

is consistent with this structure, showing a parent peak at  $m/e$  249 and the base peak at  $m/e$  95 (the allylic methylcyclohexenyl cation).

Initial excitation of the *p*-benzoquinone and inter-system crossing to the triplet is probably followed by O-C coupling to produce the more favorable "diradical species" **6** (or a similar intermediate).<sup>5</sup> Instead of undergoing ring closure to an oxetan, **6** loses a  $\text{NO}_2\cdot$ , which is immediately trapped by the phenoxy radical **7**. It is not known whether the  $\text{NO}_2$  radical becomes attached directly to the benzene ring or to the oxygen to yield a phenyl nitrate, which rearranges to the *o*-nitrophenyl compound **8**. The low yield may be partially attributed to loss of  $\text{NO}_2$  from the solvent cage before recombination can occur.

Although photolytic fragmentation of nitro compounds has been observed before, this photochemical addition reaction appears to be the first case involving transfer of a nitro group.

### Experimental Section

**3-Nitro-2-methylcyclohexene (2).**—Nitration of 29 g of 1-methylcyclohexene with nitric acid-acetic anhydride as described by Bordwell and Garbisch<sup>6</sup> led to 22.4 g of a mixture of nitro acetate and nitro nitrate, as well as of nitro olefin **2**, which on refluxing with a benzene solution of 1,4-diazabicyclooctane fractional distillation, monitored by glc, afforded 8.9 g of 3-nitro-2-methylcyclohexene (**2**), bp 48–49° (0.3 mm), and a mixture of nitro acetate and nitro nitrate. The latter (8.5 g) was refluxed with a benzene solution of 1,4-diazabicyclooctane to yield, after work-up with water, 2.7 g of a 2:3 mixture of nitro olefins **1** and **2**, bp 42–44° (0.2 mm), as determined by glc.

**Irradiation of Nitro Olefins 1 and 2.**—A solution of 150 mg of a 2:3 mixture of **1** and **2** (see above) in 10 ml of cyclohexane was irradiated at 3660 Å and the course of the reaction was monitored by glc, using triglyme as an internal standard. Initial conversion of **1** and **2** was evident during the first 6 hr; then polymer formation was observed with concomitant slow disappearance of **1** and **2**.

**4-(2'-Methylcyclohex-2'-enoxy)-2-nitrophenol (8).**—3-Nitro-2-methylcyclohexene (**2**, 5.3 g) and *p*-benzoquinone (7.8 g) were dissolved in benzene (110 ml). The solution was deoxygenated by bubbling through  $\text{N}_2$  and then irradiated at 3130 Å in the Rayonet reactor. The reaction was followed by tlc [silica gel/50%  $\text{CH}_2\text{Cl}_2$ :50% petroleum ether (bp 60–70°)]. After 47 hr the solution was evaporated to a dark oil containing some solid. Pentane was added and the mixture was filtered to yield a yellow-brown solution, containing the product, and an almost black solid. Distillation of the solution under reduced pressure removed the solvent and unchanged nitro olefin. The residue was chromatographed on silica gel in petroleum ether containing increasing concentrations of benzene. The yellow-orange solution was evaporated to an oil which was crystallized by dissolution in petroleum ether and cooling to Dry Ice temperature. The yield of yellow crystalline **8** was 365 mg (4%).

*Anal.* Calcd: C, 62.64; H, 6.07; N, 5.62. Found: C, 62.37; H, 6.02; N, 5.46.

**Registry No.**—**1**, 36601-70-4; **2**, 36291-55-1; **4**, 106-51-4; **8**, 36601-72-6.

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(5) The photosensitized conversion of **2** to **1** followed by photoaddition of benzoquinone has not been ruled out.

(6) F. G. Bordwell and E. W. Garbisch, Jr., *J. Amer. Chem. Soc.*, **82**, 3588 (1960).

