solvent and recrystallization from dilute acetone gave 9.15 g (25.6%) of pure **10**, mp 74–76°. The combined mother liquors contained **8**, **10**, and **11** in approximately equal amounts as seen by visual estimation on a thin layer chromatogram.

Reaction of 11 with 1.—A solution 3.5 g (10 mmol) of **11** in 50 ml of THF was treated with a solution of 10 mmol of **1** in 50 ml of THF and the resulting black solution was stirred under dry nitrogen overnight at room temperature. The reaction mixture was then poured over ice and 2.5 g (97.4%) of yellow crystalline **8**, devoid of **11** and **10** (mp 109–113°, lit.[3] 115–116°), was removed by filtration. The same result was obtained when the reaction mixture was heated under reflux and also when phenyllithium was substituted for **1** in the reaction.

Registry No.—4-(β-Phenylmonophenethyl)pyridine hydrochloride, 15813-15-7; **4**, 15856-53-8; **4** 2HCl, 15813-16-8; **10**, 15814-97-8; **11**, 15814-98-9; **11** HCl, 15813-17-9.

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The Chlorination of Diethyl Acetylenedicarboxylate with Ferric Chloride

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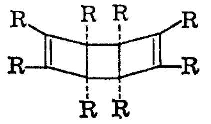
We recently became interested in the synthesis of *syn*-octacarbethoxytricyclo[4.2.0.0^{2,5}]octadiene (I) in connection with some photochemical studies. Since the aluminum chloride catalyzed tetramerization of 2-butyne to the octamethyl derivative II had been reported,[1] it was felt that a similar Lewis acid catalyzed reaction of diethyl acetylenedicarboxylate (III) should lead to the desired tetramer (I). To avoid the possibility of undesirable side reactions between aluminum chloride and the diester,[2] ferric chloride was chosen as the Lewis acid. Instead of producing I, however, ferric chloride served as a stereospecific chlorinating agent to yield diethyl dichlorofumarate (IV).



I, R = $-CO_2C_2H_5$
II, R = $-CH_3$

When a solution of III in cyclohexane was added to a stirred suspension of anhydrous ferric chloride in the same solvent, a viscous, amorphous complex which adhered to the walls of the flask was formed. Complex formation could be monitored by gas chromatography of the supernatant liquid, and appeared to be essentially complete after 1.5 hr. Continued stirring of the reaction mixture, followed by hydrolysis, produced a mixture of starting material and one major volatile product. That this product was not the expected tetramer (I) was demonstrated by its mass spectrum, which displayed a peak for the molecular ion at 239.9947, and suggested the formula $C_8H_{10}O_4Cl_2$. This formula was confirmed by combustion analysis and additional molecular weight data. The nmr spectrum exhibited *only* the characteristic signals for the grouping $-OCH_2CH_3$. Only two structures accommodated this data, diethyl dichloromaleate and diethyl dichlorofumarate (IV). Unequivocal proof that the product was not the maleate derivative was obtained by comparison of its glpc retention time with that of authentic diethyl dichloromaleate, prepared from the commercially available dichloromaleic anhydride. Earlier workers[3] had demonstrated that the acid-catalyzed esterification of this anhydride proceeds without isomerization. In addition, the well-defined separation of the two isomeric esters on gas chromatography gave assurance of the stereospecificity of the chlorination.

The chlorination of benzene derivatives,[4] alcohols,[5] and esters[5] by ferric chloride have been reported. Since there appeared to be no previous reports of chlorination of acetylenic compounds by ferric chloride,[6] however, a cursory investigation of the reaction mechanism was made. The dependence of the yield of diethyl dichlorofumarate (IV) upon reaction parameters is summarized in Table I.

Table I

Reaction time, hr	Moles of $FeCl_3$/ mole of III	% yield of IV
1.5	8.71	4.3
17	2.03	7.7
17	4.13	20.5
16	8.42	19.7
45	9.76	30.4

The physical state of the intermediate complex makes extreme emphasis upon the effect of varying the $FeCl_3$/III ratio on the yield of IV unjustifiable. It is not inconceivable that a significant amount of ferric chloride became occluded in the sticky complex during the early stages of the reaction, and was thereby effectively removed from the reaction media.

