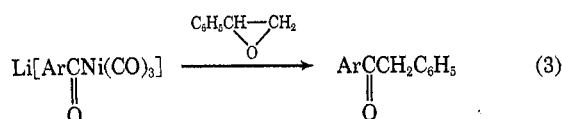
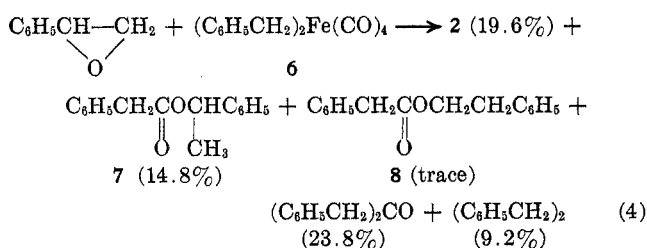




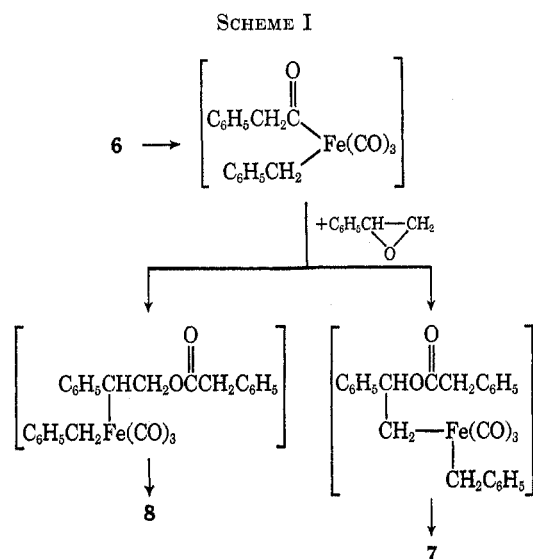
formed prior to the formation of 2 and heating of the compound results in the formation of 2. The formation of 3 in reaction 1 and 5 in reaction 2 is important in spite of the low yields, for they are the sole products, respectively, formed by the addition of the aryl group in the nickel complex to styrene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



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

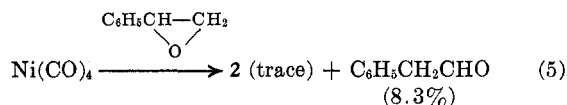


6 (reaction 4). In the formation of the esters 7 and 8, the sequences shown in Scheme I seem to be probable.

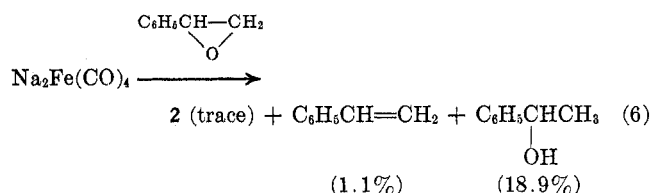


When propylene oxide was used instead of styrene oxide, isopropyl phenylacetate, and *n*-propyl phenylacetate were produced. The formation of the  $\gamma$ -lactone 2 was not explained in terms of the attack of the benzyl or the phenylacetyl group to styrene oxide, for in the analogous reaction using *p*-methylbenzyl bromide instead of benzyl halide as a partner in the reaction with iron tetracarbonyl 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.

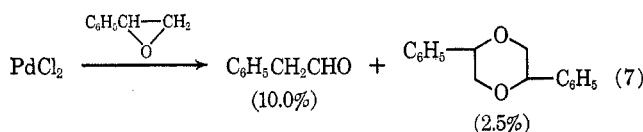
On the other hand, in the case of nickel carbonyl, styrene oxide was transformed to 2 (trace amount) and phenylacetaldehyde (8.3%) but not to acetophenone.