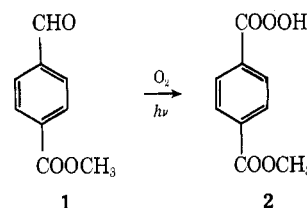
## Photooxidative Synthesis of *p*-Methoxycarbonylperbenzoic Acid, a Stable and Convenient Reagent for Epoxidation and Baeyer-Villiger Oxidation<sup>1</sup>

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During the course of the photooxidation study of methyl *p*-formylbenzoate (**1**), a simple synthesis of *p*-methoxycarbonylperbenzoic acid (**2**) has been found.



The present note describes the synthesis and chemical behavior of **2** as one of the useful reagents for epoxidation of olefins and Baeyer-Villiger oxidation of carbonyl compounds.

Photooxidation of benzaldehyde is well known as a typical autooxidation, yielding benzoic acid readily.<sup>2</sup> Jorissen and van der Beek first succeeded in isolating perbenzoic acid in 63% yield, by exposing a solution of benzaldehyde in acetone to sunlight.<sup>3</sup> Swern, Findley, and Scanlan prepared perbenzoic acid in 40% yield by employing ultraviolet radiation and carbon tetrachloride.<sup>4</sup> *p*-Bromobenzaldehyde, *p*-chlorobenzaldehyde, and *m*-chlorobenzaldehyde, however, yield little or no peracid when similarly treated.<sup>5</sup>

The photooxidation of **1** afforded mainly *p*-methoxycarbonylbenzoic acid along with a trace of the peracid in the solvents such as acetic acid, formic acid, chloroform, acetone, and benzene, consuming about 0.5 molar equiv of oxygen. However, 1 molar equiv of oxygen was rapidly consumed in the case of carbon tetrachloride,<sup>6</sup> and the reaction product consisted of essentially *p*-methoxycarbonylperbenzoic acid (**2**) which was isolated in a pure crystalline form. The yield was 80–95%.

Differential thermal analysis showed that the peracid began to decompose at 125°, the exothermic decomposition reached its maximum at 134°, and the endothermic point was at 218°, corresponding to the melting point<sup>7</sup> of *p*-methoxycarbonylbenzoic acid. The peracid **2** is as stable as *m*-chloroperbenzoic acid, and showed less than 5% decomposition after 1-year storage at 10°.

(1) Presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April 1968.

(2) H. J. L. Bächström, *J. Amer. Chem. Soc.*, **49**, 1460 (1927).

(3) W. P. Jorissen and P. A. A. van der Beek, *Recl. Trav. Chim. Pays-Bas*, **46**, 42 (1927).

(4) D. Swern, T. W. Findley, and J. T. Scanlan, *J. Amer. Chem. Soc.*, **66**, 1925 (1944).

(5) P. A. A. van der Beek, *Recl. Trav. Chim. Pays-Bas*, **51**, 411 (1932).

(6) It is very important to remove any trace of heavy metal ion from the solvent and the starting aldehyde. Otherwise, the yield of **2** is markedly decreased by autooxidation of the aldehyde with heavy metal ions.

(7) M. J. S. Dewar and J. P. Schroeder, *J. Org. Chem.*, **30**, 2296 (1965).

The reactivity of 2 was investigated by the reactions to carbon-carbon double bonds and carbonyl compounds, and the results are shown in Table I. The

TABLE I  
REACTIVITY OF *p*-METHOXYCARBONYLPERBENZOIC ACID

Olefin or ketone	Yield of oxidation product, %	Yield with perbenzoic acid, %
Cyclohexene	90	100 <sup>c</sup>
1-Methylcyclohexene	77	50-75 <sup>c</sup>
1,5,9- <i>cis,trans,trans</i> -Cyclododecatriene	76 <sup>a</sup>	64-90 <sup>d</sup>
4-Vinylcyclohexene	72 <sup>b</sup>	82 <sup>e</sup>
Styrene	60	69-75 <sup>c</sup>
Cyclopentanone	74	70-80 <sup>f</sup>
Cyclohexanone	64	71 <sup>f</sup>
Acetophenone	85	50-80 <sup>g</sup>

