been reported and previous attempts to hydrogenate tetraphenylmethane catalytically have resulted in the formation of tricyclohexylmethane and dicyclohexylmethane as major products. No tetracyclohexylmethane was isolated.[1] It has been suggested that the steric requirements of the cyclohexyl group prevent the bonding of four such bulky groups to a single carbon atom.[2]

This laboratory has demonstrated that tetraphenylmethane in the presence of 5% rhodium on charcoal may be catalytically hydrogenated, with surprising ease considering the expected steric situation, at a relatively mild temperature of 100° to give 80% of the theoretical yield of tetracyclohexylmethane, m.p. 282°.

Microanalytical data for carbon and hydrogen are accurate enough to rule out the possibility of residual double bond unsaturation but spectral confirmation seemed desirable in view of slightly low molecular weight values by vapor osmometry (339 and 332, compared to the theoretical 344.6). The ultraviolet absorption spectrum in cyclohexane solution from the visible down to 205 mμ showed no bond with an absorptivity (molar extinction coefficient) even as great as 2.3 l. mole-cm.$^{-1}$. This very high transparency in this region rules out any possibility of existence of phenyl or conjugated olefinic unsaturation. In addition, the exceedingly simple absorption spectrum taken in carbon tetrachloride solution over the infrared region from 2 to 13 μ shows no absorption from 4000 to 3000, 2500 to 2000, or 2000 to 1500 cm.$^{-1}$, thus, respectively, ruling out any hydrogen on unsaturated carbon, hydrogen on silicon, and/or any unsaturated bonds to carbon.

Dehydrogenation of tetracyclohexylmethane to tetraphenylmethane can be effected in the presence of 10% palladium on charcoal at temperatures above 259°. However, extensive fragmentation occurs at these conditions. Although the presence of tetraphenylmethane in small amounts in such dehydrogenation reaction mixtures was demonstrated by comparison with an authentic sample through a capillary column gas chromatograph, it was not possible to isolate a useful quantity of the pure compound.

In view of the steric strain involved, tetracyclohexylmethane has demonstrated remarkable thermal stability. Melting occurs at 282° without decomposition However, the stability in the presence of catalyst is reduced, thereby necessitating relatively mild conditions for hydrogenation. Previous workers[1] appear to have used overly harsh conditions which led to cleavage. These factors probably account for past erroneous conclusions interpreting the steric requirements to be unfavorable to the formation and stability of tetracyclohexylmethane.

Atomic models, Stuart–Briegleb and Fisher–Hirschfelder–Taylor, allow construction of the molecule with difficulty and suggest that the conformations of the cyclohexyl groups may be partially frozen. Stereochemical and X-ray crystal studies to clarify this point are now in progress.

Experimental

Hydrogenation of Tetraphenylmethane.—Into a 1-l. stainless steel liner were placed 3.2 g. (0.01 mole) of tetraphenylmethane (K & K Laboratories), 1 g. of 5% rhodium-on-charcoal catalyst, and 150 ml. of methylcyclohexane. The liner was placed inside an American Instrument Co. superpressure rocking reactor and the assembly was flushed three times with hydrogen by pressurization to 1200 p.s.i. and subsequent venting to atmospheric pressure. The assembly was heated to 100° and pressurized to 1250 p.s.i. with hydrogen, and rocking of the assembly was started. After 16 hr., the heat and rocking mechanism were turned off and the assembly was allowed to cool to room temperature. The reaction mixture was filtered through an extraction thimble and the residue was extracted with methylcyclohexane for 8 hr. in a Soxhlet apparatus. The solvent was removed under vacuum and the residue was recrystallized twice from cyclohexane. After overnight drying at 100° in a vacuum oven there was obtained 2.75 g. (80% of theory) of tetracyclohexylmethane, m.p. 282°.

Anal. Calcd. for $C_{25}H_{44}$: C, 87.13; H, 12.87; mol. wt., 344.6. Found: C, 87.35; H, 12.87; mol. wt. (Mechrolab osmometer), 339, 332.

Moderate-to-strong infrared absorption peaks in the 2–13-μ region for solutions in carbon tetrachloride were observed in a Perkin-Elmer Model 521 spectrophotometer at (in cm.$^{-1}$) 2920 (3.42 μ), 2843 (3.52 μ), 1438 (6.95 μ), and 1055 (9.48 μ); weak bands at 1327 (7.54 μ), 1303 (7.67 μ), 950 (10.53 μ), and 880 (11.36 μ). The ultraviolet spectrum, taken with a Cary Model 11 spectrophotometer over the region 205–700 mμ, showed no band with an absorbance (optical density) as high as 0.01 for a 4.34×10^{-3} molar solution of tetracyclohexane in spectroquality cyclohexane.

