left only a small residue on evaporation, suggesting that most of the ethyl metaphosphate decomposed during the distillation.

All of the 1,2-dibromopropane was recovered using the standard procedure. Even when the reaction mixture was refluxed for 5 hr, 86% of the dibromide survived. In both runs, provision was made to collect evolved propene over water, but none was produced. The experimental data are summarized in Table II.

Registry No.—Triethyl phosphite, 122-52-1.

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Formation of α,β -Diphenyl- γ -butyrolactone from Styrene Oxide by the Action of Organo **Transition Metal Complexes**

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Received February 9, 1970

It has been known that epoxides are transformed to the corresponding ketones by the action of cobalt tetracarbonyl anion or dicobalt octacarbonyl.¹ In the presence of carbon monoxide, carbon monoxide insertion reactions occur to give β -hydroxy carboxylic acid esters in alcohol solution² and α,β -unsaturated acids in benzene solution.³ Furthermore, under the oxo conditions, α,β -unsaturated aldehydes are produced.⁴ Although the interesting reaction behaviors of σ -organometallic compounds toward olefins, acetylenes, ketones, or aldehydes have been evealed during these 10 years, the reactivity of alkyl or acyl transition metal complexes toward epoxides has not yet been defined. However, the facility with which π -methallylnickel bromide reacts with styrene oxide to give 2-methyl-4phenyl-5-hydroxypentene-1⁵ suggests that the analogous reactions of alkyl or acyl transition metal complexes might be important in organic synthesis.

Lithium acylmetal carbonylates, prepared by the reaction between organolithium compounds and metal carbonyls, are efficient nucleophilic acylating agents, and many useful organic reactions using these reagents, such as syntheses of aldehydes,⁶ acyloins,⁷ α -diketones,⁷ unsymmetrical ketones,⁷ and 1,4-dicarbonyl compounds⁸ have been reported. The reaction of lithium aroylnickel carbonylate with styrene oxide was carried out and it was found that the product is not the expected aroylphenylethyl alcohol but α,β -diphenyl- γ butyrolactone, which seemed to be produced by dimerization and hydrogen abstraction of styrene oxide. In this paper, we report the formation of α,β -diphenyl-

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 γ -butyrolactone from styrene oxide by the action of lithium aroylnickel carbonylate or dibenzyliron tetracarbonyl, which is a new type of transformation of olefin oxide and would promise a unique synthetic route to lactones from olefin oxides.

Results and Discussion

Styrene oxide undergoes reaction with lithium benzoylnickel carbonylate (1) to give trans- α,β -diphenyl- γ -butyrolactone (2, 19.3%), benzyl phenyl ketone (3, trace), benzoin (23.5%), and benzoic acid (9.0%). The latter two compounds are produced by the hydrolysis of 1,7 and the former two seem to be the products derived from the reaction between styrene oxide and 1.

The formation of 2 was not explained by the combination of benzoyl group in 1 with styrene oxide; so, in order to clarify whether the phenyl groups in 2 came from styrene oxide or 1, an analogous reaction was carried out using lithium *p*-toluoylnickel carbonylate (4) instead of 1.

$$C_{6}H_{5}CH-CH_{2} + Li[p-CH_{8}C_{6}H_{4}CNi(CO)_{8}] \xrightarrow{\Delta} 2 (17.0\%) +$$