From the low yield of IV after a reaction time of 1.5 hr (complex formation complete), it was inferred that chlorination was not simply a result of the hydrolysis of the complex. This experiment also demonstrated that chlorination occurred more slowly than complex formation, a hypothesis which was substantiated by the dependence of the yield of IV on reaction time. Finally, when diphenylacetylene was treated with ferric chloride for 22 hr, no reaction occurred. Thus it appeared that the carbethoxy groups were involved in the chlorination reaction.

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(3) N. R. Eldred and D. M. Yound, *J. Amer. Chem. Soc.*, **75**, 4338 (1953).

(4) P. Kovacic and N. O. Brace, *ibid.*, **76**, 5491 (1954).

(5) M. Dangyan, *J. Gen. Chem. USSR*, **8**, 1780 (1938); *Chem. Abstr.*, **33**, 4957 (1939).

(6) For a recent review of additions to acetylenes, see E. Winterfeldt, *Angew. Chem. Intern. Ed. Engl.*, **6** (5); 423 (1967). See also F. Behlmann, *Angew. Chem.*, **69** (3), 82 (1957), and G. Chavanne, *Bull. Soc. Chem. Belges*, **26**, 287 (1912).

The initial complex probably results from coordination of ferric chloride at each of the carbonyl oxygens.[7] It would be reasonable to expect the complexed carbonyl groups to assume the *anti* conformation with respect to each other. Chlorine transfer in this conformation from the complexed Lewis acids to the neighboring acetylenic carbons would then yield the observed product.

Experimental Section

The diethyl acetylenedicarboxylate used in this study was purchased from Farchan Research Laboratories (Wickliffe, Ohio) and was used without further purification. The sublimed anhydrous ferric chloride powder and the cyclohexane were Matheson Coleman and Bell analytical reagent grade. Gas chromatography was performed on a Barber-Coleman Model 5000 gas chromatograph with 6 ft × 0.25 in. 10% SE30 on 60–80 Chromosorb W columns. The check for volatile products was carried out by programming column temperature from 100–270°, while the quantitative gas chromatography was done isothermally at 125° using hexamethylbenzene as a standard.

Reaction of Diethyl Acetylenedicarboxylate with Ferric Chloride. General Procedure.—To a stirred suspension of 1.6260 g (9.41 mmol) of anhydrous ferric chloride in 10 ml of cyclohexane was added dropwise over 35 min a solution of 0.790 g (4.64 mmol) of diethyl acetylenedicarboxylate in 10 ml of cyclohexane. After stirring for 17 hr, the cyclohexane solution was decanted onto 10 g of ice. The residue in the reaction flask was dissolved in ice water and added to the cyclohexane above. The organic layer was separated and saved and the aqueous layer extracted once with 30 ml of cyclohexane. The combined organic layers were dried over anhydrous magnesium sulfate, the dessicant removed by filtration, and the filtrate concentrated to a volume of *ca.* 10 ml on a rotary evaporater without the application of heat. Hexamethylbenzene (0.1280 g) was added and the composition of the solution was found by quantitative gas chromatography to be 0.086 g of IV (7.7%) and 0.56 g of III. A pure sample of IV was obtained by preparative gas chromatography using a 5 ft × $^3/_8$ in. 5% SE 30 on 60–80 Chromosorb W at 100°. The analytical sample had $n^{25}\text{D}$ 1.4672.

Anal. Calcd for $C_8H_{10}Cl_2O_4$: C, 39.84; H, 4.18; Cl, 29.42; mol wt, 241. Found: C, 39.75; 39.85; H, 4.03, 4.14; Cl, 29.25; 29.28; mol wt, 246 (osmometry).

