3-nitrotoluene at measurable rates below 227°. Thus, it seems clear that electron-withdrawing substituents at the 2 position will significantly increase the rate of decarboxylation of 3-pyridinecarboxylic acid only.

Experimental Section

Starting material, unless otherwise specified, is 2-amino-x-methylpyridine (x = 3, 4, and 5) purchased from Reilly Tar and Chemical Corp., Chicago, Ill. The apparatus and procedure used to collect the kinetic data has been described previously.[5] Melting points were determined with a Fisher-Johns block and are uncorrected.

Preparation of 2-Nitro-3-pyridinecarboxylic Acid.—This compound was prepared *via* oxidation of the amino group[8] followed by oxidation of the methyl group[9] of 2-amino-3-methylpyridine. It had mp 156° (lit.[10] mp 156°).

Anal. Calcd for $C_6H_4N_2O_4$: C, 42.8; H, 2.4; N, 16.7. Found: C, 42.7; H, 2.9; N, 16.4.

Preparation of 2-Nitro-4-pyridinecarboxylic Acid.—2-Nitro-4-pyridinecarboxylic acid was synthesized from 2-amino-4-methylpyridine by the same procedure as above. It had mp 174° (lit.[10] mp 175°).

Anal. Calcd for $C_6H_4N_2O_4$: C, 42.8; H, 2.4; N, 16.7. Found: C, 42.7; H, 2.3; N, 16.4.

Preparation of 2-Nitro-5-pyridinecarboxylic Acid.—This compound was prepared from 2-amino-5-methylpyridine by the same procedure as used to make 2-nitro-3-pyridinecarboxylic acid. It had mp 183° (lit.[10] mp 183°).

Anal. Calcd for $C_6H_4N_2O_4$: C, 42.8; H, 2.4; N, 16.7. Found: C, 42.4; H, 2.5; N, 16.3.

Preparation of 2-Chloro-3-pyridinecarboxylic Acid.—2-Chloro-3-pyridinecarboxylic acid was synthesized *via* diazotization of the amino group[11] followed by oxidation of the methyl group[9] of 2-amino-3-methylpyridine. It had mp 200–201° (lit.[10] mp ~192–193°).

Anal. Calcd for $C_6H_4ClNO_2$: C, 45.7; H, 2.5; N, 8.9. Found: C, 45.4; H, 2.8; N, 9.2.

Preparation of 2-Chloro-4-pyridinecarboxylic Acid.—This compound was prepared from 2-amino-4-methylpyridine by the same procedure as above. It had mp 249–251° (lit.[10] mp 245°).

Anal. Calcd for $C_6H_4ClNO_2$: C, 45.7; H, 2.5; N, 8.9. Found: C, 45.4; H, 2.8; N, 9.2.

Preparation of 2-Chloro-5-pyridinecarboxylic Acid.—2-Amino-5-methylpyridine was diazotized and oxidized to prepare 2-chloro-5-pyridinecarboxylic acid by the same procedure as used to make 2-chloro-3-pyridinecarboxylic acid. It had mp 194–195° (lit.[10] mp ~199°).

Anal. Calcd for $C_6H_4ClNO_2$: C, 45.7, H, 2.5; N, 8.9. Found: C, 45.9; H, 2.8; N, 9.0.

Preparation of 2-Bromo-3-pyridinecarboxylic Acid.—2-Bromo-3-pyridinecarboxylic acid was synthesized *via* diazotization[12] followed by oxidation[9] of 2-amino-3-methylpyridine. It had mp 254° (lit.[10] mp 249–250°).

Anal. Calcd for $C_6H_4BrNO_2$: C, 35.6, H, 2.0; N, 6.9. Found: C, 35.3; H, 2.0; N, 6.5.

3-Pyridinecarboxylic Acid.—This compound was purchased from Reilly Tar and Chemical Corp. It had mp 234° (lit.[10] mp 236°).

Anal. Calcd for $C_6H_5NO_2$: C, 58.5; H, 4.1; N, 11.4. Found: C, 58.1; H, 4.0; N, 11.3.

