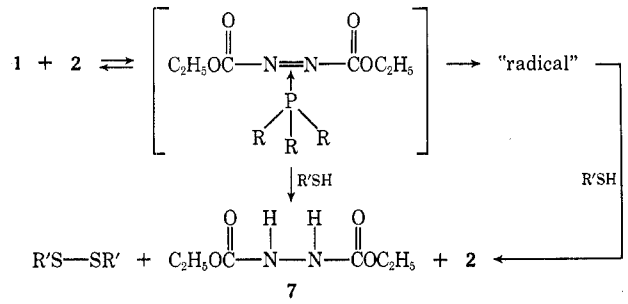
Although the mechanism of the oxidation reaction is still not completely elucidated, the reaction can be represented by he following scheme.



In order to extend the reaction, amines, which might become electron donors, were used in the place of trivalent phosphorus compounds in the above reactions. This investigation will be reported in a next paper.

Experimental Section

Reagents.—Diethyl azodicarboxylate was prepared by the procedure of Rabjohn.[12] The other reagents were purchased from Wako Pure Chemical Industries, Ltd., and purified in general methods. Thin layer chromatography was carried out on Wakogel B-O and was developed with *n*-hexane. For column chromatography Wakogel C-300 (silica gel) or alumina (300 mesh) was used. The silica gel and the alumina were activated by heating at 120° for 2 hr. Sulfur-containing compounds were detected by a spray of *ca.* 0.5% w/v 2,6-dibromo-*p*-benzoquinone-4-chloroimine in cyclohexane[13] or with iodine vapor.

General Procedure of the Oxidation of Mercaptans with Diethyl Azodicarboxylate and Triphenylphosphine.—A solution of diethyl azodicarboxylate (5×10^{-3} mol) in 5 ml of THF was added dropwise to a solution of triphenylphosphine (5×10^{-3} mol) and a mercaptan (1×10^{-2} mol) in 5 ml of THF with vigorous stirring. After 2 hr at 25°, the THF was removed. The residue was washed with 10 ml of dry ether to give diethyl hydrazodicarboxylate as white needles: 0.83–0.78 g; mp 129–131°, undepressed on admixture with an authentic sample.[12] Each disulfide was isolated from the filtrate and purified by the following procedures.

A. Di-*n*-propyl Disulfide.—After removal of the ether, di-*n*-propyl disulfide was obtained by distillation at reduced pressure, bp 72° (14 mm) (75%). Redistillation gave an analytical sample, bp 192–194°, n^{20}D 1.4977. (lit.[14] bp 194°, n^{20}D 1.4980).

Anal. Calcd for $C_6H_{14}S_2$: C, 47.94; H, 9.34. Found: C, 48.23; H, 9.20.

From the residue of the distillation, triphenylphosphine was isolated and was recrystallized from ethanol, 1.16 g (88.5%), mp 79°.

B. Di-*n*-dodecyl Disulfide.—The mother liquid was completely evaporated under reduced pressure and the residue was separated into di-*n*-dodecyl disulfide (1.90 g, 95%, mp 34°), the recovered mercaptan (trace), and triphenylphosphine (1.22 g, 93.2%, mp 76–77.5°) by silica gel column chromatography (3.0 × 40 cm; eluate, *n*-hexane).

When the mole ratio of the mercaptan–triphenylphosphine was changed, the products were also purified by the same procedure. The yields of the disulfide are summarized in Table I.

When *n*-dodecyl mercaptan was allowed to react with 1 in the presence of triethyl phosphite for 2 hr at room temperature in the dark, nearly quantitative yields of di-*n*-dodecyl disulfide and **3** were obtained by the same procedure described above (Table I).

C. Dibenzyl Disulfide.—Ethanol–ether (1:1) was added to the residue resulting from removal of ether. Dibenzyl disulfide was obtained by filtration and purified by recrystallization from ethanol, 1.19 g (97%), mp 68–69°. The filtrate was evaporated to give triphenylphosphine which was recrystallized from ethanol, 1.19 g (91%), mp 72–74°.

