

SECTION C, PHYSICAL SCIENCES

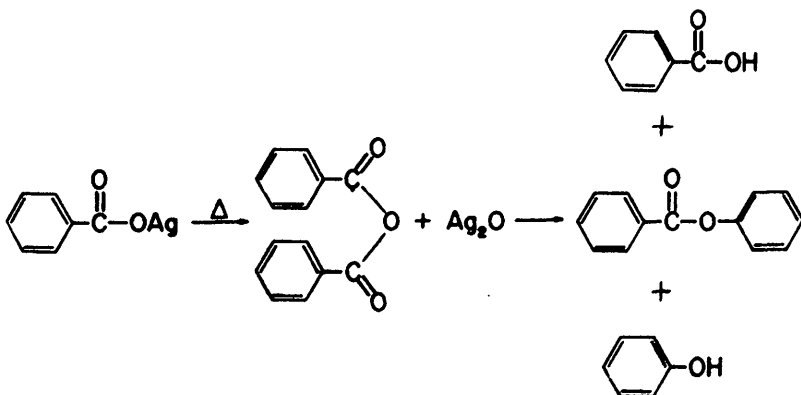
Photolysis of Silver Benzoate in Cyclohexene¹K. DARRELL BERLIN and DON E. GIBBS²

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Thermal decomposition of benzoyl peroxide is known to generate phenyl and benzoyloxy radicals. This fact and the photosensitivity of silver salts of carboxylic acids suggested that the photolysis of silver benzoate might be a convenient source of the radicals cited, possibly near room temperature. Neither the photolysis nor the pyrolysis of silver benzoate in liquid media had hitherto been reported, and it would be of interest to elucidate the mechanisms involved.

If the photolysis of silver benzoate proceeds by a free-radical mechanism, it might well be expected to give products (Table I) similar to those obtained from the pyrolysis, which is known to involve free radicals. The thermal decomposition of benzoyl peroxide in cyclohexene has been examined (Farmer and Michael, 1942). As cited previously benzoyl peroxide decomposes by a radical mechanism in cyclohexene and the products are given in Table I. Clearly, benzoyloxylation occurred to give both allylic and vinylic type esters. In addition phenylation resulted in the formation of phenyl-substituted cyclohexenes. More recently, Noma and Tsuchida (1948), heated benzoyl peroxide in cyclohexene at 60° for 200 hours and obtained 1- and 2-cyclohexenyl benzoate, cyclohexyl benzoate, and polymers with two, three, and eight six-membered rings substituted with benzoyloxy groups.

The second mechanism to be considered for the photolysis of silver benzoate is similar to that postulated to explain the pyrolysis of silver benzoate (Kamevskaya *et al.*, 1936), which is outlined in Fig. 1. The important feature was the appearance of benzoic anhydride, the presence of which was reasonably well established.

Fig. 1. Pyrolysis of silver benzoate (Kamevskaya *et al.*, 1936).

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This paper reports the analysis of the photolysate obtained from silver benzoate in cyclohexene. In addition several compounds were synthesized for comparison with the components of the photolysis mixture. It should be noted that in all of the previous work, gas chromatography was not utilized in analyzing the products. In the results recorded herein, analysis of the reaction mixtures was performed by means of a gas chromatography unit with a hydrogen flame detector cell. Identification of all individual products from the photolysates was substantiated by mixed injection with pure compounds that had been synthesized by alternative routes and identified by elemental analyses and comparison of infrared spectra. Several new substituted cyclohexene derivatives were prepared and characterized.

Photolysis of freshly prepared silver benzoate in reagent-grade cyclohexene (less than 0.5% impurity by gas chromatography) was accomplished with a Hanovia lamp using quartz apparatus. The total conversion of silver benzoate was 10% or less. The residual silver benzoate and metallic silver were removed by filtration and the filtrate was analyzed directly on two separate gas chromatography columns. Benzoic acid and metallic silver were the major components, and six other products were found in various quantities. The results are shown in Table I.

