expected components with the exception of vinyl 3-(penta-1,4-dienyl)ether (II). During the course of the reaction, it was noted that the carbonyl absorption in the infrared spectrum increased in its intensity and that the area of the peak in the gas chromatograms attributed to 4,6-heptadienal increased in size. The reaction was essentially complete within 10 days as ascertained by the disappearance of the divinylcarbinol peak in the gas chromatograms. 4,6-Heptadienal (III) was isolated by distillation in a yield of 70%.

Reaction of Divinylcarbinol with Vinyl Isobutyl Ether.—A mixture of 10.0 g. (0.119 mole) of divinylcarbinol, 49.0 g. (0.5 mole) of vinyl isobutyl ether, 1.2 g. of mercuric acetate, and 0.4 g. of sodium acetate was heated to reflux for a period of 3 hr. After cooling, 1.5 g. of anhydrous potassium carbonate was added, and the major part of the excess vinyl isobutyl ether was removed at reduced pressure. Distillation of the residue gave 9.50 g. (72%) of 4,6-heptadienal and 0.73 g. of an unidentified viscous residue.

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A Novel Fragmentation of *trans*-π-Bromocamphor

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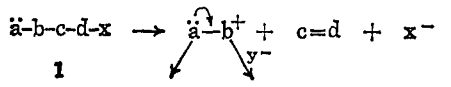
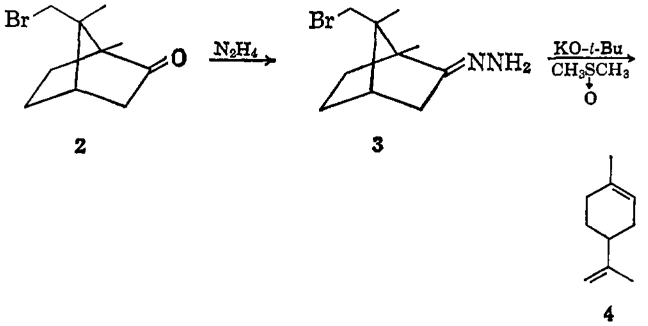
Fragmentation reactions, although commonly encountered in the form of reverse Michael and reverse aldol condensations, have only recently been recognized as a general class of reactions. Grob[1,2] first applied the term fragmentation to a reaction in which a molecule symbolized by **1** undergoes solvolytic cleavage to form two fragments as shown in eq. 1. The atoms



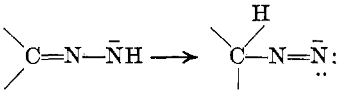
(1)

a–d must be able to form a double bond; x is a typical leaving group, *i.e.*, halogen, OTs, $^+NR_3$, etc., and a must be an atom or group of atoms capable of donating electrons either by resonance or inductive effects, *i.e.*, alkyl, aryl, OR, NR_2, etc. Grob[3] has shown that this reaction may occur by either a one-step concerted mechanism or a two-step mechanism depending on the reaction conditions. The reaction may be catalyzed by both acid and base.[4–6] Regardless of the exact nature of the reaction, Grob[1,2] and subsequent workers[5] have shown that for optimum results the bonds being broken (*i.e.*, d–x and b–c) should be parallel and coplanar.

We wish to report the novel fragmentation of *trans*-π-bromocamphor (**2**) during an attempted Wolff–Kishner reduction of this ketone. Treatment of the hydrazone (**3**) of **2** under Wolff–Kishner conditions as modified by Cram[7] yields, as the only volatile product, limonene (**4**), identified by comparison with an authentic sample.



Fragmentation of **3**, instead of reduction to the yet unknown π-bromobornane, is a consequence of this system possessing the specific steric requirements of the fragmentation reaction.[8] The Wolff–Kishner reduction is believed[9] to be at least a two-step process with the rate-determining step the transfer of a hydrogen atom either intra- or intermolecularly from the



nitrogen terminal of the hydrazone anion to the carbon terminal. The transfer is most probably intermolecular with at least two molecules of solvent present in the transition state.[9] Assuming the transfer of hydrogen to place the $-\mathrm{N}{=}\underset{\cdot\cdot}{\bar{\mathrm{N}}}:$ group in the *endo* position[10] and that the bromo group has the conformation shown in **2a** (Figure 1), the specific steric requirements[1,5] for fragmentation of **3** are met, and the cleavage may be depicted as shown in Scheme I.