D. Diphenyl Disulfide.—Diphenyl disulfide (1.08 g, 96%, mp 60°) and triphenylphosphine (0.13 g, 99.5%, mp 70–74°) were separated by alumina column chromatography (3.0 × 40 cm; eluate, benzene) and purified by recrystallization from ethanol.

Spectra.—Absorption spectra were recorded on Hitachi recording spectrometer EPS-3T type with quartz cell of optical path 1.0 cm. A solution of diethyl azodicarboxylate was mixed with a solution of triphenylphosphine at 0°, and then the mixed solution was allowed to warm to room temperature. All measurements were performed at room temperature.

Registry No.—**1**, 1972-28-7; **2a**, 603-35-0; **2b**, 122-52-1; *n*-propyl mercaptan, 107-03-9; *n*-dodecyl mercaptan, 112-55-0; benzyl mercaptan, 100-53-8; phenyl mercaptan, 108-98-5.

Acknowledgment.—We are pleased to acknowledge helpful discussions wirh Drs. I. Ichikizaki and T. Hoshi.

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Nitration Studies. XVII. Conversion of Carboxylic Acid Derivatives to Nitroalkanes

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Acetyl nitrate has been known for some time as a dangerously explosive compound.[3] Its decomposition under controlled conditions seems not to have been studied previously. We have found that when diluted it undergoes smooth thermolysis to give carbon dioxide and nitromethane (eq 1). In the same way higher acyl

$$CH_3CO_2NO_2 \xrightarrow[\text{solvent}]{290^\circ} CH_3NO_2 + CO_2 \quad (1)$$

nitrates give the corresponding nitro alkanes containing one less carbon atom. This new synthesis provides a ready preparation for nitroalkanes of various types in yields which compare favorably with or exceed those of other methods (see Table I).

Acyl nitrates may be prepared by a number of different methods. Fortunately they need not be isolated for purposes of this synthesis, but may be used in the presence of an excess of one reactant or an added solvent. We have employed the following methods of preparation (eq 2–6). Each method offers certain

$$\text{A.}\quad (RCO)_2O + N_2O_4 \longrightarrow RCO_2NO_2 + RCO_2NO \quad (2)$$

$$\text{B.}\quad (RCO)_2O + HNO_3 \longrightarrow RCO_2NO_2 + RCO_2H \quad (3)$$

$$\text{C.}\quad (RCO)_2O + N_2O_5 \longrightarrow 2RCO_2NO_2 \quad (4)$$

$$\text{D.}\quad (RCO)_2O_2 + N_2O_4 \longrightarrow 2RCO_2NO_2 \quad (5)$$

$$\text{E.}\quad RCOCl + AgNO_3 \longrightarrow RCO_2NO_2 + AgCl\downarrow \quad (6)$$

advantages and disadvantages relative to the others. Thus, for example, method E can be used when the corresponding acid anhydride is not readily available

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TABLE I

NITROALKANES FROM CARBOXYLIC ACID DERIVATIVES

Carboxylic acid	Method	Acid derivative/nitrating agent, mol ratio	Temp, °C	Nitroalkane	Conversion, %[a]
Acetic	A[b]	0.133	105	Nitromethane	26
	B	8	280		54
	C	4	280		50
	D[b]	5	240		24
	E[d]	1	235		45
Propionic	A[b]	0.133	105	Nitroethane	50
	B	8	280		62
Valeric	B	8	280	1-Nitrobutane	56
Octanoic	B	2.5	280	1-Nitroheptane	60
Cyclohexane	B	3	290	Nitrocyclohexane	48
	C[c]	2	280		39
	F	...[f]	290		20
2-Methylbutyric	C	3	290	2-Nitrobutane	50
Pivalic	B	8	290	*tert*-Nitrobutane	30
	C	2	240		23
2,2-Dimethylbutyric	E[d]	1	240	*tert*-Nitropentane	18
Dimethylmalonic	E[d]	1	240	2,2-Dinitropropane	24
4-Chlorobutyric	B	2	230[e]	3-Chloro-1-nitropropane	15
Benzoic	C	8	270	Nitrobenzene	Trace
	E[d]	1	240		11.3
p-Toluic	E[d]	1	270	*p*-Nitrotoluene	23.4

