[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

Solvent Effects in the Oxidation of Camphor Hydrazone by Mercuric Oxide

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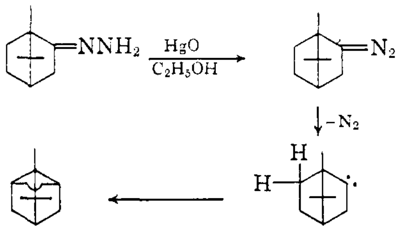
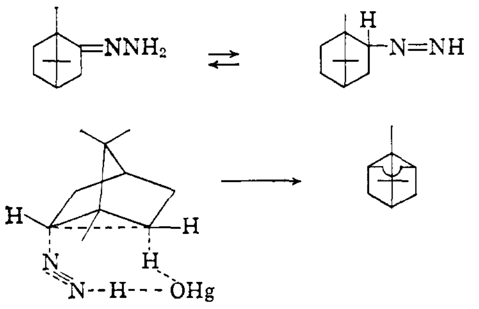
The rate at which camphor hydrazone is oxidized by mercuric oxide has been shown to be of the same order of magnitude for a variety of reaction solvents. When ethanol-d_1 was used as a solvent, no deuterium was incorporated in the tricyclene produced. These findings support the mechanism proposed by Meerwein for this reaction, and also have a bearing on the related alkaline decomposition of camphor tosylhydrazone. The nature of the heterogeneous step of this oxidation is briefly discussed.

In 1920 Meerwein reported[2] that the oxidation of camphor hydrazone with mercuric oxide gave the hydrocarbon tricyclene as the major product. Meerwein considered this unusual reaction to proceed by way of a carbene intermediate, which in turn was generated presumably from the corresponding diazo compound, as shown in equation 1.[3,4] Very little subsequent work has been done; the mechanism has accordingly been tacitly accepted.



(1)

Our interest in this reaction can be attributed to two factors. First, although it is certainly attractive, the Meerwein mechanism does not represent a unique rationale for the facts. Indeed, it appeared to us that a preliminary tautomerism of the hydrazone followed by decomposition on the mercuric oxide surface was a reasonable alternative (Equation 2).



(2)

Second, the alkaline decomposition of tosylhydrazones to olefinic and cyclic hydrocarbons has excited recent interest,[5-9] and is thought to proceed by way of an intermediate diazo compound similar to that proposed by Meerwein. The evidence cited by Shechter and Whiting suggests that the reaction solvent may affect the manner in which this intermediate decomposes. Thus a study of the course of camphor hydrazone oxidation in different solvents appeared likely to be of value.

RESULTS AND DISCUSSION

The rate of nitrogen evolution during the oxidation was determined for a variety of reaction solvents, and was found to be constant over a major portion (70–80%) of the reaction. It can be seen from Table I that at comparable temperatures the relative rate constants for different solvents were all within an order of magnitude of each other. An increase in the reaction temperature resulted in an increase of the rate of oxidation which corresponded to an enthalpy of activation of about 20 kcal. per mole. In each instance the volatile reaction products consisted of more than 97% tricyclene, only traces of camphene being observed.[10] This similarity of reaction rate and product composition in widely different solvents is in complete agreement with the Meerwein mechanism, but would be unexpected if a proton transfer immediately preceded the rate determining step (Equation 2).

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[1] Supported by the National Science Foundation, Undergraduate Research Participation Program.

[2] H. Meerwein and K. v. Emster, *Chem. Ber.*, **53**, 1915 (1920).

[3] The ability of carbenes to react with carbon hydrogen bonds is well known. W. von E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *J. Am. Chem. Soc.*, **78**, 3224 (1956).

[4] V. Heubaum and W. A. Noyes, *J. Am. Chem. Soc.*, **52**, 5070 (1930) observed that the red diazo compound obtained from bornylamine decomposed rapidly at room temperature to give tricyclene and nitrogen.

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

[6] L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959).

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

[8] C. H. DePuy and D. H. Froemsdorf, *J. Am. Chem. Soc.*, **82**, 634 (1960).

[9] L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **82**, 1002 (1960).

[10] Less volatile substances account for a significant portion of the organic material, particularly when older samples of hydrazone are used.