Preparation, Determination of Per Cent Composition and Kinetics of 2-Amino- and 2-Acetamido-3-pyridinecarboxylic Acid Mixture.—This mixture was synthesized *via* acetylation[11] followed by oxidation[13] of 2-amino-3-methylpyridine. In the oxidation step partial hydrolysis of the amide linkage took place. The per cent composition was determined by titrating a given amount of sample with standardized NaOH and solving two simultaneous equations. The mixture was found to be 15% 2-acetamido-3-pyridinecarboxylic acid and 85% 2-amino-3-pyridinecarboxylic acid. The kinetics were run as described above; however, a twofold excess of the mixture was used as compared to the above acids in an effort to determine if any CO_2 was evolved. The reaction was run for over 1 hr. During this time no CO_2 was detected.

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[10] E. P. Oliveto, *Heterocycl. Compounds*, **14** (3), Chapter 10 (1962).

[11] S. M. McElvain, "The Characterization of Organic Compounds," Rev. Ed., Macmillan, New York, N. Y., 1964, p 210–201.

[12] L. C. Craig, *J. Amer. Chem. Soc.*, **56**, 231 (1934).

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Preparation and Photolysis of Esters of Perphthalic Acid[1]

Mark R. DeCamp[2] and Maitland Jones, Jr.*

Department of Chemistry, Princeton University, Princeton, New Jersey 08540

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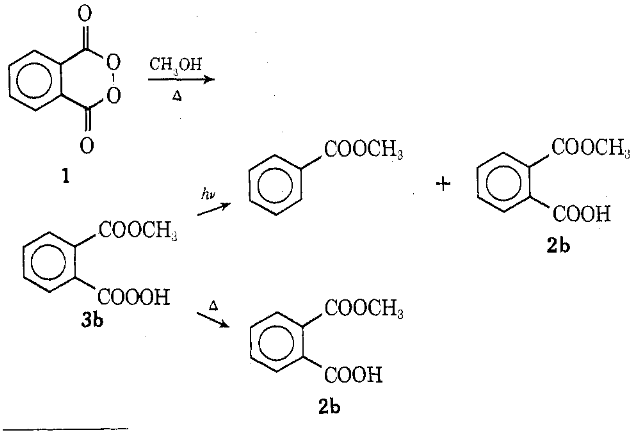
Phthaloyl peroxide (1)[3,4a] has long been recognized as a highly reactive species. Greene and coworkers discovered the facile addition of **1** to unsaturated systems[4b–f] and attributed its reactivity to the inherent strain of a planar six-membered array containing a peroxide linkage. Horner and Brüggemann[5] studied thermal decompositions of **1** in a variety of substrates and found that the reactivity and rate of decomposition of **1** was considerably greater than that of its acyclic relative, benzoyl peroxide. Although they allude to the basic hydrolysis of **1**,[6] Horner and Brüggemann do not report any further reactions with hydroxylic oxygen nucleophiles. Greene[4a] also briefly mentioned the slow dissolution of **1** in water "with concomitant hydrolysis to monoperphthalic acid." We describe here the reaction of **1** with water and alcohols to give monoperphthalic acid and its esters. We further report the photolytic decomposition of these compounds.

Upon overnight refluxing of **1** in methanol, a quantitative conversion to phthalic acid monomethyl ester (**2b**) was effected. Ester **2b** was identified by inspection of spectra, conversion to phthalic anhydride on gas chromatography, and formation of dimethyl phthalate



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[2] National Science Foundation Trainee, 1970–1971; *Petroleum Research Fund Fellow*, 1971–1972.

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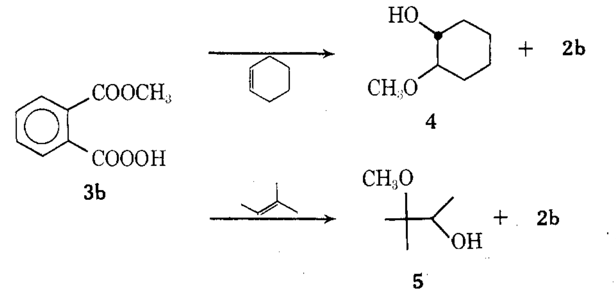
[4] (a) F. D. Greene, *ibid.*, **78**, 2246 (1956); (b) *ibid.*, **78**, 2250 (1956); (c) F. D. Greene and W. W. Rees, *ibid.*, **80**, 3432 (1958); (d) F. D. Greene, *ibid.*, **81**, 1503 (1959); (e) F. D. Greene and W. W. Rees, *ibid.*, **82**, 890 (1960); (f) *ibid.*, **82**, 893 (1960).

[5] L. Horner and H. Brüggemann, *Justus Liebigs Ann. Chem.*, **635**, 22 (1960).

