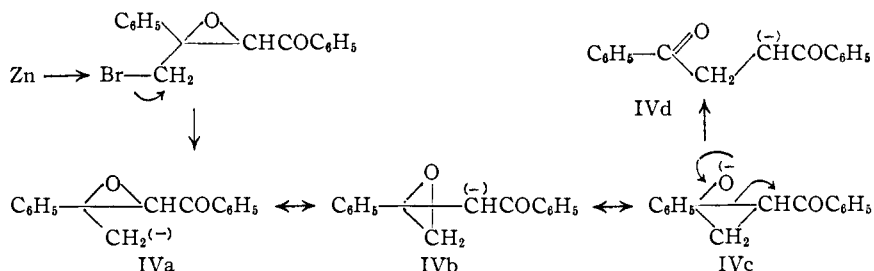




spondence of their infrared spectra with the spectra of the diphenacyl bromides indicates that they, too, are isomeric epoxyketones analogous to IIa and IIb.

The debromination of the diphenacyl halides by the action of metals and alcohol to yield 1,2-dibenzoyl ethane is readily explicable on the basis of the epoxyketone structures (IIa and IIb). This conversion can be pictured as involving interaction of the metal with the halogen atom, as shown below, leading to the anion IVa where the charge may be distributed over forms such as IVb-c. Rearrangement to the more stable anion IVd followed by uptake of a proton would yield the product, 1,2-dibenzoyl ethane.



**The *cis-trans*-Relationship of the  $\alpha$ - and  $\beta$ -Diphenacyl Halides.**—Widman first pointed out that in the case of both bromides and chlorides, the  $\alpha$ -form could be readily converted to the  $\beta$ -form by the action of base in the presence of halide ion, and we have found that, although the  $\alpha$ -diphenacyl halides appear to be formed first under the conditions of the condensation, the  $\alpha$ -form can be isolated as the major product only by rapid working-up of the reaction mixture; otherwise the  $\beta$ -isomer is formed exclusively. The preferred formation of the  $\beta$ -isomer under these conditions suggests that this isomer is the more stable and is hence *trans*-IIb. (Examination of models<sup>13</sup> of the isomeric diphenacyl bromides indicates somewhat more crowding in the model where the phenyl and benzoyl groups are *cis* compared to the model where the bulky groups are *trans*.) On the other hand, the slightly stronger general absorption in the ultraviolet (Table I) of  $\alpha$ -diphenacyl bromide and of the related low-melting dypnone oxide finds close analogy in Cromwell's<sup>14</sup> studies on the ethyl-

TABLE I  
ULTRAVIOLET ABSORPTION SPECTRAL DATA<sup>a</sup>

Epoxy ketone	$\lambda_{\max}$	$\epsilon$
$\alpha$ -Diphenacyl bromide	252	15,600
$\beta$ -Diphenacyl bromide	250	13,100
Dypnone oxide (low-melting)	249	16,600
Dypnone oxide (high-melting)	247	13,300

<sup>a</sup> Solvent is absolute ethanol.

(13) Inasmuch as the standard Fischer-Taylor-Hirschfelder molecular models do not permit the formation of an ethylene oxide ring, we have constructed this system in the following manner: the carbon and oxygen atoms were made with atomic radii corresponding to those in the standard set; the bond angles and interatomic distances were modified to accommodate the three membered oxide ring, based on the data of G. L. Cunningham, A. W. Boyd, W. D. Gwinn and W. I. LeVan, *J. Chem. Phys.*, **17**, 211 (1949). The assumption is made that no significant error arises from the use of these values in a system where the hydrogen atoms, attached to the oxide ring, are replaced by more bulky substituents.

(14) N. H. Cromwell and co-workers, *THIS JOURNAL*, **73**, 1044 (1951); *J. Org. Chem.*, **17**, 415 (1952).

imine ketones, where, in each case, forms to which *trans*-structures were assigned based on chemical evidence, absorbed at slightly longer wave lengths with higher intensities than the corresponding *cis*-isomers. Cromwell has interpreted his results on the basis of hyperconjugation of the three-membered ring with the substituent aryl and aroyl groups. The somewhat lower general absorption of the *cis*-relative to the *trans*-forms was ascribed to a steric inhibition of hyperconjugation whereby the steric requirement for interaction between the aryl and aroyl groups through the three-membered ring is met to a lesser degree in the *cis*-case than in the *trans*.

If this interpretation is valid,<sup>15</sup> consideration of the above epoxyketones along the same lines would favor assignment of *cis*-structures to the higher melting forms.

