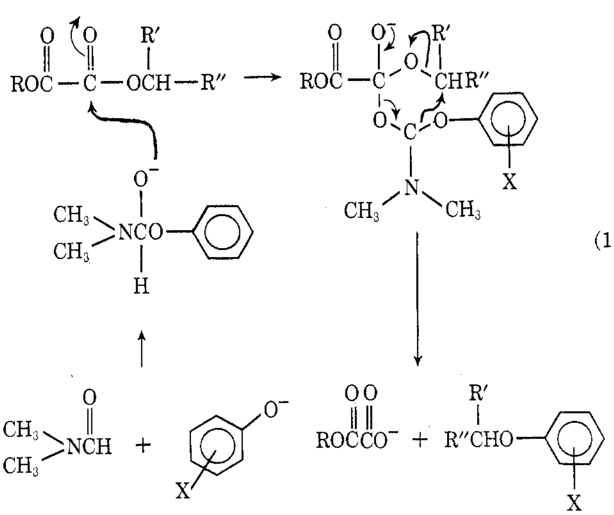

(1)

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 C_6H_6. This solution was washed twice with 200 ml of H_2O and dried (Na_2SO_4), 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 $C_8H_9NO_3$: 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 Et_2O 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 C_6H_6 and washed with 100 ml of H_2O. The organic solution was dried (Na_2SO_4) 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 $C_8H_9NO_3$: 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 $C_8H_9NO_3$: 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 C_6H_6 and washed twice with 200 ml of H_2O. The C_6H_6 solution was dried (Na_2SO_4) 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 $C_{15}H_{16}O$: 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 C_6H_6 and washed twice with 200 ml of H_2O. The C_6H_6 solution was dried (Na_2SO_4) 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 H_2O and aqueous $NaHCO_3$ and dried (Na_2SO_4), 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 H_2O, 10% NaOH, and water, and dried (Na_2SO_4) 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 [$(C_{10}H_{10}Ti)_2$] 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.

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[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 extention 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.

TABLE I

REACTIONS OF TITANOCENE WITH ORGANIC HALIDES

Organic halide	Registry no.	Mole ratio of titanocene:halide[a]	Product	Yield, %[b]
1,2-Dibromocyclohexane	5401-62-7	1.0:1.0	Cyclohexene	42.5
Benzyl chloride	100-44-7	1.0:1.0	Dibenzyl	18.6
Benzal chloride	98-87-3	1.0:3.6	*cis*-Stilbene	2.9
			trans-Stilbene	14.0
			dl-Stilbene dichloride	9.2
Benzotrichloride	98-07-7	1.0:2.0	*cis*-Dichlorostilbene	15.9
			trans-Dichlorostilbene	8.9
			1,2-Diphenyl-1,1,2,2-tetrachloroethane	7.0
			Biphenyl[c]	
meso-Stilbene dichloride	15951-99-2	1.0:1.0	*trans*-Stilbene	64.0
meso-Stilbene dibromide	13440-24-9	1.0:1.0	*trans*-Stilbene	73.6
trans-1,2-Dibromostilbene	20432-10-4	1.0:2.0	Diphenylacetylene	23.2
trans-1,2-Diiodostilbene	20432-11-5	1.0:2.0	Diphenylacetylene	34.2

[a] Mole ratio calculations are based on titanocene *monomer*. [b] Yields were based on the assumption of abstraction of two halogen atoms per titanium atom of titanocene. Theoretical yields of individual products were based on the assumption that they were the sole products. [c] No yield was calculated for this product. See Experimental Section for the extent of its formation.

The aromatic halides which titanocene failed to dehalogenate included *o*-dichlorobenzene, *o*-dibromobenzene, *p*-nitrobromobenzene, and *p*-bromoanisole. In all these cases the starting materials were recovered following reaction attempts under different conditions.

Of the green complexes formed by titanocene in the dehalogenation reactions, the chloro complex proved to have the greatest air stability. Regardless of the organic chlorine compound used, it analyzed consistently for a formula of $C_{20}H_{19}Ti_2Cl_4$. Based on this formula the yields of the titanium product were usually almost quantitative. This compound is not monomeric judging from its insolubility in the common solvents. Reproducible elemental analyses could not be obtained for the somewhat less stable analogous bromide complexes, but the data and other observations suggest a similar dimeric structure.

The mechanisms of these reactions have not been established.