[a] Conversions are based on nitrating agent, except for method A where conversions are based on acid anhydride. [b] Excess N_2O_4 used as solvent. [c] Nitromethane was used as solvent. [d] Acetonitrile was used as solvent. [e] 4-Chlorobutyric anhydride carbonized at 280–290°. [f] Mole ratios: cyclohexanecarboxylic acid–acetic anhydride–HNO_3 were 1:1:2.5. Product contained a 25% yield of nitromethane also.

(*e.g.*, in preparing *gem*-dinitroalkanes), but it is considerably more costly than the other syntheses. Method C provides high conversions of acyl radicals to nitroalkanes (since 2 mol of nitroalkane are expected per mol of reacted anhydride) but necessitates the prior preparation of dinitrogen pentoxide. Method B is probably the simplest to employ on a laboratory scale, since the reactants are readily available and the by-product acid can easily be reconverted to its anhydride. Actually method B may be extended and made even more convenient (method F) by using mixtures of carboxylic acids and acetic anhydride with nitric acid[4] to obtain mixtures of nitromethane with higher nitroalkanes. In this case equilibrium is apparently rapidly established between the two carboxylic acids, their anhydrides, and acyl nitrates, as, for example in eq 7.

$$\text{F.}\quad RCO_2H + 2(CH_3CO)_2O + HNO_3 \rightleftharpoons RCO_2NO_2 + CH_3CO_2NO_2 + 3CH_3CO_2H \quad (7)$$

Yields of RNO_2 depend in part on the relative amount of acetic anhydride employed. An excess is usually desirable.

Decarboxylative nitration may be accomplished satisfactorily and with little or no danger of explosion in the presence of an excess of nitrating agent, an excess of carboxylic acid derivative, or an inert solvent (*e.g.*, a nitroalkane, acetonitrile, or a perchloroalkane). Optimum temperatures lie in the 270–300° range. At lower temperatures, *e.g.*, 100°, acyl nitrates decompose in part to oxides of nitrogen and the corresponding carboxylic acid anhydride[3] (eq 8 and 9). To avoid losses due to these reactions, the acyl nitrates should be heated rapidly to the higher range of temperatures. Thus, although an autoclave and slow heating may be used, better yields of nitroalkanes are obtained with a heated, packed column and a controlled flow of reactants.

$$2RCO_2NO_2 \xrightarrow{100^\circ} (RCO)_2O + N_2O_5 \quad (8)$$

$$N_2O_5 \xrightarrow{100^\circ} N_2O_4 + {}^1/_2O_2 \quad (9)$$

Mechanism of Reaction.—The facts of decarboxylative nitration are in accord with a free-radical process initiated by a thermolytic cleavage of a nitrogen–oxygen bond in the acyl nitrate followed by a series of reaction leading to nitroalkanes and other products (eq 10–17).

$$RCO_2NO_2 \longrightarrow RCO_2\cdot + NO_2\cdot \quad (10)$$

$$RCO_2\cdot \longrightarrow R\cdot + CO_2 \quad (11)$$

$$R\cdot + RCO_2NO_2 \longrightarrow RNO_2 \text{ and } RONO + RCO_2\cdot \quad (12)$$