Varying the duration of photolysis did not alter the types of products found. Although slow decomposition of the silver salt was observed at room temperature by deposition of a silver mirror, the most practical rate of reaction resulted near 70 C, the boiling point of the mixture. When heated at 70 C in the absence of ultraviolet light, the mixture contained only traces of the decomposition products, all of which were identical to those found in the photolysate. Addition of cuprous chloride resulted in the formation of metallic copper within a few minutes but again analysis of the supernatant liquid showed only the components previously identified. Thus, the silver-oxygen bond undergoes rapid cleavage by heat. Apparently a metathetic exchange reaction occurs with cuprous chloride. However, the facile reduction of cuprous ion to metallic copper is not easily explained and may well involve electron transfer *via* radicals.

Only two differences were found when the products in the photolysate were compared to the ingredients of the mixture resulting from decomposition of benzoyl peroxide in cyclohexene (Table I). 1-Phenylcyclohexene was obtained as a minor product from the photolysate but was not reported in the experiments with benzoyl peroxide. More important, however, was the fact that the photolysate did not contain cyclohexyl benzoate, which had been recorded as a major component in the reaction with benzoyl peroxide. Our results were reproducible, and the data suggest a different mechanism in the photolysis process. If the mechanism were similar to that suggested for the pyrolysis of silver benzoate (Kamevskaya *et al.*, 1936), formation of benzoic anhydride might be expected; however, the anhydride was not detected in any of the photolysis solutions regardless of exposure time. Under similar conditions, but with anisole as solvent (Berlin and Gibbs, 1964), benzoic anhydride decomposes to give phenylation products. Consequently, it is not possible to state definitively the overall mechanism of the photolysis at present. The data obtained are more easily rationalized by assuming a radical mode of decay. Efforts are underway to complete this study.

EXPERIMENTAL

Photolysis Procedure.—Photolysis was conducted in a 100 ml quartz flask equipped with a reflux condenser. The ultraviolet source was a Hanovia mercury lamp which emitted radiation from 1849 to 4000 Ang-

TABLE 1. THE DECOMPOSITION OF SILVER BENZOATE AND OF BENZOYL PEROXIDE IN CYCLOHEXENE
 Symbols: p, present; a, absent; d, doubtful; —, no analysis

| Compound | Pyrolysis of Silver Benzoate | | Benzoyl Peroxide | | Photolysis of Silver Benzoate, 70 C ^o |
|---------------------------------------|------------------------------|-----------------------------|-----------------------------|-----------------------------|--|
| | 140 C, 6 hrs. ^a | 60 C, 200 hrs. ^b | 60 C, 200 hrs. ^b | 60 C, 200 hrs. ^b | |
| 1-Phenylcyclohexene | — | — | — | — | p |
| 3-Phenylcyclohexene | p | — | — | — | — |
| 3-Cyclohexylcyclohexene | — | — | — | — | a |
| Dicyclohexyl | d | — | — | — | a |
| Cyclohexyl benzoate | p | — | p | — | a |
| Cyclohexenyl benzoate | p | — | p | — | p |
| Benzolic acid | p | — | — | — | p |
| Benzene | p | — | — | — | — |
| 3, 3'-Dicyclohexenyl | p | — | — | — | — |
| 1-Cyclohexenyl benzoate | — | — | — | p | — |
| Benzoyloxycyclohexane | — | — | — | p | — |
| Polymers | — | — | — | — | — |
| Phenylcyclohexane | d | — | — | — | — |
| Cyclohexane | d | — | — | — | — |
| 2-(2-Cyclohexenyl)cyclohexyl benzoate | p | — | — | — | a |

^aFarmer and Michael, 1942.

^bNoma and Tsuchida, 1948.

^cBerlin and Gibbs, 1964.

stroms, with the intensity at 8130 Angstrom being about 250 microwatts at 20 in. In a typical photolysis experiment 1.3 g (0.0056 mole) of silver benzoate suspended in 20 ml of cyclohexene was photolyzed for a total of 26 hours. In one of two experiments in which cuprous chloride (0.5 g) was used, 1.0 g of silver benzoate in 20 ml of cyclohexene was irradiated for 4 hours with rapid stirring.