Experimental Section

Materials.—Titanocene was synthesized by the method described by Watt, Baye, and Drummond[4] and used without sublimation. The organic halides were purified by recrystallization or fractional distillation till they had sharp melting points or were gas chromatographically pure. All solvents (benzene, THF, toluene, pentane) were distilled over calcium hydride, $LiAlH_4$, or Na–K alloy and stored under argon.

Analyses.—Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Fritz-Pregl-Strasse, West Germany. Gas chromatographic analyses were carried out on a Hewlett-Packard F & M Model 5754B gas chromatograph using 6 ft × 0.125 in., SE-30 columns.

Apparatus.—All the dehalogenations were carried out in a 100-ml, round-bottom, three-necked flask equipped with reflux condenser, constant pressure dropping funnel, magnetic stirrer, and an inlet for argon free of oxygen or moisture. The apparatus was evacuated, flame dried, and filled with argon prior to each reaction.

Calculations.—A mole of titanocene was based on the monomer, $C_{10}H_{10}Ti$, for mole ratio and per cent yield calculations. The theoretical yields are based on the assumption of abstraction of two halogen atoms per titanium atom in titanocene and the formation of $C_{20}H_{19}Ti_2X_4$ complexes.

Reaction of Titanocene with 1,2-Dibromocyclohexane.—Titanocene (5.0 g, 28 mmol) was stirred in 15 ml of toluene, and a solution of 1,2-dibromocyclohexane (6.45 g, 26.7 mmol) in 25 ml of toluene was added dropwise within 10 min. After an initial exothermic period the reaction was continued for 24 hr at room temperature. Volatiles were vacuum distilled from the flask and collected in a Dry Ice–acetone cooled receiver. The residue, a stable greenish solid, weighed 9.0 g (95%) after drying. The distillate was fractionally distilled in a spinning band column and fractions boiling at 80–82, 82–85, and 85–108° were collected. These fractions were found by gas chromatography to contain 99, 79, and 8% cyclohexene, respectively. These correspond to a total of 0.93 g of cyclohexene (42.5% yield) based on the calibration of the chromatograph.

Reaction of Titanocene with Benzyl Chloride.—To titanocene (1.0 g, 5.6 mmol) stirred in 15 ml of benzene, a solution of benzyl chloride (1.43 g, 11.3 mmol) in 5 ml of benzene was added dropwise. The reaction mixture was then stirred for 12 hr at room temperature. The contents were then exposed to air and filtered. The green filter cake was further washed with benzene and petroleum ether (bp 30–60°). The insoluble, green solid weighed 1.38 g (99%) after drying under vacuum. The filtrate was concentrated, reslurried in pentane, and passed through a silica gel column. From the concentrated, cooled eluate crystals were separated and recrystallized from pentane. After drying, the purified crystals, identified as dibenzyl, weighed 0.19 g (mp 52–52.5°), corresponding to a yield of 18.6%.

Reaction of Titanocene with Benzal Chloride.—To a well-stirred slurry of titanocene (4.00 g, 22.4 mmol) in 20 ml of pentane was added a solution of benzal chloride (13.00 g, 80.0 mmol) in 10 ml of pentane within a 10-min period. The reaction was exothermic. The contents were stirred for 16 hr at room temperature, exposed to air, and filtered. The green filter cake was washed several times with pentane and dried under vacuum. The filtrate was distilled under vacuum to remove the pentane and the excess benzal chloride. The residue was treated with hot pentane and filtered. Evaporation of the filtrate gave a residue weighing 1.35 g which was shown (gc, ir) to consist of 4.3% *cis*-stilbene, 20.9% *trans*-stilbene, 38.2% *dl*-stilbene dichloride, and 34.6% benzal chloride.

The dried, insoluble green solids were extracted by benzene in a Soxhlet extraction apparatus, dried (4.30 g, 77%), and analyzed.

Anal. Calcd for $C_{20}H_{19}Ti_2Cl_4$: C, 48.34; H, 3.85; Ti, 19.28; Cl, 28.53. Found: C, 48.02; H, 3.86; Ti, 19.52; Cl, 28.23.

Reaction of Titanocene with Benzotrichloride.—A solution of benzotrichloride (11.80 g, 60.2 mmol) in 18 g of THF was slowly added dropwise to titanocene (5.35 g, 30.0 mmol) in THF (18 g). After the initial exothermic reaction, the mixture was stirred for 8 hr at room temperature and then exposed to air and evaporated to dryness. The residue was extracted with boiling pentane several times and the remaining insoluble green solid was dried under vacuum (7.5 g, 100%). The pentane extracts were combined and the pentane was removed. The residue (2.10 g) consisted (gc, ir) of 28.2% *cis*-dichlorostilbene, 15.8% *trans*-dichlorostilbene, 32.0% 1,2-diphenyl-1,1,2,2-tetrachloroethane, 13.4% biphenyl,[5] and 10.6% of the starting benzotrichloride.