$$O$$

$$4$$

$$C_{6}H_{5}CH_{2}CC_{6}H_{4}CH_{3}-p + (p-CH_{3}C_{6}H_{4})_{2}CO + (p-CH_{3}C_{6}H_{4}C-)_{2}$$

$$O$$

$$5 (1.7\%) (21.0\%) (trace)$$

$$(2)$$

After the reaction was complete, the ether was evaporated and the benzene-soluble part was distilled under reduced pressure. Then, 2 was obtained in a similar yield to that from reaction J, and the formation of benzyl p-tolyl ketone 5 corresponded to the formation of 3. Di-p-tolyl ketone and p,p'-bitolyl are the products formed by thermal decomposition of 4.7 The fact that 2 was obtained in both reactions 1 and 2 in similar yields shows that the aroyl group in 1 or 4 is not incorporated into the structure of 2, and so 2 mol of styrene oxide is transformed to 1 mol of 2 with the aid of the aroylnickel carbonylate complex. As the reaction mixture before distillation (bath temp 200-250°) under reduced pressure does not show a peak due to the carbonyl group of the γ -lactone at 1780 cm⁻¹, heating is necessary for the formation of 2 in addition to the aroylnickel carbonylate complex. By column chromatographic separation of the residual oil after removal of the solvent, the crude material, which had a peak at 3600-3200 cm⁻¹ and no peaks in the carbonyl region (2100-1630 cm⁻¹), was obtained from the methanol eluate, and this material, which could not be purified by recrystallization, was transformed to 2 by heating above 200°. This suggests that an alcoholic compound is

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formed prior to the formation of 2 and heating of the compound results in the formation of 2. The formation of 3 in reaction 1 and 5 in reaction 2 is important in spite of the low yields, for they are the sole products, respectively, formed by the addition of the aryl group in the nickel complex to styrene oxide, but the mechanism is still open to question.

$$\begin{array}{ccc} \text{Li}[\text{ArCNi}(\text{CO})_3] & \xrightarrow{C_6H_6\text{CH}-\text{CH}_2} & \text{ArCCH}_2C_6\text{H}_5 \\ \| & & \| \\ O & & O \end{array}$$
(3)

Further, to establish the formation of γ -lactone from styrene oxide by the action of metal complexes, the reactions of styrene oxide with dibenzyliron tetracarbonyl, nickel carbonyl, iron tetracarbonylate anion, and palladium dichloride were carried out. Styrene oxide gives 2 and α - and β -phenylethyl phenylacetate (7 and 8) by the reaction with dibenzyliron tetracarbonyl

$$C_{6}H_{5}CH-CH_{2} + (C_{6}H_{5}CH_{2})_{2}Fe(CO)_{4} \longrightarrow 2 (19.6\%) + 6$$

$$C_{6}H_{5}CH_{2}COCHC_{6}H_{5} + C_{6}H_{5}CH_{2}COCH_{2}CH_{2}C_{6}H_{5} + 0$$

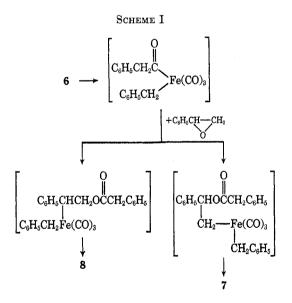
$$C_{6}H_{5}CH_{2}COCHC_{6}H_{5} + C_{6}H_{5}CH_{2}COCH_{2}CH_{2}C_{6}H_{5} + 0$$

$$T (14.8\%) \qquad 8 (trace)$$

$$(C_{6}H_{5}CH_{2})_{2}CO + (C_{6}H_{5}CH_{2})_{2} \qquad (4)$$

$$(23.8\%) \qquad (9.2\%)$$

6 (reaction 4). In the formation of the esters 7 and 8, the sequences shown in Scheme I seem to be probable.



When propylene oxide was used instead of styrene oxide, isopropyl phenylacetate, and *n*-propyl phenylacetate were produced. The formation of the γ -lactone 2 was not explained in terms of the attack of the benzyl or the phenylacetyl group to styrene oxide, for in the analogous reaction using *p*-methylbenzyl bromide instead of benzyl halide as a partner in the reaction with iron tetracarbonylate anion, 2 was also produced in a similar yield (14.9%). Styrene oxide (2 mol) is transformed to 2 as well as in the case of reaction 1 or 2.

On the other hand, in the case of nickel carbonyl, styrene oxide was transformed to 2 (trace amount) and phenylacetaldehyde (8.3%) but not to acetophenone.

$$Ni(CO)_{4} \xrightarrow{C_{6}H_{5}CH-CH_{2}} 2 \text{ (trace)} + C_{6}H_{5}CH_{2}CHO \qquad (5)$$

$$(8.3\%)$$

From the reaction of styrene oxide with disodium iron tetracarbonylate, 2 (trace amount), styrene (1.1%), and α -phenylethyl alcohol (18.9%) were obtained (reaction 6). Therefore, nickel carbonyl or disodium iron

$$Na_{2}Fe(CO)_{4} \xrightarrow{C_{6}H_{6}CH-CH_{2}} 2 \text{ (trace)} + C_{6}H_{5}CH=CH_{2} + C_{6}H_{5}CHCH_{3} \quad (6)$$

