mol.) of 1,4-bis-4(phenylbutadienyl)benzene was refluxed with 20 ml. of *o*-dichlorobenzene for 3 hr. The mixture was cooled and a trace of crystalline solid was filtered and discarded. The filtrate was refluxed with 100 ml. of absolute alcohol containing 5 g. of potassium hydroxide. The solvent was practically evaporated under nitrogen and the damp residue was extracted with water. The aqueous layer was separated from water insoluble matter by the addition of a little ether. The intense yellow aqueous phase was treated with a little decolorizing carbon, filtered, and the filtrate was then neutralized with dilute hydrochloric acid and then made basic again by the addition of 5 g. of sodium carbonate. Thirty g. of potassium ferricyanide was dissolved in 200 ml. of water and the two solutions were mixed. The mixture rapidly turned milky, but the very finely divided precipitate could not be satisfactorily filtered. The suspension was centrifuged and the deposited solid was washed several times by centrifugation. The precipitated solid was dried in a vacuum oven to give 3.6 g. (theory 3.8 g.) of a green tinged solid. An analytical sample was prepared by subliming 0.3 g. at 0.2 mm. and 300°. The yellowish solid melted at 380–390° on the hot bar. Further purification was carried out by recrystallizing the product from dimethylsulfoxide from which it was obtained as large well defined leaflets. The infrared and ultraviolet spectra were consistent with the structure of quinquephenyl. No carbonyl bands could be detected in the infrared.

*Anal.* Calcd. for $C_{30}H_{22}$: C, 94.24; H, 5.76. Found: C, 94.19, 94.27; H, 5.95, 5.96.

The over-all yield of sublimed quinquephenyl in several preparations was 50% based on 1,4-bis(4-phenylbutadienyl)benzene.

*Preparation of 4,4''''-dimethylquinquephenyl.* This synthesis was carried out as described for the preparation of quinquephenyl only using 3.63 g. (0.010 mol.) of 1,4-bis[4-(*p*-tolyl)butadienyl]benzene instead of 1,4-bis(4-phenylbutadienyl)benzene. The total products (17.3 g.) from four experiments on this scale were combined and sublimed at 350° and 0.07 mm. The light yellow crystalline sublimate weighed 6.9 g. (42%), m.p. > 400°. This could be recrystallized from tetramethylenesulfone to give light yellow leaflets.

*Anal.* Calcd. for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.59, 93.65; H, 6.48, 6.57.

*Preparation of 2',3'''-dimethylquinquephenyl.* The synthesis of this compound was carried out as described for the preparation of quinquephenyl only using 3.63 g. (0.010 mol.) of 1,4-bis(3-methyl-4-phenylbutadienyl)benzene in place of 1,4-bis(4-phenylbutadienyl)benzene. The yield of crude product was 4.7 g. This was sublimed at 210° and 0.05 mm. The colorless sublimate weighed 3.5 g. (85%), m.p. 217–218°.

*Anal.* Calcd. for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.57, 93.61; H, 6.43, 6.48.

*Attempted nitration of p-quinquephenyl.* One-half g. of *p*-quinquephenyl was heated for 1 hr. with 100 ml. of concentrated nitric acid under reflux. Five ml. of concentrated sulfuric acid was added and heating continued for 26 hr. At the end of this time there was some crystalline solid present which was removed by filtration. It was washed with water and a little acetone and dried in the vacuum oven. Weight 0.1 g. (A).

The mother liquor was poured into water and the resulting fluffy precipitate filtered, washed with water and dried in the vacuum oven. Weight 0.4 g (B).

The infrared spectra of both A and B are quite similar both showing nitro groups present, but impossible to determine sites of substitution since both *m*- and *p*-substitution appear. (B) shows some carbonyl (probably acid) present.

*Preparation of 1,6-diphenylhexatriene.* A mixture of 8.0 g. (0.019 mol.) of triphenylcinnamylphosphonium chloride, 2.6 g. (0.020 mol.) of cinnamaldehyde, 50 ml. of ethanol, and 100 ml. of 0.2*M* lithium ethoxide reacted rapidly with separation of a pastel pink solid. This product was recrystallized from xylene in the presence of iodine to give the all-*trans*-diphenylhexatriene as pale yellow leaflets, m.p. 206–207° (hot bar). The yield of pure product was 0.90 g. and product of lesser purity (m.p. 180–185°) was 2.2 g. An analytical sample melting at 203° was obtained by recrystallization from cyclohexane-benzene mixture.