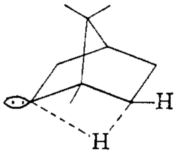
TABLE I

Reaction Solvent	Reaction Temperature	Relative Rates[a,b] of Oxidation
Ethanol	78°	1.0
Cyclohexane	80°	1.0
Cyclohexene	81°	0.94
Diglyme[c]	78°	1.2
Triethylamine[c]	78°	1.0
Heptane	98°	2.5
Toluene	95°	2.2
Xylene	95°	2.0
Xylene	120°	12
Diglyme[c]	120°	10

[a] All the rate measurements were made using three grams of camphor hydrazone in twenty five milliliters of solvent and eight grams of mercuric oxide. [b] These constants were taken from the linear portion of a plot of nitrogen evolved *vs.* time. [c] The oxidations in these solvents exhibited an anomalous decrease in rate for a brief period shortly after the beginning of the reaction.

Additional evidence was furnished by carrying out the oxidation using O-deuterated ethanol as the solvent. The tricyclene thus obtained was found to contain no significant amount of deuterium. This finding completely rules out a preliminary tautomerism of the type proposed above.

The contrast between the selectivity of the intermediate carbene advanced by Meerwein and the striking nonselectivity of methylene[3] suggests enhanced stability of the transition state (I) for the 1:3 hydrogen shift leading to tricyclene.



I

Indeed, it has recently been observed[11] that hydrazone oxidation in systems having less favorable geometry for such a shift results in much smaller cyclopropane: olefin ratios. It is also of interest to note that oxidation of the hydrazone from *exo*-trimethylene-2-norbornanone gave no product analogous to tricyclene.[12] In this case the authors point out that the trimethylene bridge would strain the tetracyclic product.

The decomposition of tosylhydrazones has generally been effected in strongly alkaline media at temperatures near 200°. Shechter and Whiting have reported[6,7] that decomposition of camphor tosylhydrazone in protonic solvents yields camphene as the major product, while decomposition in aprotic solvents leads to tricyclene in nearly quantitative amounts. These workers proposed that diazocamphane was a common intermediate, and that the variation in product composition was due to further reaction of this intermediate by two competing paths. In aprotic solvents the mechanism of decomposition would be essentially that proposed by Meerwein. Protonic solvents, on the other hand, could protonate the diazo intermediate giving a diazonium salt (or its equivalent) which would then rearrange to a variety of products.[13] By this reasoning, however, solvolytic protonation of the thermally unstable diazocamphane[3] should occur far more readily in the relatively neutral refluxing ethanol solutions used in this study than in the higher temperature alkaline mixtures used by Shechter and Whiting. The findings reported in this article therefore argue strongly against such a protonation,[14] provided the Meerwein mechanism for the oxidation is correct. Although this has not been shown unequivocally to be so, it is the only mechanism written to date which is in agreement with all of the facts.

During our study of the oxidation of camphor hydrazone, we were impressed by the constant rate of nitrogen evolution observed for a major portion of the reaction. This regularity was not expected, as the oxidation is rather complex and the mercuric oxide surface is continuously being destroyed as the reaction progresses. Additional evidence was therefore acquired, which we feel is pertinent to the heterogeneous (rate determining) step:

1. The rate of oxidation was roughly proportional to the amount of mercuric oxide used. 2. The rate of oxidation was insensitive to the addition of mercury in amounts up to one equivalent. 3. When cyclohexane was used as a solvent, the addition of an equivalent amount of water (with respect to the hydrazone used) had no effect on the rate of oxidation, but the removal of all traces of water from the reaction (a molecular sieve was used in situ) resulted in a fivefold reduction of the rate. 4. The rate of oxidation in ethanol solutions was not affected by either the addition or removal of water.

In view of the complexity of this reaction system, a detailed description of the heterogeneous phase must await a more thorough investigation. However, a brief presentation of a mechanism which is consistent with many of the facts may be of some interest. If it is assumed that the concentration of hydrazone molecules adsorbed at active sites on the mercuric oxide surface is small compared to hydrazone available in solution, and if each

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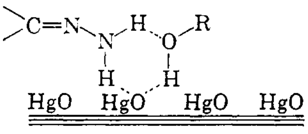
(11) R. L. Young, *Diss. Abstr.*, **20**, 1882 (1959).

(12) L. Kaplan, H. Kwart, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **82**, 2341 (1960).

(13) W. Hückel and F. Nerdel, *Ann.*, **528** 57 (1937) have shown that nitrous acid treatment of bornylamine results in camphene, camphene hydrate, and α-terpineol as the major products.

(14) Whiting and Powell[7] report that thermal decomposition of diazocamphane in 2-ethoxyethanol gives mixtures rich in camphene, particularly at lower temperatures. This result provides good support for the protonation mechanism, but conflicts with the earlier work of Heubaum and Noyes,[4] who found that decomposition of diazocamphane in ethereal hydrogen chloride solutions gave tricyclene as the major product.

time an active site is destroyed by reacting a new one is produced, the reaction system would be expected to exhibit zero order kinetic behavior.[15] A transition state (II) for reaction at an active site can be written so that the water (or alcohol)



II

molecule involved in the six membered cyclic complex is well situated to activate an adjacent mercuric oxide site, after reacting.

