a Teflon stirrer, and a pressure-equalizing dropping funnel. One neck of the flask was equipped with a rubber serum cap through which gas was admitted *via* a hypodermic needle which allowed the gas to pass over the mixture. When no purging gas was used, the Dry Ice condenser was replaced by an air-cooled condenser, and the ether was allowed to reflux so that a small amount constantly escaped from the top of the condenser which was protected from the atmosphere by a drying tube containing Drierite.

The Grignard reagents listed in Table I were prepared by the dropwise addition of the organic halide to a 10% excess of the magnesium metal in ether so that the final Grignard solution was approximately $2N$ in RMgX. When all of the halide had been added, the solution was heated under reflux from 2–3 hr., allowed to cool to room temperature, and was transferred to rubber serum-capped bottles by means of a hypodermic syringe. One-milliliter samples were titrated with $0.1N$ hydrochloric acid and with $0.1N$ silver nitrate using the Volhard method.[3]

ROHM & HAAS CO.
BRISTOL, PA.

(3) W. Reiman, III, J. D. Neuss, and B. Naiman, *Quantitative Analysis*, McGraw-Hill Book Co., Inc., New York, 1951, p. 270.

A Test for Peroxides in Vinyl Ethers

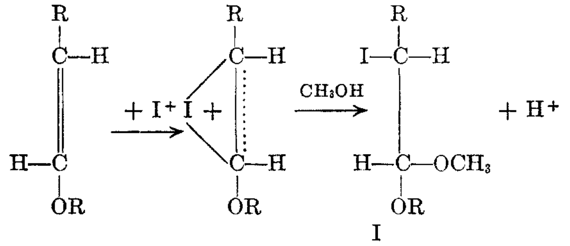
R. K. SUMMERBELL AND D. KAREN ANDERSON HYDE

Received April 8, 1960

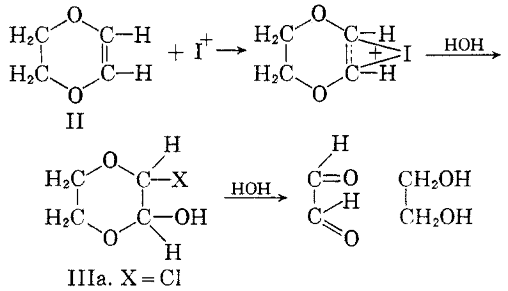
The hazards involved in evaporating or distilling ethers that contain peroxides are well recognized. In safety conscious laboratories a routine test is employed periodically to make certain that samples of ethers that have developed a dangerous peroxide content are discarded. The usual test[1] is to add acidified or neutral aqueous or alcoholic iodide to the suspected sample, or *vice versa* and a brown coloration is positive. The test is readily performed quantitatively.[2a,b] The purpose of this note is to point out that this test as usually performed is not valid in the presence of vinyl ethers and to suggest a modified procedure with which vinyl ethers do not interfere.

The reason for the failure of the usual form of the test is the immediate reaction of the liberated iodine with the vinyl ether. We became interested in the reaction when, during preliminary studies of the relative rates of iodine liberation by isomeric tetrachlorinated dioxanes,[3] we noticed that addition of water caused a rapid fading of the iodine color. Apparently the double bonded product from which vicinal halogens had just been removed by iodide ions was in turn adding back the iodine. The related parent compound, dioxene, was found to react with aqueous iodine as fast as mixing took place. It was then realized that a dioxene was a type of vinyl ether and that the observed reaction was closely related to the valuable quantitative method of Siggia and Edsberg[4] for determination of vinyl ethers by titration with aqueous methanolic iodine. These authors do not mention interference by peroxides, perhaps because it is so obvious, nor did they have occasion to point out the corollary: *that vinyl ethers would negate the usual peroxide test.* In view of the increasing commercial availability of vinyl ethers and the extreme hazards of handling ethers that contain peroxides, we think the corollary should be emphasized.

There is some evidence available concerning the course of these related reactions. Siggia and Edsberg[4] isolated an iodine-containing organic product from the reaction of methanolic iodine with butyl vinyl ethers, the analysis of which was consistent with the formula of an iodoacetal, I. The following mechanism explains this result:



In the case of our modified vinyl ether, II, the reaction would proceed further:



IIIa. X = Cl
b. X = I

We have identified the glyoxal and the ethylene glycol by isolation of appropriate derivatives. The intermediate, IIIb, is the iodine analogue of one postulated by Salomaa.[5] To account for the first order kinetics of the hydrolysis of *trans*-2,3-dichloro-*p*-dioxane,[6] he proposed that the hydrolysis of IIIa was much more rapid than that of the parent dichloro compound. The iodine compound, IIIb, should hydrolyze even faster. There is no evidence for the formation of an intermediate diiodo

---

(1) *Reagent Chemicals*, Am. Chem. Soc. Specifications (1955), American Chemical Society, Washington, D. C.