Gas Chromatography.—Chromatographic analyses were made in a Hy Fi Aerograph apparatus (Wilkins Instruments, Inc.) with hydrogen flame detector using a column of 10% silicone rubber on acid-washed Chromosorb W ($\frac{1}{8}$ in by 8 ft) and/or with 10% SE-30 on a similar column.

Infrared Spectroscopy.—All spectra were recorded with a Beckman IR-5 spectrophotometer. Solids were examined in KBr pellets while the liquids were measured as films.

Silver Benzoate.—To a mixture of 31.0 g (0.25 mole) of benzoic acid and 100 ml of water was added 40 ml of concentrated ammonium hydroxide with vigorous stirring. After the mixture was neutralized with about 1.0 g of benzoic acid, 38.5 g (0.25 mole) of silver nitrate in 100 ml of water was added with rapid mixing. The white precipitate was removed by suction filtration, washed with 500 ml each of water, methanol, and ether, successively. The salt was dried by pressing it on a filter since oven drying caused some decomposition; yield was quantitative. The traces of residual moisture could be removed by recrystallization of the salt from pyridine, but traces of the amine were always present and thus the sample was too impure for the photolysis reaction.

3-Cyclohexylcyclohexene.—3-Bromocyclohexene (11.27 g, 0.07 mole) in 25 ml of carbon tetrachloride was added dropwise with stirring during 1 hour to ice-cold cyclohexyl Grignard reagent made from 32.60 g (0.20 mole) of bromocyclohexane and 3.1 g (0.12 g-atom) of magnesium. The resulting grey semisolid was heated at reflux 2 hours and then decomposed with 100 ml of 10% aqueous ammonium chloride. The upper layer was separated and dried over calcium chloride and then fractionally distilled to yield a liquid, bp 71.5 C/2 mm, reported bp 236-7.5 C/755 mm (Schrauth and Gorig, 1902); yield was 2 g (17%). Absorption maxima (film): 3.32 microns (H-C=), 3.46 microns (H-C), and 6.11 microns (C=C).

1-Phenylcyclohexene.—1-Phenylcyclohexanol was made by adding cyclohexanone (49 g, 0.50 mole) in 100 ml of ether dropwise over a period of 1 hour to chilled phenyl Grignard reagent prepared from 0.50 mole of bromobenzene and 0.60 g-atom of magnesium in 200 ml of ether. Decomposition of the reaction mixture with aqueous ammonium chloride yielded an organic phase which was concentrated to a yellow oil; this solidified after standing for a day. The product was recrystallized from n-heptane to give 21.8 g of crystals melting at 60 C (25% yield).

The alcohol thus prepared, 21.8 g (0.12 mole), was heated with about 30 g of freshly fused potassium hydrogen sulfate at 110-140 C for 1.5 hours. The solid reaction mixture was powdered and washed with ether. Distillation of the combined washings gave 16.9 g of a clear, thin oil, bp 67.5-72 C/0.3 mm (yield 86% based on 1-phenylcyclohexanol). The chromatographically-pure fraction used as an analytical standard had a boiling range of 69-70 C/0.3 mm, n_D^{20} 1.5665; reported data 128-9 C/19 mm, n_D^{20} 1.5692 (Baddeley *et al.*, 1956; Mixer and Young, 1956). The infrared spectrum was identical to that published. Although the olefin was reported previously, its preparation was not well described and yields were lower than reported here.

3-Cyclohexenyl Benzoate. Method I.—*t*-Butyl perbenzoate was made (Miles and Surgenor, 1946) by the simultaneous addition of 14.05 g (0.10 mole) of benzoyl chloride and 7.2 g (0.13 mole) of potassium hydroxide in 17 ml of water to a rapidly stirred mixture of 12.8 ml (0.11 mole) of *t*-butyl hydroperoxide and 7 ml of water at 8-12 C, over a period of 45 minutes. After this mixture had been stirred for 11 hours, the upper layer was washed with 5% sodium bicarbonate and dried over magnesium sulfate. It was fractionated to yield a clear liquid, bp 90-100 C/3-4 mm, n_D^{20} 1.4995. Yield, 2 g (10%). To a chilled mixture of 0.53 g (0.006 mole) of cyclohexene and 0.80 g (0.004 mole) of *t*-butyl perbenzoate was slowly added 0.1 g of cuprous bromide (Kharasch and Sosnovsky, 1958). The resulting green mixture was stirred for a few minutes at room temperature and was extracted with benzene. Evaporation of the benzene left an oil which was chromatographed on alumina and distilled, bp 83-4.5 C/0.07 mm; n_D^{20} 1.5382, yield 5%. No physical data were reported for this ester previously. Absorption maxima (film): 3.91 microns (H-C=), 5.85 microns (C=O), 6.0 microns -shoulder (C=C), 4.15 microns (C₆H₅-).