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



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).<sup>9</sup>



It is interesting to note that styrene oxide is transformed to *trans*- $\alpha,\beta$ -diphenyl- $\gamma$ -butyrolactone by the action of lithium aroylnickel carbonylate or dibenzyliron tetracarbonyl in contrast to the reaction of styrene oxide with  $\pi$ -methallylnickel bromide,<sup>5</sup> in which case the epoxide ring was cleaved as a result of the addition of the methallyl group to form 2-methyl-4-phenyl-5-hydroxypentene-1. A study of the mechanism of the  $\gamma$ -lactone formation reaction, which remained unexplored because of the lack of structure determination of the precursor to the  $\gamma$ -lactone, and further studies of the reaction between  $\sigma$ -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<sup>-1</sup>, carrier gas He, 15 cc min<sup>-1</sup>) 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<sup>-1</sup>).

**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.<sup>7</sup> 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  $-60^{\circ}$  to room temperature. Benzene (100 ml) was added to this solution and the mixture was stirred for 5 hr at  $50-60^{\circ}$ . 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  $50-100^{\circ}$  (5 mm), 1.6 g; 2, bp  $100-180^{\circ}$  (5 mm), 9.4 g; 3, bp  $180-200^{\circ}$  (5 mm), 6.6 g; and 4, bp  $200-210^{\circ}$  (2 mm), 2.4 g. Most of fraction 1 consisted of the recovered styrene oxide. Recrystallization of fractions 2 and 3 from petroleum ether (bp  $30-60^{\circ}$ )-benzene gave *trans*- $\alpha,\beta$ -diphenyl- $\gamma$ -butyrolactone (**2**) [mp  $96-96.5^{\circ}$ ; white crystals; *m/e* 238, 193, 179, 116;  $\nu_{C=O}$   $1780\text{ cm}^{-1}$ ; nmr (CDCl<sub>3</sub>)  $\tau$  6.05 (2 H), 5.1-5.8 (2 H), 2.75 (10 H) (*Anal.* Calcd for C<sub>16</sub>H<sub>14</sub>O<sub>2</sub>: 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  $\alpha,\beta$ -diphenyl- $\gamma$ -hydroxybutyric acid: mp  $147-148^{\circ}$ ; white crystals; *m/e* 256, 238, 179, 137;  $\nu_{C=O}$   $1690\text{ cm}^{-1}$ ;  $\nu_{O-H}$   $3600-3300\text{ cm}^{-1}$ . Reduction of **2** with lithium aluminum hydride gave 2,3-diphenyl-1,4-butanediol: mp  $102-102.5^{\circ}$ ; white crystals; *m/e* 242, 212, 194, 180, 165;  $\nu_{O-H}$   $3400\text{ cm}^{-1}$ ; nmr (CDCl<sub>3</sub>)  $\tau$  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  $3600-3200\text{ cm}^{-1}$  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  $200^{\circ}$ .

**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  $-30^{\circ}$ . 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  $-30^{\circ}$  to room temperature and then for 4 hr under reflux 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  $80-140^{\circ}$  (0.4 mm), 2.0 g; 2, bp  $140-200^{\circ}$  (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%),  $\alpha$ -phenylethyl phenylacetate **7** (2.2 g, 14.8%), and  $\beta$ -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  $\alpha$ -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 Propylene Oxide with Dibenzyliron Tetracarbonyl.**—Propylene oxide (14.0 g, 0.24 mol) and benzyl iodide (13.1 g, 0.06 mol) were used and an analogous reaction was car-

ried 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  $10^{\circ}$  and then for 5 hr at  $50^{\circ}$ . 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 ( $2750, 1730\text{ cm}^{-1}$ ) and nmr ( $\tau$  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 reflux 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%),  $\alpha$ -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  $60-82^{\circ}$  (12 mm), 0.62 g; 2, bp  $100-134^{\circ}$  (1.5 mm), 0.89 g; 3, bp  $150-210^{\circ}$  (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  $180-180.5^{\circ}$  (lit.<sup>9</sup>  $174-175^{\circ}$ ); white plates; *m/e* 240, 149, 120, 104, 91. *Anal.* Calcd for C<sub>18</sub>H<sub>18</sub>O<sub>2</sub>: 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;  $\alpha,\beta$ -diphenyl- $\gamma$ -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 Ketal<sup>1</sup>

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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  $\alpha$ -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.