<sup>a</sup> Reacted with only one of trans double bonds. <sup>b</sup> 4-Vinylcyclohexene oxide. <sup>c</sup> D. Swern, "Organic Reactions," Vol. VII, R. Adams, Ed., Wiley, New York, N. Y., 1953, p 378. <sup>d</sup> Peracetic acid was used: G. Wilke, *Angew. Chem.*, **69**, 397 (1957). <sup>e</sup> F. C. Frostick, Jr., B. Phillips, and P. S. Starcher, *J. Amer. Chem. Soc.*, **81**, 3350 (1959). <sup>f</sup> S. L. Friess, *ibid.*, **71**, 2571 (1949). <sup>g</sup> S. L. Friess and A. H. Soloway, *ibid.*, **73**, 3968 (1951).

yields of the epoxidation and Baeyer-Villiger reaction ranged from 60 to 90% and 64 to 85%, respectively, generally corresponding to the reactivity of perbenzoic acid and monoperoxyphthalic acid. The peracid 2 is fairly soluble in dioxane, ethanol, acetone, acetonitrile, and *N,N*-dimethylformamide, and less soluble in chloroform, benzene, and ether.

The by-product of the reaction is *p*-methoxycarbonylbenzoic acid, which is far less soluble than 2, and may be separated easily since it precipitates out from the reaction system when a suitable solvent is employed.

Although a more extensive application of the peracid 2 to other organic compounds is necessary, the fact that 2 may be simply prepared and is relatively stable is sufficient to commend it as a new convenient reagent for epoxidation and Baeyer-Villiger oxidation.

#### Experimental Section

All melting points are uncorrected. The ir spectra were obtained on a Hitachi EPI-S2 spectrophotometer and the nmr spectra on a Varian A-60 spectrometer.

A 2-kW mercury quartz lamp made by Toray Engineering Laboratories was used without any filter.

**Preparation of Methyl *p*-Formylbenzoate (1).**—The method of Lieberman and Connor was applied to the oxidation of methyl *p*-methylbenzoate.<sup>8</sup>

The crude aldehyde, 52 g (43.8%), was recrystallized from ether or subjected to column chromatography with Woelm neutral alumina (activity I) using ether as an eluent, showing mp 62-63°. <sup>9</sup>

**Preparation of *p*-Methoxycarbonylperbenzoic Acid (2).**—Methyl *p*-formylbenzoate (1) (2 g) and 50 ml of carbon tetrachloride were placed in a cylindrical glass reactor (50 mm diameter × 250 mm length) equipped with a gas inlet tube connected to a gas buret. The reaction mixture, which was a suspension, was vigorously shaken under an atmosphere of oxygen and irradiated with the 2-kW high-pressure mercury lamp.

Oxygen (290 ml) was absorbed in 0.5 hr at room temperature (theoretical volume was 298 ml at 25°). The material which separated as white crystalline powder was collected and dried. The product was confirmed to be mainly *p*-methoxycarbonylperbenzoic acid (2) (2.0 g, 84% yield). An iodometric titration

showed that the purity of the crude product was about 90%. No explosion occurred by heating in a capillary tube and no decomposition point was observed. The peracid thus obtained was pure enough for general oxidation reactions, but, if a purer product is desired, it may be recrystallized from methanol: ir (KBr) 3268 (OH), 1730 cm<sup>-1</sup> (COOOH); nmr (dioxane) δ 3.91 (s, 3, OCH<sub>3</sub>), 8.09 (s, 4, aromatic), and 12.36 (s, 1, OH).

**Anal.** Calcd for C<sub>9</sub>H<sub>8</sub>O<sub>5</sub>: C, 55.10; H, 4.11; mol wt, 196. Found: C, 55.21; H, 4.11; mol wt, 179 (Rast).