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(4) G. W. Watt, L. J. Baye, and F. O. Drummond, Jr., *J. Amer. Chem. Soc.*, **88**, 1139 (1966).

(5) Biphenyl, which was not present in the reactants, was produced in carefully repeated experiments; its mode of formation is presently unknown.

After additional extraction of impurities with benzene in a Soxhlet extraction apparatus and drying, the green solid was submitted for elemental analysis.

Anal. Calcd for $C_{20}H_{19}Ti_2Cl_4$: C, 48.34; H, 3.85; Ti, 19.28; Cl, 28.53. Found: C, 48.39, 48.43; H, 3.83, 3.84; Ti, 19.34, 19.35; Cl, 28.31, 28.33.

Reaction of Titanocene with *meso*-Stilbene Dichloride.—*meso*-Stilbene dichloride (0.50 g, 2.0 mmol) and 9 ml of benzene were added separately to a solution of titanocene (0.36 g, 2.0 mmol) in 5 ml of benzene with stirring. The reaction was exothermic with considerable foaming. After the reaction mixture had been stirred for 24 hr at room temperature, the contents were exposed to air and filtered. The green filter cake was washed with benzene and dried; it weighed 0.4 g (80%). The filtrate was evaporated to dryness and the residue was extracted with boiling petroleum ether. From the combined extracts three crystalline crops were collected, combined, and dried under vacuum. The dry, flaky crystals, which were identified as *trans*-stilbene, were recrystallized from petroleum ether. The final product weighed 0.23 g, mp 122–124° (lit.[6] mp 124°), corresponding to a yield of 64.0%.

Reaction of Titanocene with *trans*-Diiodostilbene.—Benzene (30 ml) was added to a solid mixture of titanocene (1.20 g, 6.74 mmol) and *trans*-diiodostilbene (1.45 g, 3.36 mmol). The mixture was stirred for 24 hr at room temperature. The contents were then filtered and the brownish-green filter cake was washed with benzene. The filtrate was evaporated to dryness and the residue was extracted with boiling pentane. The pentane extracts were combined and evaporated. The remaining residue was recrystallized from pentane and dried. The product, identified as diphenylacetylene, weighed 0.41 g, mp 60–61° (lit.[7] mp 64°), corresponding to a yield of 34.2% based on titanocene and 68.6% based on *trans*-diiodostilbene used in the reaction.

Registry No.—Titanocene, 1271-29-0.

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[6] "Handbook of Chemistry and Physics," 48th ed, Chemical Rubber Co., Cleveland, Ohio, 1967, p C-546.

[7] Reference 6, p C-321.

Preparation of *N*,*N*-Bis(2-fluoro-2,2-dinitroethyl)amides

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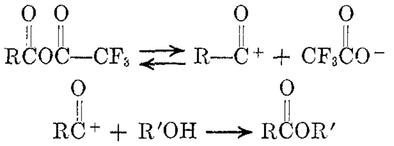
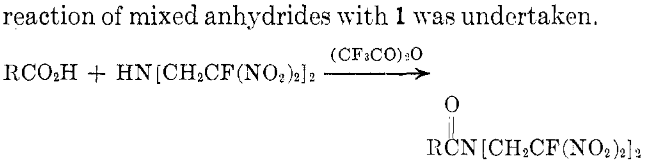
In a recent paper by Adolph and Kamlet[1] the preparation of bis(2-fluoro-2,2-dinitroethyl)amine (**1**) was reported. These authors showed that **1** was weakly basic; it could be recrystallized unchanged from trifluoroacetic acid, was insoluble in 50% sulfuric acid, and did not form isolable salts with mineral acids.[2] The weak nucleophilic properties of the amine **1** toward protons appear to parallel equally weak nucleophilic properties toward carbon. Attempts to prepare amides by the reaction of **1** with anhydrides or acyl chlorides or by ester amination, under usual conditions, proved fruitless.