That the bromo group in fact does possess the conformation **2a** is shown by the n.m.r. spectrum of *trans*-π-bromocamphor (**2**). The signals due to the two methyl groups in **2** appear at τ 9.06 (bridgehead methyl) and at 8.99 (bridge methyl). The latter signal is a doublet (J = 1.0 c.p.s.) as a result of long-range coupling.[11] The bromomethylene hydrogens appear as an AB quartet with two doublets centered at τ 6.40 and 6.80 (J_{AB} = 10 c.p.s.). The doublet at lower field shows further splitting (J = 1.0 c.p.s.), while the doublet at higher field shows no such secondary splitting. This unequivalent secondary coupling suggests that the conformation of **2** is maintained in

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[1] C. A. Grob in "Theoretical Organic Chemistry" (papers presented to the Kekule Symposium organized by the Chemical Society, London, Sept. 1958) Butterworth and Co. (Publishers) Ltd., London, 1959, p. 114 ff.

[2] C. A. Grob and W. Baumann, *Helv. Chim. Acta*, **38**, 594 (1955); C. A. Grob, *Experientia*, **13**, 126 (1957).

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[4] J. English, Jr., and F. V. Brutcher, Jr., *J. Am. Chem. Soc.*, **74**, 4279 (1952); H. E. Zimmerman and J. English, Jr., *ibid.*, **76**, 2294 (1954).

[5] (a) R. B. Clayton and H. B. Henbest, *Chem. Ind.* (London), 1315 (1953); (b) R. B. Clayton, H. B. Henbest, and M. Smith, *J. Chem. Soc.*, 1982 (1957).

[6] M. F. Clarke and L. N. Owen, *ibid.*, 2103 (1950).

[7] D. J. Cram, M. R. V. Sahyun, and G. R. Knox, *J. Am. Chem. Soc.*, **84**, 1734 (1962).

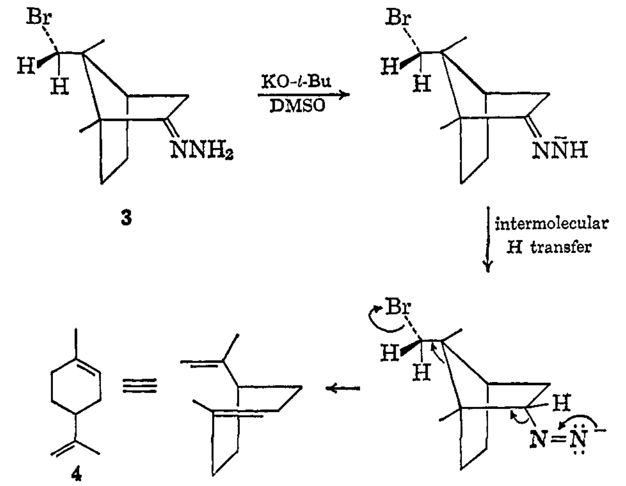
[8] Compare this result with the steroidal systems in ref. 5b.

[9] H. H. Szmant and C. M. Harmuth, *J. Am. Chem. Soc.*, **86**, 2909 (1964), and references cited therein. For a review of the Wolff–Kishner reduction, *cf.* D. Todd, *Org. Reactions*, **4**, 378 (1948).

[10] This assumption is reasonable since the *endo* isomer is the thermodynamically favored product. For example, isobornylcarboxylic acid is converted by base to bornylcarboxylic acid. W. F. Erman, *J. Am. Chem. Soc.*, **86**, 2887 (1964).

[11] S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

SCHEME I

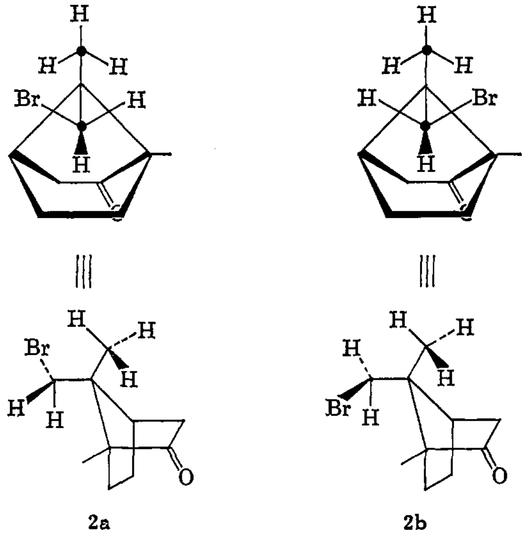


such a manner as to allow "zigzag" type coupling of only one of the hydrogens α to the bromo group with the bridge methyl group.[11–14] There are two conformations of **2** which would be capable of the specific long-range coupling described above, *i.e.*, **2a** and **2b**. Conformation **2b** would not be so favorable as **2a** owing to the additional interaction of the bromine atom with the bridgehead methyl group. Fragmentation would also be more favored from conformation **2a** than from **2b**.[1,5] Formation of the hydrazone **3** would not affect the conformation of the π-bromomethylene group, so that in the reaction of **3** with potassium *t*-butoxide the stereochemistry is the same as in the starting ketone.