One should be careful in using the peracid, since it irritates the nasal membranes and causes sneezing. The yield of the peracid is greatly influenced by the purity of methyl *p*-formylbenzoate and the presence of heavy metal ions.

**Reaction with Cyclohexene.**—In a 300-ml three-necked flask equipped with a mechanical stirrer, a thermometer, and a dropping funnel were placed 6.112 g of 2 and 200 ml of chloroform. Cyclohexene (2.544 g) dissolved in 20 ml of chloroform was added dropwise to the suspension, keeping the temperature below 20°. After addition, it was allowed to stand overnight with stirring at this temperature.

Precipitates of *p*-methoxycarbonylbenzoic acid (4.650 g) were removed by filtration and the filtrate was washed two times with 100 ml of 10% aqueous sodium carbonate solution, with 2 g of sodium hydrogen sulfite in 100 ml of water, and with a saturated aqueous solution of sodium chloride. After drying, the solvent was removed at atmospheric pressure, and an oily residue was distilled under reduced pressure to obtain 2.763 g of 7-oxabicyclo-[4.1.0]heptane as a colorless oil. The yield was 90%.

**Reaction with Cyclopentanone.**—In a 300-ml erlenmeyer flask equipped with a dropping funnel, 7.632 g of 2 and 150 ml of chloroform were placed and the flask was cooled in an ice bath. Then cyclopentanone (1.628 g) dissolved in 30 ml of chloroform was added to the solution. After addition, the mixture was magnetically stirred under cooling for 4 hr and allowed to stand for 4 days at room temperature. Precipitates of *p*-methoxycarbonylbenzoic acid (6.63 g) were removed by filtration and the filtrate was washed two times with 100 ml of 10% aqueous sodium carbonate solution and washed with a saturated aqueous solution of sodium chloride. After drying, the solvent was removed at atmospheric pressure, and an oily residue was distilled under reduced pressure to obtain 1.437 g of 5-pentanolate as a colorless oil. The yield was 75%. The same procedure was applied to other olefins and carbonyl compounds.

Registry No.—2, 28276-78-0.

#### The Conversion of Podocarpic Acid to an 18-Nor Steroid

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The use of podocarpic acid<sup>1</sup> (1a) and other resin acids as starting materials for the synthesis of steroids has been investigated by several groups.<sup>2-5</sup> We now report the synthesis of an 18-nor steroid (5b) from 1a.

(1) J. L. Simonsen and D. H. R. Barton, "The Terpenes," University Press, Cambridge, 1961, Vol. III, p 472.

(2) Cambie and his coworkers<sup>2</sup> devised a route for removing the geminal methylcarboxyl group in podocarpic acid and producing a Δ<sup>4</sup>-3-one system in ring A; their final product was 12-methoxy-18,19-bisnorpodocarpa-4,8,11,13-tetraen-3-one. Davis and Watkins<sup>4</sup> converted the methyl ether of methyl podocarpate to 4β-methoxycarbonyl-4α-methyl-12-methoxy-18-norandrost-8,11,13-trien-15-one, a steroid with ring C aromatic, and also the corresponding D-homo steroid.

(3) C. R. Bennett and R. C. Cambie, *Tetrahedron*, **23**, 927 (1967); R. C. Cambie and W. A. Denny, *Aust. J. Chem.*, **22**, 1699 (1969); C. R. Bennett, R. C. Cambie, R. A. Franith, and T. J. Fullerton, *ibid.*, p 1711.

(4) B. R. Davis and W. B. Watkins, *Tetrahedron*, **24**, 2165 (1968); *Aust. J. Chem.*, **21**, 1611 (1968).

(5) J. W. Huffman, *J. Org. Chem.*, **35**, 478 (1970).

(8) S. L. Lieberman and R. Connor, "Organic Syntheses," Collect. Vol. 11, Wiley, New York, N. Y., 1955, p 441.

(9) H. B. Hass and M. L. Bender, *J. Amer. Chem. Soc.*, **71**, 1767 (1949).