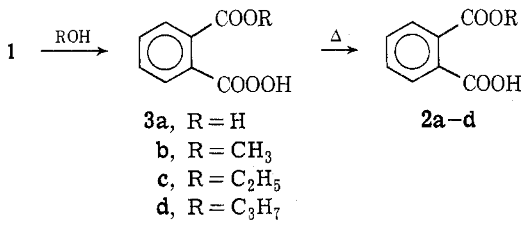
[6] Phthaloyl peroxide was dissolved in 0.1 *M* NaOH to form sodium phthalate and the sodium salt of monoperphthalic acid.

upon treatment with diazomethane. However, if **1** is merely dissolved in methanol and left to stand in the dark at room temperature, a new compound **3b** is formed. Formation of **3b** is rapid in neat methanol, but may be monitored conveniently by nmr spectroscopy in dilute solution. Mild thermolysis or photolysis converts **3b** to **2b**.

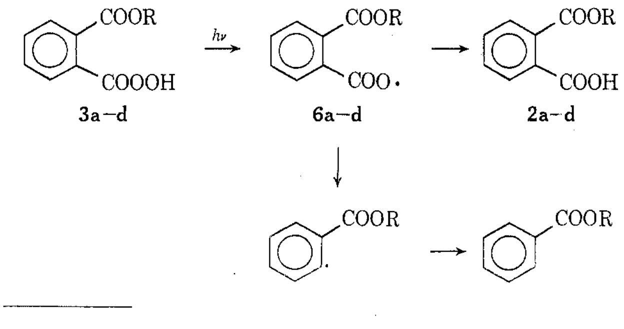
The new compound **3b** was identified as the methyl ester of perphthalic acid by the following spectral and chemical properties. The nmr spectrum of **3b** in CCl_4 contains an aromatic multiplet (δ 7.4–8.0, 4 H) and a singlet (δ 3.8, 3 H). Both the infrared spectrum (1735, 1700 cm^{-1}) and the ultraviolet spectrum (282, 276 nm) are very similar to the corresponding spectra of **2b**. Addition of cyclohexene or 2-methyl-2-butene to a methanolic solution of **3b** produced **2b** and the corresponding hydroxy ethers **4** and **5**. These latter compounds, which were presumably formed by methanolysis of an initially formed epoxide, were identified by comparison with authentic samples.



An entirely analogous reaction took place upon addition of water or other alcohols to **1**, as either monoperphthalic acid or the appropriate ester was formed. Although ortho-substituted perbenzoic acids are well known,[7] this appears to be the first report of an ester of perphthalic acid.



Irradiation of a methanolic solution of **1** through Pyrex with a 450-W medium-pressure mercury arc resulted in quantitative conversion to methylbenzoate and **2b**. A rational mechanism for this reaction involves decomposition of initially formed **3b**. Although the photolysis of perbenzoic acid itself seems not to have been reported, in our hands this process produced benzoic acid and benzene. Similarly the photolysis of *m*-chloroperbenzoic acid provided *m*-chlorobenzoic acid and chlorobenzene. A reasonable explanation for each of these reactions is that the oxygen–oxygen bond suffers photolytic cleavage to a benzoyloxy radical which is capable of hydrogen abstraction or decarboxylation. Peracetic acid has long been known as a photochemical source of hydroxy radicals.[8] The radical **6b** is also presumably the intermediate in the thermolysis of **1** in methanol.[9] Solutions of **1** in water, ethanol, and 1-propanol were also irradiated. In each case products analogous to those above were formed. Photolysis in 2-propanol followed a similar course, but in this case some products of the photodecomposition of **1**[11] were noted. Irradiation of **1** in *tert*-butyl alcohol resulted only in photolysis of the starting material. The latter two cases reflect an increasing inability to form perphthalate esters, presumably because of steric hindrance in the addition of the alcohol to **1**.



Experimental Section[14]

Phthaloyl Peroxide (1).—The preparation of 1 by a modification of Greene's[4a] procedure has been described elsewhere.[12] Peroxide synthesized by this method is a fluffy white solid, mp 125° (lit.[4a] mp 126°). *Warning:* On one occasion freshly prepared 1 was detonated with explosive violence upon touching with a metal spatula. Prior to the explosion it had been noted that the peroxide was particularly crystalline. As with any peroxide, 1 should be handled with the utmost respect.