(2) (a) K. V. Kopatnur and M. Jelling, *J. Am. Chem. Soc.*, **63**, 1432 (1941).

(b) Union Carbide Chemical Co. *Ethers and Oxides* Booklet number 4764B (1957).

(3) A qualitative difference in rates was first observed by Milton Cooper, Ph.D. dissertation, Northwestern University, 1955.

(4) S. Siggia and R. L. Edsberg, *Anal. Chem.* **20**, 762 (1948).

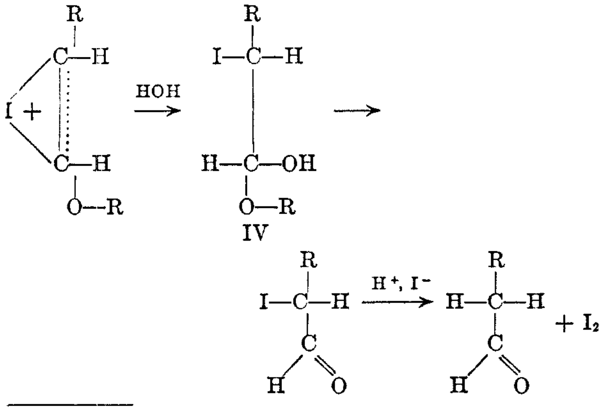
(5) P. Salomaa, *Acta. Chem. Scand.*, **8**, 744 (1954).

(6) R. K. Summerbell and Hans E. Lunk, *J. Am. Chem. Soc.*, **79**, 4802 (1957).

compound as proposed some years ago in a related situation.[7]

The proposed mechanism led us to the prediction that the use of a solvent less polar than aqueous methanol would materially reduce the velocity of iodine uptake by vinyl ethers. This was found to be the case. As the ratio of methanol to water was increased, the reaction tended to become more quantitative[8] with ordinary vinyl ethers, but also to take considerably more time to reach completion. By using a solvent of sufficiently low dielectric content, it should be possible to so reduce the rate of iodine uptake that interference with the usual peroxide test would be inconsequential. Peroxide-free dioxane was found to be the solvent of choice for this purpose, as considerable water must be admixed before the rate of uptake of iodine becomes appreciable. The use of pure dioxane as the major solvent component thus serves as a single and practical modification of the iodide test for peroxides in ethers, a modification that makes the test valid in the presence of vinyl ethers.

We have made several incidental observations concerning the Siggia and Edsberg method. It does not work at all for 2,3-diphenyl-*p*-dioxene.[9] This compound was not only inert to aqueous methanolic iodine, in which it was insoluble, but also to aqueous methanolic iodine solutions, in which it was completely soluble. Failure of this type of vinyl ether to react is probably due to the stabilization of the double bond by resonance with the phenyl groups. The general inferiority of water to methanol as a solvent may be due to the tendency toward halogen-catalyzed polymerization,[10] particularly when two phases are permitted, or even when the limit of solubility is approached. In some cases, Siggia and Edsberg observed a somewhat unsatisfactory end point due to reappearance of iodine on standing. This could be due to air oxidation, but also could be caused by the following sequence:



As both water and methanol are present and competing for the carbonium ion, some of the unstable hemiacetal, IV, as well as the acetal that was actually isolated, I, would form. The iodine regeneration from this source can be prevented by buffers which reduce the hydrogen ion concentration. The reported failures[4] of the method in the case of lauryl vinyl ether and octadecyl vinyl ether result because if water is present, two phases and polymerization result, while if water is excluded, the initial attack of positive iodine is so slow that no reaction is observed. Probably at least one component of the solvent must be capable of participation in the reaction,[11] explaining the failure of the determination using carbon tetrachloride.[4]

EXPERIMENTAL

Aqueous iodine and dioxene. Standard iodine solutions, approximately 0.1*M*, containing also 80 g. of iodate-free potassium iodide per l. were prepared by exact weighing of pure iodine. Arsenious oxide and sodium thiosulfate solutions for back titration were standardized against the iodine solutions.

Dioxene, 0.0123 mole, dissolved in 150 ml. of water containing sodium acetate–acetic acid buffer required 0.0117 moles of iodine for an iodine/ether ratio of 0.951 to give a pale coloration. In a similar experiment when no buffer was used, the iodine/ether ratio was 0.931. Substitution of methanol for part of the water did not change the iodine/ether ratio. Rapid addition of excess iodine and back titration with sodium thiosulfate gave an iodine/ether ratio of 0.949.