Analysis: C₁₁H₁₆O₂; calculated: C, 77.20; H, 6.98
Found C, 76.82; H, 6.99.

2-Cyclohexenyl Benzoate. Method II.—3-Bromocyclohexene (Ziegler *et al.*, 1942) was obtained by adding 89 g (0.05 mole) of *N*-bromosuccinimide and 2 g of benzoyl peroxide to a boiling solution (rapidly stirred) of 100 ml (1.1 mole) of cyclohexene, 2 g of benzoyl peroxide, and 350 ml of carbon tetrachloride. Within 30 minutes, the *N*-bromosuccinimide had been replaced by a pure white solid. This mixture was cooled and filtered. Removal of the solvent under aspirator pressure on a steam bath yielded a dark brown liquid.

3-Bromocyclohexene in 30 ml (0.1 mole) of carbon tetrachloride was added in small portions with swirling to 20 g (0.083 mole) of silver benzoate in 50 ml of benzene. Filtration of the solid and concentration of the filtrate under aspirator pressure gave a yellow oil, which was fractionated into benzoic acid and a colorless liquid identical to the product obtained by method I. The product was more easily purified and was obtained in higher yield (42%).

Cyclohexyl Benzoate.—While a mixture of 10 ml (0.10 mole) of cyclohexanol, 20 ml of pyridine, and 30 ml of benzene was stirred vigorously, 14 ml (0.12 mole) of benzoyl chloride was added over a period of 15 minutes. The reaction mixture was filtered and the filtrate was fractionated to give a colorless liquid, bp 140-3 C/7 mm, n_D^{20} 1.5175; reported bp 132-3 C/15 mm (Mengelberg, 1954). This product was also found to be pure by gas chromatography, yield 19 g (93%). Absorption maxima (film): 5.88 microns (C=O), 14.09 microns (C₆H₅-).

Analysis: C₁₁H₁₈O₂; calculated: C, 76.44; H, 7.90
Found C, 75.95; H, 7.64.

2-(2-Cyclohexenyl)cyclohexyl Benzoate.—2-(2-Cyclohexen-1-yl)cyclohexanol was synthesized (Pelton, 1951) by adding 50 ml (0.50 mole) of cyclohexanone in small portions with stirring to a white gel made from 50 ml (0.50 mole) of cyclohexanol, 27.0 g of sodium hydroxide, and 6.0 ml of water. After being heated under vigorous reflux for 2.5 hours, the reaction mixture was filtered and washed with benzene and ether. Fractional distillation gave a colorless liquid, bp 90-5 C/0.4 mm, n_D^{20} 1.5010; reported bp 135-45 C/20 mm (Pelton, 1951).

To a rapidly stirred mixture of 27.3 g (0.135 mole) of the alcohol, 20 ml of pyridine, and 15 ml of benzene was added 19 ml (0.15 mole) of

benzoyl chloride. After being stirred for 1 hour, the mixture was filtered and the filtrate was concentrated to an oil on a steam bath. Vacuum distillation of the oil gave a product, bp 168-70 C/2 mm, n_D^{20} 1.5375, yield 88 g (86% based on the alcohol). Absorption maxima (film): 5.84 microns (C=O), 6.06 microns (C=C), 14.12 microns (C_6H_5).

Analysis: $C_{10}H_{10}O$; calculated: C, 80.28; H, 8.45
Found C, 80.08; H, 8.38.

Dicyclohexyl.—This compound is available from the literature by a reliable method (Laber, 1954). Comparison of infrared spectra showed the synthetic compound to be identical to that published.

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