Preparation of Esters of Monoperphthalic Acid (3b–d).—1 (0.16 g, 1.0 mmol) was dissolved with stirring in 10 ml of the appropriate alcohol at room temperature. The crude esters could be obtained by removal of the solvent at reduced pressure, but no attempts were made to purify these potentially dangerous compounds. The esters were prepared and used *in situ* in the transformations which follow.

***trans*-2-Methoxycyclohexanol (4) and 3-Methoxy-3-methylbutan-2-ol (5).**—A methanolic solution of 1 was prepared as above. Several milliliters of cyclohexene were added and the solution was stirred for 1 hr at room temperature. Following concentration under reduced pressure, 4 was isolated by preparative glpc (retention time 2 min at 130°) and compared to an authentic sample. Compound 5 was formed by the same procedure using 2-methyl-2-butene as the substrate. It was isolated by preparative glpc (retention time 5 min at 90°), and compared to an authentic sample. Pure samples of 4 and 5 were prepared by the acid-catalyzed methanolysis of the corresponding epoxides.

Photolyses of 3a–d.—Alcoholic solutions of the esters of perphthalic acid (3b–d) were prepared as described above. A solu-

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[7] D. Swern, Ed., "Organic Peroxides," Vol. I, Wiley, New York, N. Y., 1970, p 436.

[8] D. L. Heywood, B. Phillips, and H. A. Stansbury, Jr., *J. Org. Chem.*, **26**, 281 (1961).

[9] **6b** has been implicated in the thermolysis of the dimethyl ester of peroxydiphthalic acid.[10] In that study a major product was phthalic anhydride, which under our conditions would have been converted to the corresponding monoester of phthalic acid. However, either photolysis or thermolysis of the methyl ester **3b** in ethanol failed to produce any of the appropriate ethyl esters. Thus our results suggest that the radical **6b** is not prone to intramolecular cyclization.

[10] G. I. Nikishin, E. K. Starostin, and B. A. Golovin, *Bull. Acad. Sci. USSR, Ser. Chem.*, **5**, 869 (1971); *Izv. Akad. Nauk SSSR, Ser. Khim.*, **20**, 946 (1971).

[11] Photolysis of PPO in the presence of dilute alcohols affords phenylalkyl ethers from the addition of benzyne[12] to the alcohols, salicylate esters, phthalic acid, and benzoic acid.[13]

[12] M. Jones, Jr., and M. R. DeCamp, *J. Org. Chem.*, **36**, 1536 (1971).

[13] M. R. DeCamp, unpublished results.

[14] Nmr spectra were obtained with a Varian A-60A spectrometer using TMS as an internal standard; ir spectra were recorded on a Perkin-Elmer Model 237B spectrometer; uv spectra were measured with a Cary 14 recording spectrophotometer. Glpc analyses were performed on a Varian-Aerograp h A90-P using a 1-m column of 10% DC 550 silicone oil on Chromosorb P.

tion of perphthalic acid (**3a**) itself was prepared by dissolving 0.16 g of **1** in aqueous acetone. All samples, 20 ml (0.05 *M*), were irradiated at room temperature through Pyrex with a Hanovia 450-W medium-pressure mercury arc. Following drying over $MgSO_4$, where appropriate, and concentration under reduced pressure, the crude photolysates were analyzed by nmr spectroscopy and glpc. Under our glpc conditions, phthalic acid and its half esters (**2a–d**) are quantitatively converted to phthalic anhydride. The presence of the carboxyl group was confirmed in separate runs by treating the crude photoproduct with an ethereal solution of diazomethane (prepared from *N*-methyl-*N*-nitrosourea) at 0° and observing the methyl ester by nmr spectroscopy.

Registry No.—3a, 2311-91-3; **3b,** 36004-41-8.

Anomalous Ether Formation in Attempts to Transesterify Oxalate Esters with Phenoxides

Edward E. Smissman,* Michael D. Corbett,[1]
Samir El-Antably, and Kathryn C. Kroboth

Department of Medicinal Chemistry, School of Pharmacy, The University of Kansas, Lawrence, Kansas 66044

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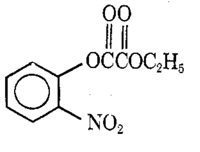
In an attempt to secure ethyl *o*-nitrophenyl oxalate (**1**) by transesterification, *o*-nitrophenol and diethyl oxalate were heated in dimethylformamide in the presence of a catalytic amount of potassium *o*-nitrophenoxide. The product isolated was not the desired mixed ester **1** but the ether, *o*-nitrophenetole (**2**), and potassium monoethyl oxalate. It was initially assumed that this anomalous ether formation was due to neighboring group participation by the *o*-nitro function. However, under identical conditions, *m*-nitrophenol produced *m*-nitrophenetole (**3**), and *p*-nitrophenol gave *p*-nitrophenetole (**4**), thus eliminating the possibility of an ortho effect by the nitro group being involved in the reaction.