Mixed trifluoroacetic–carboxylic anhydrides have been extensively used as mild reagents for preparing esters.[3] It has been postulated that the reactive species is the acylium ion, formed in equilibrium with the mixed anhydride.[4] In contrast, the main reaction course with amines involves a nucleophilic attack directly on the mixed anhydride, forming the trifluoroacetamide as the predominant product.[5] Thus, the method has been considered unsuitable for N-acylation.[3a] It seemed likely, however, that bis(fluorodinitroethyl)amine **1**, because of its lack of basic properties, would react *via* an acylium ion mechanism, if it reacted at all. Therefore an investigation of the reaction of mixed anhydrides with **1** was undertaken.



$$\mathrm{R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}{-}CF_3} \rightleftarrows \mathrm{R{-}\overset{O}{\overset{\|}{C}}{}^+} + \mathrm{CF_3\overset{O}{\overset{\|}{C}}O^-}$$

$$\mathrm{R\overset{O}{\overset{\|}{C}}{}^+} + \mathrm{R'OH} \longrightarrow \mathrm{R\overset{O}{\overset{\|}{C}}OR'}$$



$$\mathrm{RCO_2H + HN[CH_2CF(NO_2)_2]_2} \xrightarrow{\mathrm{(CF_3CO)_2O}} \mathrm{R\overset{O}{\overset{\|}{C}}N[CH_2CF(NO_2)_2]_2}$$

Bis(fluorodinitroethyl)amine **1** reacted at ambient temperature with the mixed anhydride formed by the addition of acetic acid to trifluoroacetic anhydride. The reaction, as judged by tlc analysis,[6] was complete and essentially quantitative in 24 hr. The reaction time for the mixed anhydride of butyric acid was 48 hr and for isobutyric acid 192 hr at ambient temperature. Pivalic acid was completely unreactive. That steric factors can play an important and even overriding role is not unexpected in view of the bulky nature of the amine.

With acrylic acid, a 69% yield of *N*,*N*-bis(2-fluoro-2,2-dinitroethyl)acrylamide (**5**) was obtained after 4 days at ambient temperature. Fumaric and succinic acid did not react under these conditions, presumably because of the formation of the unreactive cyclic anhydrides.[3a] Ethyl fumarate, however, gave a 44% yield of ethyl *N*,*N*-bis(2-fluoro-2,2-dinitroethyl)fumaramate (**6**) after 5 days at 80°. Chloroacetic acid required a longer reaction period of 25 days at 80°, while dichloroacetic acid was unreactive at 100° for periods up to 13 days. In contrast to dichloroacetic acid, a 71% yield of ethyl *N*,*N*-bis(2-fluoro-2,2-dinitroethyl)oxamate was isolated from the reaction of the mixed anhydride of ethyl oxalate with **1** after 5 days at 100°.

For an acylium ion mechanism it would be expected that electronegative substituents on the carboxylic acid would inhibit the reaction by lowering the equilibrium concentration of both the mixed anhydride and the acylium ion. In general the experimental results are in accord with this expectation. However, an examination of the collected results in Table I indicates that ethyl oxalate reacts more readily than would be anticipated on the basis of inductive effects. The

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[1] H. G. Adolph and M. J. Kamlet, *J. Org. Chem.*, **34**, 45 (1969).

[2] A pK_a value of 0.4 can be calculated for **1** using Hall's correlation equation for secondary amines (ref 2a) and a σ^* value of 1.57 for the fluorodinitroethyl group (ref 2b). However, the data of Bagal and coworkers (ref 2c) indicates that amines substituted with bulky nitro groups are less basic than would be expected solely on the basis of inductive effects. A more reasonable figure for the pK_a of **1** would be ~ -0.3. (a) H. K. Hall, Jr., *J. Amer. Chem. Soc.*, **79**, 5441 (1951). (b) L. A. Kaplan and H. B. Pickard, *J. Org. Chem.*, **35**, 2004 (1970). (c) L. I. Bagal, G. I. Koldobskii, and E. S. Gerasimova, *Zh. Org. Khim.*, **3**, 2084 (1967).

[3] (a) J. M. Tedder, *Chem. Rev.*, **55**, 787 (1955); (b) R. C. Parish and L. M. Stock, *J. Org. Chem.*, **30**, 927 (1965); L. Alimirante and G. Tosolini, *ibid.*, **26**, 177 (1961).

[4] For a comprehensive discussion of the possible equilibria involved in mixed anhydrides see ref 3a.

[5] E. J. Bourne, S. H. Henry, C. E. M. Tatlow, and J. C. Tatlow, *J. Chem. Soc.*, 4014 (1952).

[6] W. H. Gilligan, *J. Org. Chem.*, **36**, 2138 (1971).