Experimental[15]

***trans*-π-Bromocamphor** (2).—This compound was prepared as described by Corey[16] from α-bromocamphor in 50% over-all yield, m.p. 94–95° (lit.[16] m.p. 93–95°). The n.m.r. spectrum has an AB quartet with one doublet centered at τ 6.40 and the second doublet centered at 6.80 (J_{AB} = 10 c.p.s., area 2 protons). The doublet at lower field has additional splitting equal to 1 c.p.s. The methyl groups appear at τ 9.06 (bridgehead methyl, singlet, area 3 protons) and 8.99 (bridge methyl, doublet, J = 1.0 c.p.s.).

Wolff–Kishner Reduction of *trans*-π-Bromocamphor (2).[7,16]—To 46 g. (0.2 mole) of *trans*-π-bromocamphor in 150 ml. of absolute ethanol were added 27 g. (0.8 mole) of anhydrous hydrazine and 12 g. (0.2 mole) of glacial acetic acid. The mixture was heated under reflux for 3 hr., the ethanol was removed under reduced pressure, and the mixture was brought to its original volume with ether. The lower hydrazine layer was removed and the reaction mixture was washed once with 10% sodium hydroxide saturated with sodium chloride solution and three times with saturated sodium chloride solution and dried over sodium sulfate.



2a **2b**

Figure 1.

The solvent was removed under reduced pressure and the crude hydrazone was reduced without further purification.

To 10 g. of potassium *t*-butoxide (MSA Research Corp.) in 25 ml. of dimethyl sulfoxide, which had been dried over molecular sieves, was added a solution of 12.5 g. of *trans*-π-bromocamphor hydrazone in 25 ml. of dimethyl sulfoxide over a 20-min. period. Nitrogen was evolved and the reaction mixture turned a deep wine red during this addition. The mixture was stirred at room temperature for 16 hr. The mixture was heated to 35–45° at which temperature the reaction became exothermic and warmed to a maximum temperature of 80° where it was maintained for an additional 3 hr. The mixture was cooled, poured into 500 ml. of ice water, acidified with dilute hydrochloric acid, and extracted with ether. The combined ether extracts were washed with 3% hydrochloric acid solution, water, and saturated sodium chloride solution and dried over sodium sulfate. The ether was removed at reduced pressure, and the residue (5.7 g.) was distilled through a 10-cm. Vigreux column. The only fraction (1.97 g., 30% yield) obtained boiled at 58–59° (12 mm.): $n^{23}\mathrm{D}$ 1.4747, single peak on gas chromatography [reported for limonene, b.p. 60.5–61° (13 mm.),[17] $n^{20}\mathrm{D}$ 1.4722[18]]. The n.m.r. and infrared spectra and the gas chromatography retention time of our isolated product were identical with an authentic sample of limonene, b.p. 59° (12 mm.), $n^{27}\mathrm{D}$ 1.4695, obtained from Eastman Organic Chemicals.

Acknowledgment.—The authors wish to acknowledge many helpful discussions with Dr. T. J. Flautt of these laboratories concerning the n.m.r. spectra. They are also grateful for helpful comments on the manuscript by Dr. P. J. Kropp.

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[14] (a) Professor Walter Meyer has also observed long-range spin–spin coupling in π-substituted camphor derivatives. Deuterium-labeling experiments, now in progress in his laboratories, should establish definitively the exact mode of coupling. We thank Professor Meyer for communicating this information to us prior to publication. (b) Tori similarly has observed long-range coupling in π-bromocamphor but has not discussed the coupling in terms of conformation. K. Tori, Y. Hamashima, and A. Takamizawa, *Chem. Pharm. Bull.* (Tokyo), in press.

[15] Melting points were determined on a micro hot-stage apparatus and are corrected. Boiling points are uncorrected. N.m.r. spectra were determined on a Varian A-60 spectrometer in deuteriochloroform or carbon tetrachloride solution using tetramethylsilane as an internal standard. Infrared spectra were determined on a Perkin-Elmer Model 137 infrared spectrometer in CH_2Cl_2 solution.

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Molecular Orbital Calculations of the Norbornyl Cation Using an Extended Hückel Theory

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Recently, Hoffmann has presented an extended Hückel theory (E.H.T.) suitable for calculations of

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