$$OH \\ (1.1\%) \quad (18.9\%)$$

tetracarbonylate is not effective for the transformation of styrene oxide to 2. As the formation of 2 from styrene oxide seems to involve the dimerization and the hydrogen abstraction processes, it is expected that palladium dichloride which causes easy hydrogen transfer may cause the analogous reaction behavior to occur, but the formation of 2 was not observed and the isolated products were phenylacetaldehyde (10.0%)and *trans*-2,5-diphenyl-1,4-dioxane (2.5%), reaction 7).⁹

$$PdCl_{2} \xrightarrow{C_{6}H_{5}CH} C_{6}H_{5}CH_{2}CHO + C_{6}H_{5} \xrightarrow{O} C_{6}H_{5} (7)$$

$$(10.0\%)$$

It is interesting to note that styrene oxide is transformed to $trans-\alpha,\beta$ -diphenyl- γ -butyrolactone by the action of lithium aroylnickel carbonylate or dibenzyliron tetracarbonyl in contrast to the reaction of styrene oxide with π -methallylnickel bromide,⁵ in which case the epoxide ring was cleaved as a result of the addition of the methallyl group to form 2-methyl-4-phenyl-5hydroxypentene-1. A study of the mechanism of the γ -lactone formation reaction, which remained unexplored because of the lack of structure determination of the precursor to the γ -lactone, and further studies of the reaction between σ -organometallic compounds and olefin oxides are continuing and will be reported in the near future.

Experimental Section

All reactions were carried out under nitrogen. Yields of 2, 3, 5, 7, and 8 and the products obtained in parts F, G, and H were calculated based on the used styrene oxide, and those of the other products were calculated based on the used organic halide. Gas-liquid partition chromatographic analyses were performed on a Yanagimoto GCG-5DH instrument using 2.5 m \times 3 mm columns packed with 5% SE-30 (column temperature 160-280°, 4° min⁻¹, carrier gas He, 15 cc min⁻¹) or on a Hitachi K53 instrument using 2.4 m \times 3 mm columns packed with Polyester DS (column temperature 160°, carrier gas He, 25 cc min⁻¹).

A. Reaction of Styrene Oxide with Lithium Benzoylnickel Carbonylate.—The ether solution (50 ml) of nickel carbonyl (17.1 g, 0.1 mol) was added dropwise to the ether solution of phenyllithium prepared from bromobenzene (15.7 g, 0.1 mol) and lithium metal (1.5 g, 0.22 g-atom) at -70 to -60° , and the mixture was stirred for 2 hr at that temperature.⁷ Then styrene

⁽⁹⁾ This compound was known to be produced by the action of tetrachlorotin on styrene oxide: R. K. Summerbell and M. J. Kland-English, J. Amer. Chem. Soc., 77, 5095 (1955).

oxide (15 g, 0.13 mol) was added to this lithium benzoylnickel carbonylate solution and the mixture was stirred for 5 hr from -60° to room temperature. Benzene (100 ml) was added to this solution and the mixture was stirred for 5 hr at 50-60°. After hydrolysis with 4 N hydrochloric acid (50 ml), the reaction mixture was extracted with ether, and this ether solution was separated by extraction with 5% aqueous sodium hydroxide to an acidic part and a neutral part. From the acidic part, benzoic acid (1.1 g, 9.0%) was obtained. The neutral part was distilled under reduced pressure after removal of the solvents to give the following fractions: 1, bp 50-100° (5 mm), 1.6 g; 2, bp 100-180° (5 mm), 9.4 g; 3, bp 180-200° (5 mm), 6.6 g; and 4, bp 200-210° (2 mm), 2.4 g. Most of fraction 1 consisted of the re-covered styrene oxide. Recrystallization of fractions 2 and 3 from petroleum ether (bp 30-60°)-benzene gave $trans-\alpha,\beta$ diphenyl- γ -butyrolactone (2) [mp 96–96.5°; white crystals; m/e 238, 193, 179, 116; $\nu_{C=0}$ 1780 cm⁻¹; nmr (CDCl₈) τ 6.05 (2 H), 5.1–5.8 (2 H), 2.75 (10 H) (Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92; mol wt, 238. Found: C, 81.00; H, 5.90); 3 g, 19.3%] and benzoin (2.5 g, 23.5%). Benzyl phenyl ketone (3, trace) was identified by glpc of fractions 2 and 3. Alkali hydrolysis (KOH-ethylene glycol) of 2 gave α,β -diphenyl- γ -hydroxybutyric acid: mp 147-148°; white crystals; m/e256, 238, 179, 137; $\nu_{C=0}$ 1690 cm⁻¹; $\nu_{O=H}$ 3600-3300 cm⁻¹. Reduction of 2 with lithium aluminum hydride gave 2,3-diphenyl-1,4-butanediol: mp 102-102.5°; white crystals; m/e 242, 212, 194, 180, 165; ν_{O-H} 3400 cm⁻¹; nmr (CDCl₃) τ 7.25 (2 H), 6.60 (2 H), 6.10 (4 H), 3.00 (10 H). As fraction 4 had no peaks at the carbonyl region of the lactone, more purification was not carried out.

