ^1H-NMR ($CDCl_3$): δ 1.02 (s, 3H), 1.04 (s, 3H), 1.18 (m, 1H), 1.22 (s, 3H), 1.48 (m, 1H), 1.7-2.1 (m, 3H); ^{13}C-NMR ($CDCl_3$): δ 10.2 (q), 19.3 (q), 21.3 (q), 27.9 (d), 29.2 (d), 29.3 (t), 38.7 (s), 43.8 (s), 51.6 (d), 213.4 (s). The IR and NMR spectra were identical with those of authentic samples kindly provided by Prof. J. K. Crandall and Dr. B. Furth.

A mixture of 370 mg of 9, 210 mg of 95% hydrazine, and 500 mg of KOH in 15 mL of absolute ethanol was heated in a sealed bomb at 170-180° for 16 h. After cooling, the contents were poured into 15 mL of water and extracted with two 15-mL portions of pentane. The extracts were dried over magnesium sulfate and concentrated, and the residue was purified by preparative GLC (10' x 3/8" column of 20% DC-710, 170°) to give 75 mg (22%) of tricyclene as a low-melting solid; ^1H-NMR ($CDCl_3$): δ 0.82 (s, 6H), 1.02 (s, 3H), 0.85-1.90 (m, 7H); ^{13}C-NMR ($CDCl_3$): δ 10.5 (q), 19.5 (d), 20.5 (q), 26.3 (s), 31.4 (t), 41.9 (d), 43.1 (s). The spectra were identical with those of an authentic sample of tricyclene prepared by the procedure of Reusch et al.[25]

5-Ketocamphene (6).- IR (CCl_4):1750, 1670, 885 cm^{-1}; ^1H-NMR (CCl_4): δ 1.00 (s, 3H), 1.10 (s, 3H), 1.5-2.2 (m, 5H), 2.95 (m, 1H), 4.50 (s, 1H), 4.70 (s, 1H); ^{13}C-NMR ($CDCl_3$): δ 27.1 (q), 28.2 (q), 36.3 (t), 41.1 (s), 44.3 (t), 44.7 (d), 62.2 (d), 102.8 (t), 160.6 (s), 215.6 (s).

Wolff-Kishner reduction of 6, as described above for tricyclenone, gave a 27% yield of camphene, identified by comparison of IR and NMR spectra with those of authentic material.

endo-2,4-Dimethylbicyclo[3.2.1]oct-2-en-7-one (14).- IR (film) 2968, 2935, 2876, 1747 (s), 1660 (w), 1456, 1408, 1160, 859, 845, 799 cm^{-1}; ^1H-NMR ($CDCl_3$): δ 0.97 (d, J=7, 3H, C4-CH_3), 1.71 (t, J=1, 3H, C2-CH_3), 1.93 (dd, J=11, 3, H_{8anti}), 2.05 (dt, J=11, 3, H_{8syn}), 2.14 (dd, J=7, 1, H_{6endo}), 2.41 (m, H_{6exo}), 2.48 (d, J=3, H_5), 2.51 (d, J=5, H_1), 2.67 (m, H_4), 5.21 (q, J=1, H_3); ^{13}C-NMR ($CDCl_3$): δ 16.6 (q, C4-methyl), 21.7 (q, C2-methyl), 34.3 (t, C8), 35.2 (d, C4), 36.3 (d, C5), 37.5 (t, C6), 51.3 (d, C1), 128 (d, C3), 132 (s, C2), 211 (s, C7); mass spectrum: m/z (relative intensity) 151 (50, M+1), 134 (11), 121 (11), 107 (100), 93 (87).

The 2,4-dinitrophenylhydrazone, after two recrystallizations from 95% ethanol, gave orange-red flakes, mp 149-150°.

The semicarbazone, recrystallized from methanol, gave tiny crystals, mp 180° d.

The p-toluenesulfonylhydrazone (17) first appeared as an oil, but crystallized when a methanol solution was kept in the freezer for several weeks. Two recrystallizations from methanol gave colorless prisms, mp 166° d.