Diethyl Dichloromaleate.—A solution of 5.2 g of dichloromaleic anhydride (0.031 mol) and 0.2 g of *p*-toluensulfonic acid in 300 ml of absolute ethanol and 150 ml of anhydrous benzene was refluxed for 12 days, using a Dean–Stark moisture trap to periodically remove 20-ml portions of the condensate. The product was worked up in the usual manner to give diethyl dichloromaleate as a clear colorless liquid, bp 70–72° (0.1 mm), which was homogeneous to vapor phase chromatography.

Registry No.—Diethyl acetylenedicarboxylate (III), 762-21-0; ferric chloride, 7705-68-0; diethyl dichlorofumarate (IV), 15649-40-8; diethyl dichloromaleate, 15649-41-9.

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Reaction of Nitro Alcohols with Sulfur Tetrafluoride[1]

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No general method is available for the synthesis of β-halo derivatives of polynitroalkanes. The preparation of 2,2,2-trinitrochloroethane and 2,2-dinitrochloropropane from mixed acetals of the corresponding alcohols and phosphorous pentachloride has been reported.[2] Sulfuryl chloride[3] has been used to convert 2,2-dinitropropanol and 2,2-dinitropropanediol into the chloro derivatives and thionyl chloride[4] was used similarly with these alcohols and with 2,2,2-trinitroethanol. Attempts to prepare 2,2,2-trinitrobromoethane from the alcohol were unsuccessful using a variety of brominating agents.[4] The nitration of 2,3-dibromopropene has been reported to give 1,2-dibromo-1,1-dinitroethane, 1,1-dinitro-2-bromoethane, and 2-nitro-2,3-dibromopropanoic acid.[5] The β-iodo and -fluoro derivatives of polynitro compounds have not been reported.

Hydroxy groups have been replaced with fluorine by the reagent, sulfur tetrafluoride, but the reaction was not used as a preparative method for simple fluoroalkanes.[6] The reactivity of hydroxylic compounds with sulfur tetrafluoride was reported to be a function of the acidity of the hydroxyl groups. Moderate yields of fluorinated products were obtained with acidic hydroxy groups such as in tropolones, but with aliphatic alcohols ethers were major by-products. Nitro groups would, therefore, be expected to enhance the reactivity of alcohols toward sulfur tetrafluoride.

It was found that 2,2,2-trinitroethanol could be converted into 2,2,2-trinitrofluoroethane at ambient temperature in 63% yield in 4 days. 2,2-Dinitropropanol and 2,2-dinitro-1,3-propanediol were less reactive, and were converted into 2,2-dinitrofluoropropane and 2,2-dinitro-1,3-difluoropropane at 85–90°, with a 46% yield after 20 hr of reaction time for the former and a 62% yield after 8 hr for the latter. Attempts to prepare 2-methyl-2-nitrofluoropropane from 2-methyl-2-nitropropanol were unsuccessful. After a reaction period of 8 hr at 110°, only starting material and a trace of material with carbonyl absorption in its infrared spectrum were found.

$$(NO_2)_3CCH_2OH \xrightarrow{SF_4} (NO_2)_3CCH_2F$$

$$CH_3C(NO_2)_2CH_2OH \xrightarrow{SF_4} CH_3C(NO_2)_2CH_2F$$

$$HOCH_2C(NO_2)_2CH_2OH \xrightarrow{SF_4} FCH_2C(NO_2)_2CH_2F$$

The nmr spectra of the latter two products showed long-range H–F coupling of 2–2.5 cps through four bonds. The nmr and ir spectra are described in the Experimental Section.

Experimental Section

2,2,2-Trinitrofluoroethane.—Sulfur tetrafluoride (103 ml at −78°) was condensed into an evacuated 300-ml stainless steel bomb containing 100 g (0.55 mol) of trinitroethanol, and the mixture was allowed to stand at ambient temperature for 4 days. The bomb was then vented through an aqueous alkali trap. The residue was dissolved in 300 ml of methylene chloride, and the solution was washed six times with 50-ml portions of water.

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[1] Supported by the Office of Naval Research.

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