B. Reaction of Styrene Oxide with Lithium p-Toluoylnickel Carbonylate.—In place of bromobenzene, p-bromotoluene (17.1 g, 0.1 mol) was used, and an analogous reaction was carried out under the same conditions as those of reaction A. After the reaction was over, the reaction mixture was extracted with hot benzene and the benzene-soluble part was distilled under reduced pressure to give 2 (3.0 g, 17.0%), benzyl *p*-tolyl ketone 5 (0.5 g, 1.7%), di-*p*-tolyl ketone (4.4 g, 21.0%), and p,p'-bitolyl (trace). The identification and the calculation of yields of the products were carried out by glpc analysis. Instead of distillation under reduced pressure, the reaction mixture was separated by alumina column chromatography, and 5, di-p-tolyl ketone, and p, p'-bitolyl were also obtained from a benzene or ether eluate. From the methanol eluate, a yellow solid (16.4 g) was obtained, and it showed a peak at 3600-3200 cm⁻¹ but no peaks at the carbonyl region. Attempts to purify this yellow solid were unsuccessful but it was transformed to 2 (2 g) by distillation under reduced pressure above 200°.

C. Reaction of Styrene Oxide with Dibenzyliron Tetracarbonylate.-To the tetrahydrofuran solution (150 ml) of disodium iron tetracarbonylate prepared from sodium dispersion (1.4 g, 0.06 g-atom) and triiron dodecacarbonyl (5 g, 0.01 mol), styrene oxide (15.5 g, 0.13 mol) was added at -40 to -30° . After stirring for 1-2 hr at that temperature, benzyl bromide (10.3 g, 0.06 mol) was added and the reaction mixture was stirred for 2 hr from -30° to room temperature and then for 4 hr under refluxing tetrahydrofuran. The solvent was removed by distillation and then the residue was extracted with hot benzene. The benzene-soluble part was distilled under reduced pressure after removal of benzene to give the following fractions: 1, bp 80-140° (0.4 mm), 2.0 g; 2, bp 140-200° (1 mm), 6.0 g. A glpc analysis of these fractions showed that fraction 1 consisted of dibenzyl ketone (1.5 g, 23.8%) and bibenzyl (0.5 g, 9.2%), and fraction 2 consisted of 2 (2.8 g, 19.6%), α -phenylethyl phenylacetate 7 (2.2 g, 14.8%), and β -phenylethyl phenylacetate 8 (trace). An analogous reaction using benzyl iodide (13.1 g, 0.06 mol) gave the same products: dibenzyl ketone (1.4 g, 22.2%), bibenzyl (1.9 g, 35.0%), 2 (2.3 g, 16.1%), 7 (0.2 g, 1.4%), and 8 (trace).

D. Reaction of Styrene Oxide with Di-(p-methylbenzyl)iron Tetracarbonyl.—In place of benzyl halide, p-methylbenzyl bromide (11.1 g, 0.06 mol) was used and an analogous reaction was carried out under the same conditions as that in part C. Products were α -phenylethyl alcohol (0.8 g, 11.1%), p,p'dimethylbibenzyl (0.8 g, 13.2%), di-(p-methylbenzyl) ketone (1.9 g, 27.9%), and 2 (1.0 g, 14.9%), which were identified by glpc analysis.

