

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 MgSO₄, 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*-nitroso-urea) at 0° and observing the methyl ester by nmr spectroscopy.

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

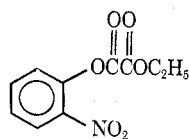
Anomalous Ether Formation in Attempts to Transesterify Oxalate Esters with Phenoxides

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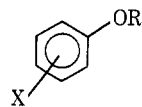
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In an attempt to secure ethyl *o*-nitrophenyl oxalate (1) by transesterification, *o*-nitrophenol and diethyl oxalate were heated in dimethylformamide in the presence of a catalytic amount of potassium *o*-nitrophenoxide. The product isolated was not the desired mixed ester 1 but the ether, *o*-nitrophenetole (2), and potassium



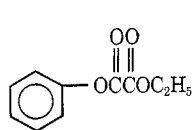
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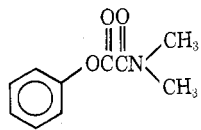
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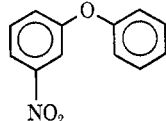
2	<i>o</i> -NO ₂	C ₂ H ₅
3	<i>m</i> -NO ₂	C ₂ H ₅
4	<i>p</i> -NO ₂	C ₂ H ₅
5	<i>p</i> -C ₆ H ₅ CH ₂	C ₂ H ₅
6	H	C ₂ H ₅
7	<i>o</i> -NO ₂	CH(CH ₃) ₂
8	<i>p</i> -C ₆ H ₅ CH ₂	CH(CH ₃) ₂



9



10



11

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.

(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.

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 decomposed² 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 McDonough⁸ 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

(2) G. J. Karabatsos, J. M. Corbett, and K. L. Krumel, *J. Org. Chem.*, **30**, 689 (1965).

(3) F. Elsinger, J. Schreiber, and A. Eschenmoser, *Helv. Chim. Acta*, **43**, 113 (1960).

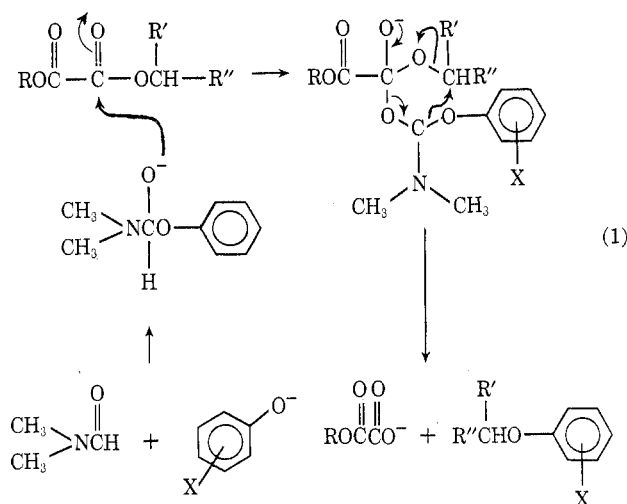
(4) A. P. Krapcho, G. A. Glynn, and B. J. Grenon, *Tetrahedron Lett.*, 215 (1967).

(5) P. A. Bartlett and W. S. Johnson, *ibid.*, 4495 (1970).

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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).



were performed by Midwest Microlab, Inc., Indianapolis, Ind., and on an F & M 185 C, H, N analyzer, University of Kansas. Unless specified otherwise, all spectra were consistent with the assigned structures.

***o*-Nitrophenetole (2).**—*o*-Nitrophenol (7.0 g, 0.05 mol), potassium *o*-nitrophenoxide (0.9 g, 0.005 mol), and 30 ml of diethyl oxalate in 120 ml of DMF were heated to 120° for 12 hr. The dark reaction mixture was cooled and combined with 200 ml of C₆H₆. This solution was washed twice with 200 ml of H₂O and dried (Na₂SO₄), and the solvent was removed *in vacuo* to give an oil. Distillation at 72–74° (0.1 mm) gave 7.8 g (85%) of 2 as a yellow liquid, *m/e* 267.

Anal. Calcd for C₈H₉NO₃: C, 57.48; H, 5.43; N, 8.38. Found: C, 56.98; H, 5.32; N, 8.39.

This reaction was then performed with potassium *o*-nitrophenoxide (8.9 g, 0.05 mol) and no *o*-nitrophenol. The dark reaction mixture was cooled and a solid was collected by filtration. Partial purification was achieved by washing with Et₂O to give potassium monoethyl oxalate as pale pink plates (5.5 g, 71%), mp 146–148°, ir (KBr) 1730 (ester C=O), 1645 cm⁻¹ (carboxylic acid anion C=O).

***m*-Nitrophenetole (3).**—*m*-Nitrophenol (3.5 g, 0.025 mol) and NaH (0.12 g of a 53.4% suspension in mineral oil, 0.025 mol) were allowed to react in 60 ml of DMF. The solution was heated to 120° for 16 hr after the addition of 20 ml of diethyl oxalate. The dark reaction mixture was combined with 100 ml of C₆H₆ and washed with 100 ml of H₂O. The organic solution was dried (Na₂SO₄) and the solvent was removed *in vacuo* to give an oil. Distillation gave a yellow oil, which solidified (2.7 g, 66%), mp 32–33° (lit. mp 34°).