Dehydrogenation of Tetracyclohexylmethane.—Into a 50-ml. test tube were placed 0.5 g. of tetracyclohexylmethane, 0.1 g. of 10% palladium on charcoal, and 1 ml. of octadecane as solvent. The top of the test tube was drawn to a capillary and the tube was then immersed in a refluxing bath of diphenyl ether (259°) for 8 hr. The mixture was extracted in a Soxhlet extractor with cyclohexane for 4 hr. and the solvent was then removed. Extensive fragmenting occurred during the high-temperature reaction period and repeated recrystallizations from common hydrocarbon and chlorohydrocarbon solvents failed to separate the components of these mixtures. However, small amounts of tetraphenylmethane were detected by gas chromatographic analysis of these mixtures at 175° on a 100 ft. × 0.01 in. capillary column coated with DC-550 silicone fluid. An authentic sample of tetraphenylmethane was used to make the chromatographic peak assignment for tetraphenylmethane in the mixture.

---

[1] V. N. Ipatiev and B. N. Dolgov, *Compt. rend.*, **185**, 210 (1927).

[2] M. Kanazashi and M. Takakusa, *Bull. Chem. Soc. Japan*, **27**, 441 (1954).

The Facile Rearrangement of Vinyl 3-(Penta-1,4-dienyl) Ether

Samuel F. Reed, Jr.[1]

Rohm and Haas Company, Redstone Arsenal
Research Division, Huntsville, Alabama

Received October 13, 1964

In connection with other work in this laboratory, the need for vinyl 3-(penta-1,4-dienyl) ether arose for use as an intermediate in the synthesis program. One of the most attractive routes to this vinyl ether was the vinyl interchange reaction between a vinyl alkyl ether and the appropriate alcohol, which has been found to be of general utility by Watanabe and Conlon[2] and used to a considerable extent by Burgstahler.[3] In this study divinylcarbinol (I) was treated with vinyl alkyl ethers under conditions of the vinyl interchange reaction in an effort to prepare vinyl 3-(penta-1,4-dienyl) ether.

---

[1] Rohm and Haas Co., Box 672, Deer Park, Texas.

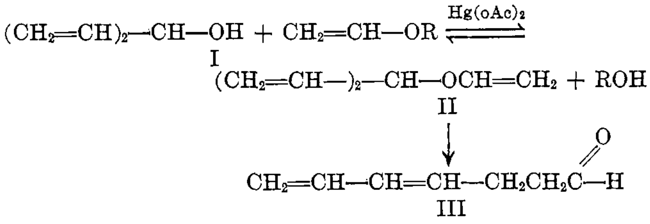
[2] W. H. Watanabe and L. E. Conlon, *J. Am. Chem. Soc.*, **79**, 2828 (1957).

[3] A. W. Burgstahler, *ibid.*, **82**, 4681 (1960).

The initial experiments were conducted employing an excess of vinyl ethyl ether at reflux with mercuric acetate as the catalyst, and sodium acetate was added to maintain neutral conditions. After refluxing for a period of 12 hr., the catalyst was neutralized with potassium carbonate, and the mixture distilled to give unreacted divinylcarbinol, b.p. 45° (48 mm.), and an unknown carbonyl compound, b.p. 40° (5 mm.). The carbonyl compound was identified as 4,6-heptadienal from its infrared, ultraviolet, and proton n.m.r. spectra, elemental analysis, and conversion to a 2,4-dinitrophenylhydrazone.

In other reactions conducted at room temperature with vinyl ethyl ether or at the reflux temperature with vinyl isobutyl ether, 4,6-heptadienal was isolated as the only product in yields of 70 and 72%, respectively. Examination of all reaction mixtures by gas chromatography prior to distillation failed to establish the presence of the desired product, vinyl 3-(penta-1,4-dienyl) ether, although, if present, it likely would have rearranged during passage through the v.p.c. column at 75°. More recent studies[4] carried out at $-10°$ have shown that the transvinylation product (II) is indeed formed and exists at this temperature as a mixture with divinylcarbinol (I) and 4,6-heptadienal (III). Evidently the vinyl ether (II) rearranges slowly to III even at this temperature.