To provide further evidence for an unequivocal assignment of *cis-trans* structures to the diphenacyl halides and related isomeric pairs, we are studying the interconversions in the epoxyketone series as

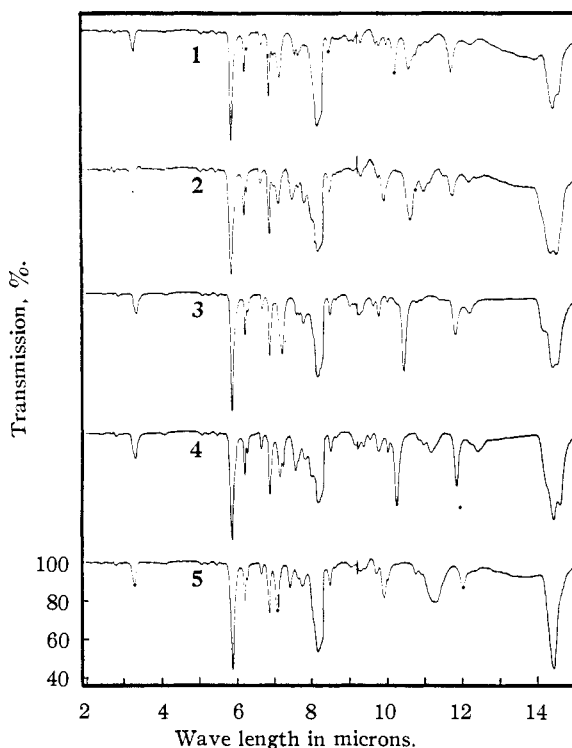


Fig. 1.—Infrared absorption spectra in chloroform solution: 1,  $\alpha$ -diphenacyl bromide; 2,  $\beta$ -diphenacyl bromide; 3, low-melting dypnone oxide; 4, high-melting dypnone oxide; 5, chalcone oxide, m.p. 89–91°.

(15) J. D. Roberts, W. Bennett and R. Armstrong (*THIS JOURNAL*, **72**, 3329 (1950)) found that in the solvolysis of nortricyclyl bromide the cyclopropane ring did not appear to contribute significantly to the stabilization of the incipient carbonium ion and they attributed the low reactivity of the halide to a steric inhibition of three-membered ring hyperconjugative resonance. However, Winstein, Walborsky and Schreiber have recently shown (*ibid.*, **72**, 5795 (1950)) that the corresponding *p*-bromobenzenesulfonate did exhibit considerable reactivity in solvolysis indicating a substantial driving force due to three ring interaction.

well as certain stereospecific reactions of the diphenacyl halides with aniline and other basic reagents.

### Experimental<sup>16</sup>

The following preparations of the diphenacyl halides are modifications of Widman's procedures.<sup>5</sup>

**$\beta$ -Diphenacyl Bromide.**—A solution of 30 g. (0.15 mole) of phenacyl bromide (Eastman Kodak Co.) in 400 ml. of absolute ethanol was cooled in an ice-bath. To this solution was added, with mechanical stirring, a solution prepared by adding 3 g. (0.13 mole) of sodium to 150 ml. of absolute ethanol. After half of the base had been added, a fine white precipitate formed and the solution began to turn orange-red. The addition was complete in 45 minutes and the mixture was allowed to stand for 12 hours at room temperature. The solid was then filtered and recrystallized from ethanol, and then from benzene. The yield of white needles, m.p. 163–164.5°, was 20 g. (83%).

*Anal.* Calcd. for  $C_{16}H_{13}O_2Br$ : C, 60.58; H, 4.13. Found: C, 61.03, 60.10; H, 4.35, 4.32.

**$\alpha$ -Diphenacyl Bromide.**—A solution of sodium ethoxide, prepared from 0.60 g. (0.026 mole) of sodium and 50 ml. of absolute ethanol, was added to 10 g. (0.050 mole) of phenacyl bromide in 80 ml. of absolute ethanol. The reaction mixture was cooled in an ice-bath and stirred mechanically. The addition was completed in 5 minutes and the solid which formed was filtered immediately (within five minutes). Two recrystallizations from ether, carried out rapidly, yielded 2 g. (25%) of tiny crystals, m.p. 128–130°.

*Anal.* Calcd. for  $C_{16}H_{13}O_2Br$ : C, 60.58; H, 4.13. Found: C, 60.46; H, 4.26.

**Dyponone Oxides.**—Dyponone (10 g., 0.045 mole) prepared according to Calloway<sup>17</sup> was dissolved in 100 ml. of methanol. To this solution, 10 ml. (0.088 mole) of 30% hydrogen peroxide together with 12 ml. of 8% sodium hydroxide was added all at once. The reaction mixture was cooled at first and then shaken for 45 minutes on a mechanical shaker. The mixture was then cooled, diluted with water, and the white solid filtered. The crude material was dissolved in about 300 ml. of ethanol and allowed to crystallize slowly.

(16) Analyses are by Micro-Tech Laboratories, 8000 Lincoln Avenue, Skokie, Ill. The infrared spectra were determined with a Perkin-Elmer double beam infrared spectrophotometer, Model 21. Ultraviolet absorption measurements were made with a Beckman Model DU Spectrophotometer.