*Anal.* Calcd. for $C_{18}H_{16}$: C, 93.07; H, 6.93. Found: C, 93,10, 93.09; H, 7.00, 7.01.

*Preparation of 1-(3-nitrophenyl)-6-phenylhexatriene.* A mixture of 5.6 g. (0.013 mol.) of triphenylcinnamylphosphonium chloride and 2.4 g. (0.013 mol.) of *m*-nitrocinnamaldehyde in 50 ml. of ethanol was treated with 80 ml. of 0.2*M* lithium ethoxide. The reaction proceeded normally and after 1 hr. it was diluted with an equal volume of water and the solid was filtered. The solid was dissolved in boiling xylene and the wet solution was dried with magnesium sulfate, decolorized, and cooled. Approximately 0.9 g. of an offcolor, yellow crystalline solid separated which was filtered and the filtrate was rejected. The solid melted in the range of 175–180°. It was recrystallized from 20 ml. of xylene to give 0.3 of stubby yellow needles, m.p. 182–184°. An analytical sample was obtained by recrystallizing again from boiling xylene followed by drying at 110° for 4 hr. This product melted at 184–185.5°.

*Anal.* Calcd. for: $C_{18}H_{15}NO$: C, 78.0; H, 5.4. Found: C, 78.36, 78.48; H, 5.68, 5.65.

*Reaction of benzaldehyde with 1,4-bis(triphenylphosphonium chloride)butene-2.* In the reaction of benzaldehyde and the subject phosphonium salt, a low melting crystalline solid was obtained which was dissolved in benzene to give a lemon yellow solution. A crystal of iodine was then added which brought about the immediate precipitation of a crystalline solid of a more orange color. This was allowed to stand in the air for a short time. However, the next day only a brown gum remained in the dish.

Only a brown resin was obtained with cinnamaldehyde.

WILMINGTON 98, DEL.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO AND THE ARGONNE NATIONAL LABORATORY]

# Beckmann Rearrangement in Hydrogen Fluoride

K. D. KOPPLE AND J. J. KATZ

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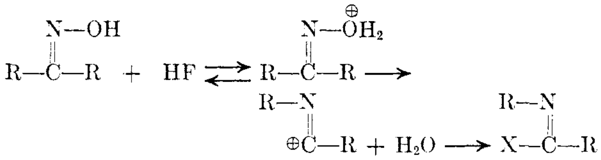
In contrast to benzophenone oxime, cyclohexanone oxime does not undergo the Beckmann rearrangement in hydrogen fluoride solution. The *O*-benzoyl derivatives of both oximes rearrange readily.

Most of the reagents that are commonly used to effect the Beckmann rearrangement of oximes, *e.g.*, concentrated sulfuric acid, polyphosphoric acid, and acid chlorides, are capable of producing esters, $R_2C{=}N{-}O{-}X$, prior to rearrangement, but whether ester formation is a necessary prelude to rearrangement is not an entirely settled question.[1] The rearrangement of benzophenone oxime by hydrogen chloride in an inert solvent probably proceeds at least in part *via* a mechanism in which water, rather than another acid, is the leaving group.[2] Although water is probably also the leaving group in the same rearrangement as carried out in concentrated aqueous hydrochloric acid,[2,3] prior ester formation is not excluded in other cases.[1,4]

We wish to report experiments in which Beckmann rearrangements are carried out in anhydrous hydrogen fluoride, a highly polar and strongly acidic solvent. The results of these experiments can be described briefly: Cyclohexanone oxime, on storage in hydrogen fluoride for 24 hr. at room temperature, does not rearrange detectably; the corresponding *O*-benzoyl derivative is converted to caprolactam. Benzophenone oxime is about 60% rearranged on 2-hr. storage in hydrogen fluoride; its benzoate reacts quantitatively in a similar period.