The products of reaction were proved by the preparation of derivatives. To a reaction mixture of dioxene titrated with aqueous iodine was added an excess of *p*-nitrophenylhydrazine hydrochloride in water. After slight warming on a steam bath, a dark orange precipitate was formed. It gave the characteristic blue color with alcoholic sodium hydroxide, and a mixed melting point with a pure example of glyoxal *p*-nitrophenyl osazone was not depressed. A solution of 7.3 g. of dioxene in water was titrated with iodine to a pale yellow end point. The total volume of the reaction solution was 150 ml. To half of this solution was added enough 20% sodium hydroxide to make the solution basic. A 1.5-ml. portion of benzoyl chloride was added, and the mixture shaken vigorously with intermittent additions of base. The dibenzoate of ethylene glycol which formed had a melting point of 71.5–72.5°. The yield was 9%. In earlier experiments, a less concentrated solution was used and no benzoate was isolated. Model experiments using the calculated amount of ethylene glycol in the present dilution gave about the same yield, but when the concentration was halved, the yield was cut to the vanishing point.

Failure of 2,3-diphenyl-p-dioxene to react. 2,3-Diphenyl-*p*-dioxene[9] (0.2072 g., 0.00087 mole) was placed in a glass-stoppered Erlenmeyer flask with 150 ml. of methanol and 10.00 ml. of 0.0923*M* iodine solution. Solution was complete. After shaking the solution for 10 min., it was titrated with sodium thiosulfate solution, 10.05 ml. being required. A blank containing 10.00 ml. of the iodine solution required exactly the same volume of thiosulfate solution. In a similar experiment in which the methanol was omitted, a suspension of the diphenyldioxene also failed to react with any aqueous iodine. The starting material was unaltered.

---

(7) V. I. Easton, *J. Applied Chem. U.S.S.R.*, **12**, 1387 (1939); *Chem. Abstr.*, **34**, 3233 (1940).

(8) Dioxene, unlike other vinyl ethers, reacted practically quantitatively with aqueous iodine.

(9) R. K. Summerbell and D. R. Berger, *J. Am. Chem. Soc.*, **81**, 633 (1959).

(10) D. D. Ely and J. Saunders, *J. Chem. Soc.*, 4167 (1952); 1668 (1954).

(11) K. Kozaki and R. A. Ogg, Jr., *J. Am. Chem. Soc.* **64**, 709 (1942).

Other vinyl ethers and aqueous iodine. Dihydropyran (0.0063 mole) was added to sodium acetate–acetic acid buffered water solution, excess standard iodine added and the excess back titrated; iodine consumed, 0.0039 mole for an ether/iodine ratio of 0.62. The ratio was raised to 0.73 in a similar experiment by the addition of 3 drops of pyridine as a polymerization inhibitor. It was raised still further to 0.91 by employing 80 ml. of methanol as the solvent. Divinyl ether (0.0109 mole), when titrated without buffer, required 0.0091 mole of iodine for a ratio of 0.83. On standing, the iodine color was regenerated. In a similar experiment buffered to pH 7 with phosphate, iodine was not regenerated. Vinyl ethyl ether, vinyl butyl ether, and dioxadiene gave iodine/ether ratios of 0.478, 0.381, and 1.58, respectively. In the latter case, even though enough methanol to ensure solution was used, an ether-insoluble solid was formed, direct evidence of extensive polymerization.

Peroxide test. A laboratory sample of ordinary dioxane from a bottle that had been in use several weeks gave a distinct yellow color when a few drops were added to an acidified aqueous solution of potassium iodide. Few samples of dioxane that have been exposed to the air and have not been specifically purified fail to give this test. When 3 drops of vinyl butyl ether was added to 1 ml. of the same dioxane, no test for peroxides could be obtained with water solutions if the volume of the water were equal to that of the dioxane. However, if only a few drops of aqueous potassium iodide and a drop of hydrochloric acid were added to a similar mixture of vinyl ether and the same dioxane, a strong test was obtained. Using mixtures of vinyl ethers and an ether known to contain peroxides, a positive test was always obtained in a 3:1 dioxane-water solution. The dioxane used as solvent was, of course, peroxide-free.[12] A negative test was always obtained when the same ether-peroxide–vinyl ether mixtures were subjected to the usual aqueous iodide test where water was present in large proportion.