EXPERIMENTAL

Analytical grade mercuric oxide (yellow), freshly prepared camphor hydrazone,[16] and carefully purified solvents were used throughout the investigation. Unless otherwise stated, the oxidations were carried out in refluxing solvents with rapid agitation by a Hershberg type stirrer. An electrically heated oil bath controlled to ±2° was used as a source of heat. The volatile products were analyzed by the infrared method of Swann and Cripwell[17] and by vapor phase chromatography using a standard 2-meter column having butyl phthalate on firebrick as the fixed phase.

d-Camphor hydrazone. The hydrazone was prepared by refluxing *d*-camphor with 4 moles of 95% hydrazine and 1 mole of acetic acid in three times its weight of absolute ethanol for 4 hr. After removing the ethanol at aspirator pressure, the reaction mixture was brought to its original volume with ether, the lower hydrazine layer was removed and the reaction mixture was washed with 10% sodium hydroxide saturated with sodium chloride followed by saturated sodium chloride alone. Removal of the solvents under aspirator pressure followed by distillation at reduced pressure gave camphor hydrazone, m.p. 55°, b.p. 68° (5 mm.), in about 75% yield.

Kinetic procedure. A solution of 3 g. of camphor hydrazone in 25 ml. of the solvent being investigated was placed in a three necked flask equipped with a Hershberg stirrer, a condenser, and a solid addition tube. The solution was then heated to the desired temperature, the stirring was begun and the mercuric oxide (8 g.) was quickly added in one portion. The nitrogen evolved was measured by a gas burette attached to the condenser. Under these conditions the apparent zero order rate constant for the reaction in refluxing ethanol was 7×10^{-4} moles/min.

Oxidation in ethanol-d_1. Ten grams of camphor hydrazone was dissolved in 20 ml. of ethanol-d_1 at room temperature. After a few minutes 20 g. of mercuric oxide was added, and the mixture was refluxed with stirring for 2 hr. Ethanol (10 ml.) was added to the cooled reaction mixture, the slurry was filtered and the clear filtrate was quickly distilled over a short path leaving the higher boiling, nonvolatile products behind. The addition of an equal volume of cold water to the distillate gave a cloudy solution which was extracted four times with pentane. Careful removal of the solvent from the dried pentane extracts left a thick oil consisting largely of tricyclene. The tricyclene was freed from traces of camphene by treatment with alkaline permanganate. Two distillations at atmospheric pressure gave 2.8 g. of tricyclene (35%), m.p. 64.5°.

DEUTERIUM ANALYSIS

Reaction Solvent	% Tricyclene-d_1
Ethanol	0.05
Ethanol-d_1	0.41[18]

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[15] K. J. Laidler, *Chemical Kinetics*, McGraw-Hill, New York, 1950, 154.

[16] Camphor hydrazone is quite hygroscopic and the hydrate decomposes to camphor azine at room temperature. We have also detected the presence of camphor in older samples.

[17] G. Swann and F. J. Cripwell, *Ind. Chem.*, **24** 573 (1948).

[18] The small but real deuterium content observed is probably due to enolization of the hydrazone prior to being oxidized.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

Cation-Exchange Resin Catalyzed Hydrolysis and Decarboxylation of Esters of Acetoacetic and Malonic Acids

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The simultaneous hydrolysis and decarboxylation of negatively substituted esters as catalyzed by cation-exchange resins was compared to similar reactions catalyzed by equivalent amounts of sulfuric acid. In the acetoacetic ester system the resin was found to be more efficient than an equivalent amount of sulfuric acid. With diethyl malonate and ethyl hydrogen malonate the resin system specifically favored the formation of ethyl acetate, seemingly a product of decarboxylation of the half-ester. Essentially no difference was obtained, however, in the relative efficiencies of the two catalysts for the overall reaction. The resin again was found to be the more effective catalyst for the hydrolysis and decarboxylation of α-ethylmalonic ester.

Esters of acetoacetic and malonic acids are usually hydrolyzed in mild alkaline solution to give the alkali metal salts of the acids. Heating the acidified solutions resulting from these hydrolyses results in decarboxylation and the formation of a methyl ketone or an acid. Acid catalyzed hydrolysis of these esters would be expected to be

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[1] Taken from the Ph.D. thesis of John A. Oscar.

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