E. Reaction of Propyrene Oxide with Dibenzyliron Tetracarbonyl.—Propyrene oxide (14.0 g, 0.24 mol) and benzyl iodide (13.1 g, 0.06 mol) were used and an analogous reaction was carried out under the same conditions as in reaction C, and isopropyl phenylacetate (0.18 g, 1.7%), *n*-propyl phenylacetate (0.14 g, 1.3%), dibenzyl ketone (1.5 g, 23.8%), and bibenzyl (2.5 g, 45.6%) were identified by glpc analysis.

F. Reaction of Styrene Oxide with Nickel Carbonyl.—A mixture of styrene oxide (2.4 g, 0.02 mol) and nickel carbonyl (3.5 g, 0.02 mol) in ether (10 ml) and benzene (10 ml) was stirred for 3 hr at 10° and then for 5 hr at 50°. After removal of the solvents and the remaining nickel carbonyl, the residual oil was distilled under reduced pressure to give phenylacetaldehyde (0.2 g, 8.3%) and 2 (trace), which were identified by glpc analysis. Phenylacetaldehyde was also confirmed by its infrared (2750, 1730 cm⁻¹) and nmr (τ 0.55) spectra. No acetophenone was detected by glpc.

G. Reaction of Styrene Oxide with Disodium Iron Tetracarbonylate.—Styrene oxide (1.56 g, 0.013 mol) was added to the tetrahydrofuran solution of disodium iron tetracarbonylate, prepared from triiron dodecacarbonyl (1.7 g, 0.0034 mol) and sodium dispersion (0.7 g, 0.03 g-atom), and the mixture was stirred for 9 hr under refluxing tetrahydrofuran. After removal of the solvent, the residue was filtered and the filtrate was distilled under reduced pressure to give styrene (0.015 g, 1.1%), α -phenylethyl alcohol (0.3 g, 18.9%), and 2 (trace), which were identified by glpc analysis.

H. Reaction of Styrene Oxide with Palladium Dichloride.— Styrene oxide (4.8 g, 0.04 mol) was added to a suspension of palladium dichloride in benzene (50 ml); the mixture was stirred for 27 hr under reflux of benzene. The mixture was filtered and the filtrate was distilled under reduced pressure after removal of benzene to give the following fractions: 1, bp 60-82° (12 mm), 0.62 g; 2, bp 100-134° (1.5 mm), 0.89 g; 3, bp 150-210° (1 mm), 1.0 g. A glpc analysis of fractions 1 and 2 showed that the recovered styrene oxide (0.5 g, 10.4%) and phenylacetaldehyde (0.48 g, 10.0%) were contained in these fractions. Recrystallization of fraction 2 from petroleum ether gave *trans*-2,5-diphenyl-1,4-dioxane: mp 180-180.5° (lit.º 174-175°); white plates; m/e 240, 149, 120, 104, 91. Anal. Calcd for C₁₀H₁₀O₂: C, 79.97; H, 6.71; mol wt, 240. Found: C, 80.69; H, 6.93. As fraction 3 had no peaks at the carbonyl region of the lactone, more purification was not carried out.

Registry No.—1, 25154-62-5; 2, 25109-89-1; 4, 25154-63-6; 6, 25154-64-7; styrene oxide, 96-09-3; di-(*p*-methylbenzyl)iron tetracarbonyl, 25154-65-8; α,β -diphenyl- γ -hydroxybutyric acid, 25109-09-4; 2,3-diphenyl-1,4-butanediol, 6583-62-6.

Acknowledgment.—The authors gratefully acknowledge the assistance of Mr. Kazumasa Kinugasa and Mr. Masaki Iwafuzi for the experimental work.

Synthesis and Some Properties of 2,2,6,6-Tetramethyl-1,4,8-trioxaspiro[2.5]octane, an Epoxy Ketene Ketal¹

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Received January 30, 1970

The synthesis of compounds such as the title compound I was undertaken because of their possible use as valuable reagents for the synthesis of a variety of α substituted acids desired for testing for biological activity. In addition, the novel functionality, epoxide and ortho ester, would make a study of their chemical reactivity of interest.

(1) This work was supported by Grant No. GM 12379 from the National Institutes of Health.