Large-scale isolation of 14.- The crude product from a run of 40 g of camphor oxime in 400 g of PPA for 1 h at 130° was distilled, collecting the volatile material boiling up to 105° at 20 mm. The distillate (29.1 g) was treated with a mixture of 29.1 g of semicarbazide hydrochloride and 72.5 g of sodium acetate trihydrate in 306 mL of 95% ethanol and 276 mL of water and kept in the refrigerator for 2 weeks. The precipitate was collected and recrystallized twice from methanol, giving 6.2 g of semicarbazone. Recovery of the ketone was accomplished by steam distilling a mixture of the semicarbazone and dilute HCl.

endo-2,4-Dimethylbicyclo[3.2.1]octa-2,6-diene (15).- A suspension of tosylhydrazone 17 (1.50 g) in 44 mL of N,N,N',N'-tetramethylethylenediamine was cooled to -78° under nitrogen and treated with 9.4 mL of 2M n-butyllithium in hexane. The mixture was held at -78° for 10 min, then allowed to warm to room temperature and magnetically stirred as thawing began. After 19 h at 25°, the mixture was cooled to 0°, treated with 110 mL of water, and extracted three times with ether. The extracts were washed with cold 5% HCl and brine, dried over $MgSO_4$, and concentrated below 25° on a rotary evaporator. The residue was distilled at 60° (20 mm) to afford 236 mg of a yellow oil, which was chromatographed on silica gel, eluting with hexane, to give 120 mg of diene 15 as a colorless oil; IR (film) 3060, 3013, 2931, 2868, 1659, 1591, 1448, 944, 732 cm^{-1}; ^1H-NMR ($CDCl_3$): δ 0.9 (d, 3H, J=7), 1.7 (m, 3H), 1.8-2.2 (m, 2H), 2.3 (m, 2H), 2.7 (m, 1H), 4.7 (m, 1H), 5.6 (dd, 1H, J=6, 3) 6.3 (dd, 1H, J=6, 3). The diene formed an instantaneous precipitate with aqueous $AgNO_3$ as described by Hoffmann and Vathke.[17]

Crystallographic

A crystal of $C_{17}H_{22}N_2O_2S$ was mounted on a Syntex P3 automated diffractometer. Unit cell dimensions (Table I) were determined by least squares refinement of the best angular positions for fifteen independent reflections ($2\theta > 15°$) during normal alignment procedures using molybdenum radiation (MoK_α=0.71069 Å). Data (2302 points) were collected at room temperature using a variable scan rate, a θ-2θ scan mode and a scan width of 1.2° below $K_{\alpha 1}$ and 1.2° above $K_{\alpha 2}$ to a maximum 2θ value of 45.0°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections and, as the intensities of these reflections showed less than 6% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization and background effects. After removal of redundant data, observed data (1625 points with ($I > 3.0\,\sigma(I)$)) were used for solution and refinement. The structure was solved for heavy atom positions using direct methods.[26] Least squares refinement[27] converged with anisotropic thermal parameters. A difference Fourier synthesis allowed location of all hydrogen positions. Hydrogen positions were included in the final refinement with isotropic thermal parameters but held invariant. A difference Fourier revealed no electron density of interpretable level. Scattering factors were taken from Cromer and Mann.[28] The final cycle of refinement - function minimized $\sum (|F_o| - |F_c|)^2$, led to final agreement factor R=6.3%, $R = (\Sigma||F_o| - |F_c||/\Sigma|F_o|) \times 100$. A weight equal to $1/\sigma F$ was introduced in the final cycles of refinement: R_w=8.4%.

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Supplementary Material Available. Tables of crystal data, positional parameters, anisotropic thermal parameters, bond angles and distances, and observed and calculated structure factors (25 pp). Ordering information is given on any current masthead page.

Dedication. This paper is dedicated, with affection and admiration, to Professor E. C. Taylor on the occasion of his 65th birthday.

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