The immediate inference from these results is that oxime esters rearrange more readily than the oximes themselves, a conclusion which is in agreement with much previous work.[4] The difference in reactivity between the two unacylated oximes is worth discussion. It is unlikely that the reaction of benzophenone oxime proceeds through *slow* formation of *N*-fluoroimine, for there is no obvious reason for cyclohexanone oxime to react in this sense so much less readily than benzophenone oxime. In addition, since *N*-chloroimines have been shown not to rearrange,[5] fluoroimines are also apt to be relatively stable once formed. The most likely path for rearrangement of benzophenone oxime in hydrogen fluoride is the obvious one.



$$R{-}\overset{\overset{\textstyle N{-}OH}{\|}}{C}{-}R + HF \rightleftharpoons R{-}\overset{\overset{\textstyle N{-}\overset{\oplus}{O}H_2}{\|}}{C}{-}R \longrightarrow \oplus\overset{\overset{\textstyle R{-}N}{\|}}{C}{-}R + H_2O \longrightarrow X{-}\overset{\overset{\textstyle R{-}N}{\|}}{C}{-}R$$

$$X = -F,\ -OH_2\oplus$$

In this formulation the protonated oxime is an intermediate, and water is lost. That cyclohexanone oxime does not rearrange under the conditions used (while benzophenone oxime does) can be ascribed to a requirement of anchimeric assistance by the phenyl group when the leaving group is water. It has been reported that in 94.5% sulfuric acid cyclohexanone oxime and benzophenone oxime rearrange at about the same rate[6]; in this case, where a sulfuric ester may be the rearranging species and sulfuric acid is lost during rearrangement, the assistance provided by the migrating phenyl group is less important. In the transition state, N—O bond breaking has proceeded farther and migration is less complete than in the hydrogen fluoride catalyzed reaction where water is the departing species.

We are indebted to Mr. Lloyd A. Quarterman for his assistance in parts of this work.

## EXPERIMENTAL

*Materials and method.* Cyclohexanone oxime, m.p. 91–92°, and benzophenone oxime, m.p. 142°, were prepared by standard procedures. *O*-benzoyl cyclohexanone oxime, m.p. 62–63°[7] and *O*-benzoyl benzophenone oxime, m.p. 100°[8] were obtained by treatment of the oximes with benzoyl chloride in pyridine, precipitation of the benzoylated products with excess water, and recrystallization from ethanol water.

Commercial hydrogen fluoride was purified in a metal-free apparatus as described elsewhere and was determined by conductivity measurements to be of purity greater than 99.95%. Reactions using hydrogen fluoride were carried out in molded poly(chlorotrifluoroethylene) tubes attached to an appropriate vacuum line.[9]

*Rearrangement of O-benzoyl benzophenone oxime.* Samples of this substance (1 g.) were treated at room temperature with hydrogen fluoride (about 3 ml. liquid) for 2 and 24 hr.; complete reaction was observed in each case. The tan powder obtained after removal of volatile material was triturated with aqueous sodium bicarbonate and then with water; dried, this crude product had m.p. 155–160° and corresponded to a 90% yield (0.6 g.) of crude benzanilide. Recrystallization from ethanol water afforded pure benzanilide, m.p. 163°.

*Rearrangement of benzophenone oxime.* A solution of benzophenone oxime, 1.00 g., in 3 ml. of hydrogen fluoride was stored 2 hr. at room temperature before removal of the solvent. The resulting powder was washed with sodium bicarbonate solution and with water, then dried. Benzanilide (0.21 g., 53%) was obtained by fractional crystallization of an aliquot (0.40 g.) from ethanol water. Another sample (0.48 g.) was boiled 20 min. with 6 ml. of 50% ethanol 3*N* in hydrochloric acid, diluted to 20 ml. with ethanol, and mixed with 15 ml. of 2,4-dinitrophenylhydrazine reagent.[10] After 20 min. at reflux there was obtained 0.27 g. (31%) of benzophenone 2,4-dinitrophenylhydrazone, m.p. 237–239°.

*Rearrangement of O-benzoyl cyclohexanone oxime.* The oxime benzoate (1.00 g.) was dissolved in 3 ml. of hydrogen fluoride at room temperature for 24 hr. The oil remaining after pumping off solvent was washed with bicarbonate solution and extracted into methylene chloride. After drying over magnesium sulfate, the methylene chloride solution was

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concentrated and the residue distilled in vacuum to give 0.38 g. (72%) of crystalline caprolactam. The product had infrared spectrum identical to that of an authentic sample of caprolactam.