(17) N. Calloway and L. Green, *THIS JOURNAL*, **59**, 809 (1937).

White needles (1.5 g.) crystallized first, m.p. 159.5–162°. Dilution of the filtrate with water yielded 6.7 g. of plates, m.p. 93–94.5°. The over-all yield was 77%.

*Anal.* Calcd. for  $C_{16}H_{14}O_2$ : C, 80.65; H, 5.92. Found (for low-melting isomer, m.p. 93–94.5°): C, 80.50; H, 6.13. (For high-melting isomer, m.p. 159.5–162°): C, 80.69; H, 5.93.

**1,3-Diphenyl-4-bromobutene-2-one-1 (III).**—A mixture of 10 g. (0.045 mole) of dyponone and 8.5 g. (0.047 mole) of *N*-bromosuccinimide (Arapahoe) was refluxed in 70 ml. of carbon tetrachloride for two hours. The solution was cooled rapidly and the succinimide filtered from the clear yellow solution. The yield of succinimide indicated nearly complete reaction. The solvent was removed under reduced pressure and the yellow oil was taken up in ethanol. Slow crystallization yielded 8.2 g. (59%) of yellow needles. After recrystallization from ethanol, the product melted 68.5–71°.

*Anal.* Calcd. for  $C_{16}H_{13}OBr$ : C, 63.81; H, 4.34; Br, 26.53. Found: C, 64.10; H, 4.66; Br, 26.80.

**1,3-Diphenyl-2,3-epoxy-4-bromobutanone-1 (II).**—Three grams (0.01 mole) of 1,3-diphenyl-4-bromobutene-2-one-1 was dissolved in 50 ml. of methanol, and 2.3 ml. (0.02 mole) of 30% hydrogen peroxide and 2.6 cc. of 8% sodium hydroxide was added all at once. The solution was cooled and stirred for 20 minutes. The voluminous white solid was then filtered. The crude material weighed 2.6 g. and melted 120–127°. Rapid recrystallization from ether yielded a product which did not depress the melting point of pure  $\alpha$ -diphenacyl bromide. The ultraviolet and infrared spectra of the two products were identical in all respects.

**The Action of Zinc and Sodium Iodide on  $\alpha$ - and  $\beta$ -Diphenacyl Bromide.**—A mixture of 5.0 g. (0.016 mole) of  $\beta$ -diphenacyl bromide, 8.0 g. (0.053 mole) of sodium iodide and 5.0 g. (0.076 mole) of zinc (washed with dilute hydrochloric acid, water and acetone) was refluxed in 200 ml. of dry methanol for 8 hours. The solution was then filtered and added to 300 ml. of cold water. The gelatinous precipitate which formed was filtered and both solid and filtrate were extracted with ether. Upon removal of the ether, 2.6 g. of oil was obtained from which 0.15 g. of white needles, m.p. 143–144.5°, was obtained by crystallization from ethanol. This product was identical (mixed melting point and infrared spectra) with authentic 1,2-dibenzoyl ethane.

Three and one-half grains of  $\alpha$ -diphenacyl bromide, and proportionate amounts of the other reagents, gave, under identical conditions, 0.35 g. of 1,2-dibenzoyl ethane.

NEW HAVEN, CONNECTICUT

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## The Decyanoethylation of Polyvinyl $\beta$ -Cyanoethyl Ether

By J. F. WRIGHT AND L. M. MINSK

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When polyvinyl  $\beta$ -cyanoethyl ether is hydrolyzed with sodium hydroxide in a water-methyl cellosolve system, a decyanoethylation to polyvinyl alcohol results rather than hydrolysis of the nitrile group to yield a polymeric acid. This decyanoethylation has been studied through isolation and analysis of the polymer. First-order reaction kinetics are followed. The rate constant is directly proportional to the concentration of catalyst and independent of the concentration of polymer. The Arrhenius activation energy,  $\Delta H$ , was found to be 30,600 cal. per combined monomer mole.

### Introduction

The cyanoethylation of alcohols is reported to be an equilibrium reaction,<sup>1</sup> and the product, in the presence of alkali, is capable of regenerating the original alcohol and a polymer of acrylonitrile as:



However, few examples of this behavior are found, the usual course of the reaction being a conversion of the nitrile group to a carboxyl. In this paper,

(1) H. A. Bruson, in "Organic Reactions," R. Adams, editor, and others, Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 90.

the results of a kinetic study of the cleavage of polyvinyl  $\beta$ -cyanoethyl ether to regenerate polyvinyl alcohol are reported. The non-polymeric fragment was not investigated. The course of the reaction was followed by isolating the polymer, after intervals of reaction time, and analyzing it for carboxyl and nitrogen.

Ethylene glycol monomethyl ether was used as the reaction medium since it is both a solvent for the polymer and water-miscible. Sodium hydroxide, in water solution, was added as the catalyst. The upper concentration of catalyst that