These results would indicate that the reaction may be represented by the following scheme. Watanabe and Conlon[2] proposed a mechanism to describe the transvinylation reaction between an alcohol and a vinyl alkyl ether and represented the reaction essentially as a reversible alkoxymercuration distinguished by the formation of an intermediate or intermediates of a symmetrical nature so that reverse reactions leading to reactants or products were possible. In view of the previous successful instances[2,3] where allylic alcohols were employed in this reaction, no immediate obvious abnormal behavior was expected when divinylcarbinol was utilized under similar conditions. Apparently the rearrangement occurs owing to the labile nature of II.



$$\underset{\text{I}}{(CH_2{=}CH)_2{-}CH{-}OH} + CH_2{=}CH{-}OR \xrightleftharpoons{Hg(oAc)_2} \underset{\text{II}}{(CH_2{=}CH{-})_2{-}CH{-}OCH{=}CH_2} + ROH$$

$$\downarrow$$

$$\underset{\text{III}}{CH_2{=}CH{-}CH{=}CH{-}CH_2CH_2C(=O){-}H}$$

The thermal rearrangement of vinyl allyl ethers to give aldehydes was first studied by Hurd and Pollack.[5] In general, these compounds are subjected to temperatures in the range of 150–250° to effect the rearrangement to their respective products. From an examination of the mechanism proposed[6] for the thermal rearrangement of vinyl allyl ethers, the product expected from the rearrangement of II is represented by III. Although other more complicated mechanisms may be suggested to explain the formation of III in this reaction, in most instances the experimental conditions and/or other factors preclude their acceptance.

It is suggested on the basis of the evidence that vinyl 3-(penta-1,4-dienyl) ether (II) is formed and immediately rearranges to 4,6-heptadienal (III) under reaction conditions. The ease of the rearrangement is attributed to the formation of the conjugated diene which acts as the driving force for the transformation. This represents the first reported study with this particular type of vinyl allyl ether and the first observation of the rearrangement of a vinyl allyl ether occurring at or below room temperature.

Experimental[7]

Divinylcarbinol was prepared by the method of Ramsden.[8] The vinyl alkyl ethers were purchased commercially and distilled prior to their use in the following reactions. Mercuric acetate was recrystallized from absolute ethanol. The proton n.m.r. spectrum of 4,6-heptadienal was obtained in a carbon tetrachloride solution (15%) on a Varian Associates A-60 instrument using a 60-Mc. probe. Tetramethylsilane was used as the external standard. The gas chromatography work was performed with an Aerograph instrument, Model A-100-C, with a 5-ft. dinonyl phthalate on Chromosorb column at 75°.

Reaction of Divinylcarbinol with Vinyl Ethyl Ether.—A solution of 1.5 g. of mercuric acetate and 0.5 g. sodium acetate in 14.5 g. (0.173 mole) of divinylcarbinol and 72.0 g. (1.0 mole) of vinyl ethyl ether was heated to reflux for a period of 12 hr. During this time the reflux temperature increased from 36.5 to 39°. Three grams of anhydrous potassium carbonate was added to the cooled solution followed by removal of the major part of the excess vinyl ether and ethyl alcohol at reduced pressure. The gas chromatogram showed the presence of vinyl ethyl ether, divinylcarbinol, and a peak of an unknown compound. The infrared spectrum of the mixture showed strong carbonyl absorption at 1733 cm.$^{-1}$. Distillation of the mixture gave 4.5 g. of divinylcarbinol (I), b.p. 45° (48 mm.), $n^{20}D$ 1.4432, and 10.67 g. (56%) of 4,6-heptadienal (III), b.p. 40° (5 mm.), $n^{20}D$ 1.4640. A small quantity (0.63 g.) of a viscous residue remained in the distillation flask. This residue was not characterized.

4,6-Heptadienal showed infrared absorptions at 1733 (carbonyl stretching vibration) and at 1610 and 1655 cm.$^{-1}$ (conjugated carbon–carbon double-bond stretching vibration) which are consistent with those expected.[9] The ultraviolet spectrum gave λ_{max} 266 mμ (ϵ 23,000). The proton n.m.r. spectrum showed a singlet at τ 0.27 (O=CH), a single peak with some structure centered at 7.58 (CH_2), and a multiplet ranging from 3.34 to 5.3 (vinyl protons of conjugated diene). The areas of the peaks were in a ratio of 1:4:5. These data strongly indicate the structure of the aldehyde isolated to be 4,6-heptadienal.

Anal. Calcd. for $C_7H_{10}O$: C, 76.36; H, 9.09. Found: C, 76.46; H, 9.16.