*Effect of hydrogen fluoride on cyclohexanone oxime.* A sample of cyclohexanone oxime (1.01 g.) was subjected to the same treatment as its benzoate as described above. In this case, the methylene chloride soluble fraction crystallized immediately on removal of solvent to give 0.23 g. (23%) of crude cyclohexanone oxime, m.p. 87°. No traces of caprolactam were detected. Since removal of hydrogen fluoride was accomplished by 150 hr. pumping at near 1$\mu$ pressure, sublimation of the oxime may account for the poor recovery.

CHICAGO, ILL.
LEMONT, ILL.

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[CONTRIBUTION FROM CHEMISTRY DEPARTMENT, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY]

# Periodate Oxidation of Compounds Related to Malondialdehyde

HERMAN L. MARDER[1] AND CONRAD SCHUERCH

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The methylene carbon of malondialdehyde bis(dimethyl)acetal and 2-deoxy-D-glucose (D-arabino-2-deoxyhexose) is oxidized to carbon dioxide *via* malondialdehyde, hydroxymalondialdehyde, and mesoxdialdehyde. Evidence is presented that this is the common oxidation route for compounds producing malondialdehyde and hydroxymalondialdehyde.

In a study of the periodate oxidation of polyvinyleneglycol (polyhydroxymethylene) and vinylene glycol–vinyl alcohol copolymers, (derived from the hydrolysis of vinylene carbonate–vinyl acetate copolymer) it became necessary to clarify the overoxidation of malondialdehyde and hydroxymalondialdehyde by periodate solutions. Although overoxidations have been studied, there are few data which show the simultaneous formation of products and consumption of periodate and some inconsistencies appear in the literature.

For orientation, we investigated the periodic acid oxidation of glucose, mannitol, inositol, glycerol and tartaric acid, and in addition, studied the oxidation of malondialdehyde bis(dimethyl) acetal and 2-deoxy-D-glucose, two compounds the oxidation of which has not been previously reported.

Under the reaction conditions reported in the experimental section, glycerol consumed 2.0 molar equivalents of periodic acid and produced 1.0 mol. of titratable acid in 1 hr. and the product and oxidant concentrations remained unchanged over a 30 hr. period. Mannitol consumed nearly 5.0 (or 4.9) mole of periodic acid in 10 hr. but produced less than the theoretical amount of titratable acid, 3.7 mole rather than 4.0. Over a 70 hr. period the yield of acid increased slightly and the periodate consumption rose to slightly more than the theoretical amount 5.1 rather than 5.0.[2] We interpret this to mean that a slight amount of overoxidation occurs probably by the mechanism discussed below.

Inositol was studied with less precision but gave evidence of overoxidation as has been reported previously and is to be discussed below. The consumption of periodate and formation of acid by glucose was quantitative in 30 hr. and unchanged over an additional 40 hr. when the reaction was carried out with periodic acid but was not quantitative with sodium periodate because of formate ester formation. The oxidation of tartaric acid (Fig. 1) consumed the theoretical 3.0 mole of periodate in less than 20 hr. but no more over 350 hr. of reaction time. Similarly the titratable acid remained unchanged over 350 hr. In this selection of polyhydric alcohols, aldehydes and acids, there was therefore no evidence of side reactions except in those cases that might produce hydroxymalondialdehyde as an intermediate, and furthermore formic acid was stable to periodate (or more correctly, mixtures of periodate and iodate[2]) over the entire 350 hr. period of our experiments.

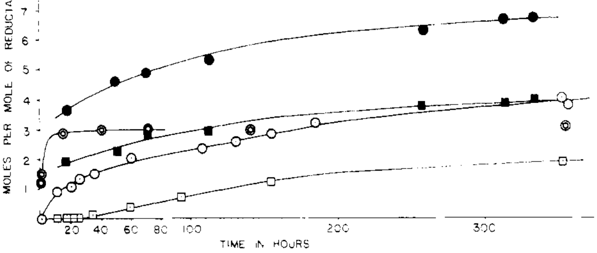

Figure 1. Oxidation of some model compounds with 0.0125$M$ periodic acid

According to published data on the rate of hydrolysis of malondialdehyde bis(dimethyl) acetal

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[1] Abstracted from a portion of a thesis presented by Herman L. Marder in partial fulfillment of the requirements of the Ph.D. degree at Syracuse University. Present address: Textile Fibers Dept., Pioneering Research Division, Wilmington 98, Delaware. E. I. du Pont de Nemours and Company.

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