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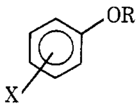
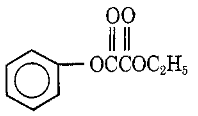


	X	R
2	*o*-NO_2	C_2H_5
3	*m*-NO_2	C_2H_5
4	*p*-NO_2	C_2H_5
5	*p*-$C_6H_5CH_2$	C_2H_5
6	H	C_2H_5
7	*o*-NO_2	$CH(CH_3)_2$
8	*p*-$C_6H_5CH_2$	$CH(CH_3)_2$



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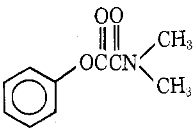

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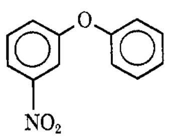

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The reaction is not limited to nitrophenols, since *p*-benzylphenol yielded *p*-benzylphenetole (**5**) and phenol gave phenetole (**6**) in good yields by the same process. The etherification also proceeded smoothly with diisopropyl oxalate to give *o*-isopropoxynitrobenzene (**7**). Di-*tert*-butyl oxalate would not undergo the reaction with *o*-nitrophenol under the conditions utilized for the etherification of the above compounds. At 150° di-*tert*-butyl oxalate decomposed[2] and no *tert*-butyl ether could be detected by tlc analysis on silica gel.

This reaction appears to be dependent on dimethylformamide, since the substitution of xylene or dimethyl sulfoxide as the solvent caused the reaction to fail.

Nucleophilic displacements of carboxylate anion from alkyl groups have been reported previously.[3–8] However, only the report by McDonough[8] describes an ether formation. On heating β-hydroxyethyl benzoate neat with an equimolar amount of diphenyl carbonate they produced β-phenoxyethyl benzoate. The scope and mechanism of this reaction was not investigated.

In order to determine if transesterification preceded ether formation, phenyl ethyl oxalate (**9**) was prepared and subjected to the conditions utilized for ether formation. When DMF was used as the solvent the half-ester half-amide **10** was obtained when either sodium methoxide or sodium ethoxide was used as the base. When sodium phenoxide was used, phenetole (**6**) was obtained and with sodium *m*-nitrophenoxide in DMF, *m*-nitrophenetole (**3**) was the product.

The above reactions were attempted using DMSO as the solvent and did not produce an isolable product.

Since the reaction requires DMF as a solvent it can be postulated that the solvent participates in the reaction. Phenyl ethyl oxalate (**9**) did not produce an ether when treated with either methoxide or ethoxide; therefore it can be concluded that transesterification does not precede ether formation.

The fact that diethyl oxalate and diisopropyl oxalate give rise to the corresponding alkyl phenyl ethers and that di-*tert*-butyl oxalate fails to give a product argues for a facile displacement reaction involving attack at the carbon attached to the ester ether oxygen. This is further substantiated in that *m*-nitrophenoxide when allowed to react with phenyl ethyl oxalate produces *m*-nitrophenetole (**3**) and not phenetole (**6**) or *m*-nitrophenyl phenyl ether (**11**).

From the above experiments a plausible mechanism (1) can be written.

Experimental Section

Melting points were obtained on a calibrated Thomas-Hoover Unimelt and are corrected. Ir data were recorded on a Beckman IR-10 spectrophotometer and nmr data on Varian Associates A-60, A-60A, and HA-100 spectrometers (TMS). Microanalyses

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[1] Taken in part from the dissertation presented by M. D. Corbett, Nov 1970, to the Graduate School of the University of Kansas in partial fulfillment of the requirements for the Doctor of Philosophy Degree.

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[7] J. L. Kice, R. A. Bartsch, M. A. Dankleff, and S. L. Schwartz, *J. Amer. Chem. Soc.,* **87,** 1734 (1965).

[8] L. M. McDonough, *Chem. Ind. (London),* 1501 (1965).