2,4-Dinitrophenylhydrazone of 4,6-Heptadienal.—Two grams of 4,6-heptadienal was added to a solution of 2.0 g. of 2,4-dinitrophenylhydrazine, 1.0 ml. of concentrated sulfuric acid, and 9.0 ml. of methanol. An immediate yellow precipitate appeared. After 30 min. the yellow solid was collected by filtration and recrystallized from 95% ethanol to give 3.87 g. of the 2,4-dinitrophenylhydrazone of 4,6-heptadienal, m.p. 101.5–102.5°.

Anal. Calcd. for $C_{13}H_{15}N_4O_4$: C, 53.60; H, 5.15; N, 19.24. Found: C, 53.47; H, 4.99; N, 19.06.

Reaction of Divinylcarbinol with Vinyl Ethyl Ether at Ambient Temperature.—A mixture of 10.0 g. (0.119 mole) of divinylcarbinol, 36.0 g. (0.5 mole) of vinyl ethyl ether, 1.2 g. of mercuric acetate, and 0.4 g. of sodium acetate was allowed to stir at ambient temperature (25–27°) for a period of 10 days. During this time, the mixture was examined at daily intervals by infrared spectroscopy and gas chromatography for the extent of reaction. The infrared spectrum of the mixture after 24 hr. showed carbonyl absorption at 1731 cm.$^{-1}$. Gas chromatograms of the mixture using a 5-ft. dodecyl phthalate column in a Perkin-Elmer instrument, Model A-100-C, showed the presence of all

---

[4] L. Boone, Rohm and Haas Co., Redstone Arsenal Research Division, Huntsville, Ala., unpublished results.

[5] C. O. Hurd and M. A. Pollack, *J. Am. Chem. Soc.*, **60**, 1905 (1938).

[6] C. O. Hurd and M. A. Pollack, *J. Org. Chem.*, **3**, 550 (1938).

[7] All boiling and melting points are uncorrected.

[8] H. E. Ramsden, *et al.*, *J. Org. Chem.*, **22**, 1602 (1957).

[9] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., pp. 40, 155.

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.

Acknowledgment.—This work was performed under the sponsorship of the U. S. Army under Contract DA-01-021 ORD-11878. Sincere appreciation is extended to Mr. L. Boone and Mrs. Carolyn Haney who supplied the proton n.m.r. spectrum of 4,6-heptadienal.

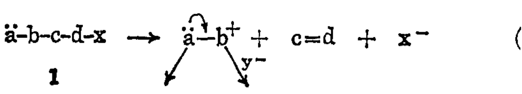
A Novel Fragmentation of *trans*-π-Bromocamphor

David H. Gustafson and William F. Erman

The Procter and Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239

Received December 2, 1964

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



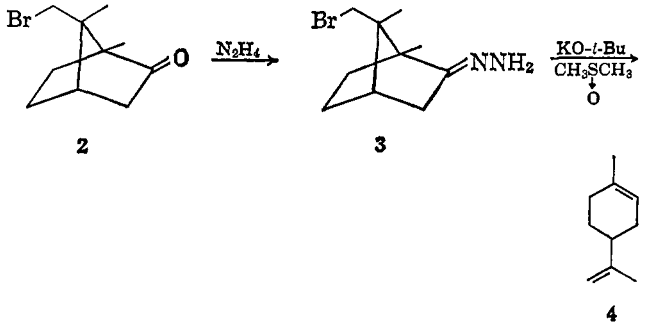
$$\ddot{a}\text{-}b\text{-}c\text{-}d\text{-}x \longrightarrow \ddot{a}{-}b^{+} + c{=}d + x^{-} \qquad (1)$$

$$\ddot{a}{-}b^{+} \longrightarrow {}^{+}a{=}b \qquad \ddot{a}{-}b^{+} \xrightarrow{y^{-}} \ddot{a}{-}b{-}y$$

1

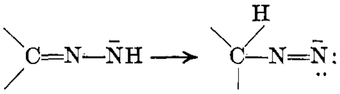
a–d must be able to form a double bond; x is a typical leaving group, *i.e.*, halogen, OTs, $^{+}NR_3$, etc., and a must be an atom or group of atoms capable of donating electrons either by resonance or inductive effects, *i.e.*, alkyl, aryl, OR, NR_2, etc. Grob[3] has shown that this reaction may occur 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.



2 **3** **4**

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 $-N{=}\bar{N}{:}$ 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.



$$>C{=}N{-}\bar{N}H \longrightarrow >\overset{H}{C}{-}N{=}\bar{N}{:}$$

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

---

[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).

[3] C. A. Grob, F. Ostermayer, and W. Raudenbusch, *Helv. Chim. Acta*, **45**, 1672 (1962); C. A. Grob and F. Ostermayer, *ibid.*, **45**, 1119 (1962).

[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).