An alternative test for the presence of peroxides in ether,[2b] the appearance of a pink or red coloration in the ether on shaking with ferrous thiocyanate solution, did not work in the presence of vinyl ethers, even though the samples under examination were known to contain large amounts of peroxides. In another experiment, a bright pink color was obtained by using a sample of typical sideshelf ethyl ether. When *n*-butyl vinyl ether was added to this test solution, the color gradually faded. The formation of black mercurous oxide on[13] shaking with a globule of metallic mercury was prevented by the presence of small percentages of vinyl ether in samples of ether that would otherwise give the test.

Acknowledgment. We wish to thank the E. I. du Pont Co. and the Research Corp. for research assistantships held by D.K.A.H.

NORTHWESTERN UNIVERSITY
EVANSTON, ILL.

---

[12] K. Hess and H. Frahm, *Ber.*, **71**, 2627 (1938); R. N. Feinstein, *J. Org. Chem.*, **24**, 1172 (1959).

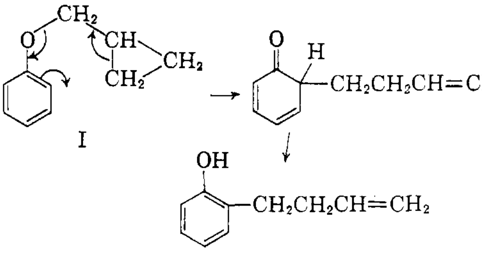
[13] C. R. Noller, *Chemistry of Organic Compounds*, W. B. Saunders Co., Philadelphia, 1951, page 139.

Attempted Thermal Rearrangement of Cyclopropylcarbinyl Phenyl Ether

HAROLD HART AND JAMES A. WREDE

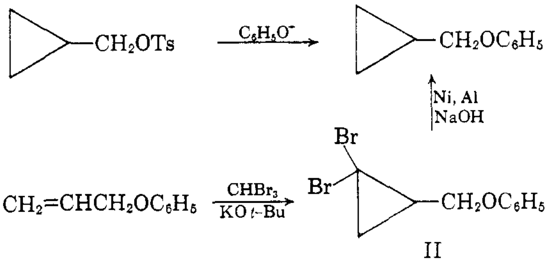
Received March 30, 1960

The cyclic nature of the transition state and the intermediacy of dienones in the Claisen rearrangement has been thoroughly established.[1] The cyclopropyl group sometimes displays chemistry similar to that of a carbon-carbon double bond.[2] It seemed possible, therefore, that the cyclopropylcarbinyl group might replace the allyl group in the Claisen rearrangement. A plausible mechanism can be envisioned and is depicted (1) for the thermal rearrangement of cyclopropylcarbinyl phenyl ether (I)



(1)

Compound I was synthesized by two independent methods: displacement by phenoxide ion on cyclopropylcarbinyl tosylate, and reduction of



2,2-dibromocyclopropylcarbinyl phenyl ether (II), the latter being prepared by the carbene reaction[3] on allyl phenyl ether.

When Compound I was refluxed (214°) for eighteen hours, or heated in a sealed tube at 300° for ten hours, it was recovered unchanged (identical infrared spectrum, negative ferric chloride test).[4] It is apparent, then, that the cyclopropylcarbinyl group does not behave like an allyl group in the Claisen rearrangement, at the ordinary tempera-

---

[1] For a review, see D. J. Cram in M. S. Newman, *Steric Effects in Organic Chemistry*, John Wiley & Sons, Inc., New York, N. Y., 1956, pp. 295–303. For subsequent work, see especially D. Y. Curtin and R. J. Crawford, *J. Am. Chem. Soc.*, **79**, 3156 (1957); F. Kalberer and H. Schmid, *Helv. Chim. Acta*, **40**, 13, 779 (1957); W. Haegele and H. Schmid, *Helv. Chim. Acta*, **41**, 657 (1958); P. Fahrni and H. Schmid, *Helv. Chim. Acta*, **42**, 1102 (1959); H. L. Goering and R. R. Jacobson, *J. Am. Chem. Soc.*, **80**, 3277 (1958); W. N. White, D. Gwynn, R. Schlitt, C. Girard, and W. Fife, *J. Am. Chem. Soc.*, **80**, 3271 (1958).

[2] For reviews, see R. A. Raphael in E. H. Rodd *The Chemistry of Carbon Compounds*, Elsevier Publishing Co., Amsterdam, 1953, Vol. IIA, pp. 25–28; E. Vogel, *Fortschr. Chem. Forsch.*, **3**, 430 (1955); E. Vogel, *Angew. Chem.*, **72**, 4 (1960).

[3] W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

[4] Compound I was readily attacked both by acid and by potassium metal; the products have not yet been identified.