Anal. Calcd for C₈H₉NO₃: C, 57.48; H, 5.43; N, 8.38. Found: C, 57.62; H, 5.71; N, 8.13.

***p*-Nitrophenetole (4).**—By a procedure analogous to that used in the preparation of 3, *p*-nitrophenetole (4) was isolated as a yellow solid (2.1 g, 51%), mp 58.5–59.5° (lit. mp 60°).

Anal. Calcd for C₈H₉NO₃: C, 57.48; H, 5.43; N, 8.38. Found: C, 57.70; H, 5.35; N, 8.30.

***p*-Benzylphenetole (5).**—*p*-Benzylphenol (9.2 g, 0.05 mol), NaH (0.23 g of a 54.4% suspension in mineral oil, 0.05 mol), and 30 ml of diethyl oxalate were heated to 120° in 120 ml of DMF for 24 hr. The reaction mixture was combined with 200 ml of C₆H₆ and washed twice with 200 ml of H₂O. The C₆H₆ solution was dried (Na₂SO₄) and the solvent was removed to give an oil. Distillation at 96–98° (0.1 mm) gave 6.9 g (60%) of 5 as a colorless oil.

Anal. Calcd for C₁₅H₁₆O: C, 84.86; H, 7.59. Found: C, 84.89; H, 7.83.

***p*-Benzylphenyl Isopropyl Ether (8).**—*p*-Benzylphenol (9.2 g, 0.05 mol), NaH (0.23 g of a 54.4% suspension in mineral oil, 0.05 mol), and 30 ml of diisopropyl oxalate were heated to 130° in 120 ml of DMF for 24 hr. The reaction mixture was combined with 200 ml of C₆H₆ and washed twice with 200 ml of H₂O. The C₆H₆ solution was dried (Na₂SO₄) and the solvent was removed to give an oil. Distillation at 102° (0.2 mm) gave 6.8 g (60%) of 8 as a colorless oil.

Phenyl Ethyl Oxalate (9).—Phenol (28.2 g, 0.3 mol) in 100 ml of dioxane was added slowly to a cold suspension of NaH (12.63 g of a 53.4% suspension in mineral oil, 0.3 mol) in 200 ml of

dioxane. After the solution was stirred for 10 min, 41 g (0.3 mol) of ethyloxalyl chloride was added slowly. The mixture was refluxed for 45 min, cooled, and filtered, the solvent was removed, and the residue was distilled at 100–105° (0.2 mm) to give 40 g (69%) of a colorless oil.

Reactions of Phenyl Ethyl Oxalate. A. With Sodium Methoxide in DMF.—Sodium methoxide (2.16 g, 0.04 mol) in 50 ml of DMF was allowed to react with 3.88 g (0.02 mol) of the diester in 50 ml of DMF. The mixture was heated at 120° for 12 hr. On cooling, 200 ml of benzene was added, the solution was washed with H₂O and aqueous NaHCO₃ and dried (Na₂SO₄), and the benzene was removed to yield an oil. The oil was found to be the phenyl half-ester *N,N*-dimethylamide of oxalic acid 10.

B. With Sodium Ethoxide in DMF.—The conditions and product were identical with those of procedure A.

C. With Sodium Phenoxide in DMF.—Sodium phenoxide (4.64 g, 0.04 mol) and the diester (3.88 g, 0.02 mol) were heated at 120° in 100 ml of DMF for 12 hr. The mixture was treated with 200 ml benzene, washed with H₂O, 10% NaOH, and water, and dried (Na₂SO₄) and the solvent was removed to give 2.4 g (50%) of phenetole (6).

D. With Sodium *m*-Nitrophenoxide in DMF.—Utilizing sodium *m*-nitrophenoxide (5.4 g, 0.04 mol) in a procedure identical with C, 2.7 g (40%) of *m*-nitrophenetole was obtained.

Registry No.—2, 610-67-3; 3, 621-52-3; 4, 100-29-8; 5, 35672-52-7; 8, 35672-53-8; 9, 15779-81-4; potassium monoethyl oxalate, 1906-57-6.

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Dehalogenation of Organic Halides by Titanocene

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The synthesis, some structural studies, and a relatively small number of chemical reactions of titanocene [(C₁₀H₁₀Ti)₂] have been reported.³ Although Watt and coworkers observed that titanocene reacted with various halogenated organic solvents, the products were not investigated. We now wish to report that titanocene is useful in effecting dehalogenation of a number of organic halides. We have found that titanocene can abstract halogens readily at room temperature from alkyl, allyl, and certain vinyl halides but not from aromatic halides. In all the dehalogenation reactions coupling and/or unsaturated products resulted from the organic halides and stable green halide complexes were formed from titanocene. The successful dehalogenations where the organic products were isolated are summarized in Table I.

(1) Member of 1969 National Science Foundation Summer Research Participation Program for College Teachers at the University of Florida and Recipient of an NSF-RPCT extension Grant 1969-1971.

(2) National Science Foundation Undergraduate Summer Research Participation Program, 1969.

(3) "Advances in Organometallic Chemistry," Vol. 9, F. G. A. Stone and R. West, Ed., Academic Press, New York, N. Y., 1970, pp 175-179.