$$R\cdot + RCO_2NO_2 \longrightarrow RCO_2R + NO_2\cdot \quad (13)$$

$$R\cdot + NO_2\cdot \longrightarrow RNO_2 \text{ and } RONO \quad (14)$$

$$R\cdot + RCO_2\cdot \longrightarrow RCO_2R \quad (15)$$

$$RONO \longrightarrow RO\cdot + NO\cdot \quad (16)$$

$$RO\cdot \xrightarrow{NO_2} \text{alcohol, aldehyde, acid, etc.} \quad (17)$$

As the weakest bond present, the N–O bond (36–40 kcal) in the acyl nitrate would be expected to break first on heating to generate an acyloxy radical[5] (eq 10). These are known to decompose rapidly to alkyl radicals[6] (eq 11). An alkyl radical may attack an acyl nitrate in at least three different ways (eq 12, 13) leading to the corresponding nitroalkane, alkyl nitrite, or symmetrical ester. Symmetrical esters were found in all cases of decarboxylative nitration studied. Other mechanisms, *e.g.*, eq 15 may obviously be proposed for their formation, but no other mechanism seems to us to be any more likely under the circumstances than the mechanism of eq 13. Alkyl nitrites are very unstable at temperatures of 100° or higher and decompose to nitric oxide and other products[7] whose variety is increased by the oxidizing agents present, such as nitrogen dioxide. Nitric oxide was also formed in all cases studied.

In order to test our hypothesis that the reaction involves radicals free enough to racemize during the course of the reaction, the decarboxylative nitration of 2-methylbutanoyl nitrate prepared from (+)-2-methylbutanoyl chloride by reaction with silver nitrate was studied. The product, 2-nitrobutane, was optically inactive. Decarboxylative halogenation as exemplified by the Hunsdiecker reaction, which probably proceeds *via* an acyl hypohalite, also occurs with racemization of the postulated alkyl radical.[8]

$$(+)\text{-}RCO_2Ag + Br_2 \longrightarrow (\pm)\text{-}RBr + CO_2$$

Comparison with Other Nitroalkane Syntheses.—The relatively high yields of primary, secondary, and tertiary nitroalkanes, the absence of isomeric nitroalkanes in the products, the ability to introduce more than one nitro group simultaneously, and the speed and ease of operation make decarboxylative nitration the most broadly applicable and for many nitroalkanes the

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best of the known syntheses. Direct nitration of alkanes loses its cost advantage as a preparative method for higher nitroalkanes because of problems in separating the many isomers and by-products formed. Replacement reactions, such as the replacement of halogen[9] or nitrate[10] groups by nitro groups, while providing good yields with primary groups, fail with tertiary alkyl groups, are irregular with secondary alkyl groups (especially cyclohexyl groups), and require special solvents and reagents to inhibit side reactions as well as starting materials which are often less readily available in pure form than the corresponding carboxylic acids. In the aromatic series decarboxylative nitration is scarcely competitive in yields with other known methods, but it does offer for the first time a process for the direct replacement of carboxyl groups by nitro groups.

Experimental Section

Apparatus.—A 21 × 2 cm glass tube packed with glass helices and wrapped with nichrome heating ribbon was employed as the pyrolysis apparatus. The temperature was controlled with the aid of a thermocouple inserted in a smaller glass tube in the reactor.

A Welsbach Style T-23 ozonator was used as the source of ozonized oxygen (110 V, 5.6 psi O_2, 0.015 ft^3/min). A 150-ml 316 stainless steel autoclave with a magnadrive stirrer was used in the experiments with N_2O_4.

Analysis by Vpc.—Throughout this work most of the conversions and yields reported were calculated from vpc analyses using the common thermal conductivity correction factor method. An F & M Model 720 dual column temperature programmed gas chromatograph was employed. Most nitroalkanes and by-products were analyzed on either a 6.0 ft, 0.25 in., 5% FFAP liquid phase on Chromosorb W, acid washed, DMCS treated column or a 16.0 ft, 0.25 in., 15% FFAP liquid phase on Chromosorb W, acid washed, DMCS treated column at a flow rate of 10 ml/16 sec. Products were identified principally by comparing their gas chromatographic retention times and infrared spectra with those of authentic samples. Mass spectral analyses were obtained when necessary.

Materials.—All anhydrides and acid chlorides were carefully distilled. Anhydrides and acid chlorides which were unavailable were prepared by techniques described in Vogel.[11] (−)-2-Methyl-1-butanol, 99% optically pure, was obtained from the Aldrich Chemical Co.

Synthesis of Acyl Nitrates. Method A.—The acid anhydride was mixed with a sevenfold excess of liquid dinitrogen tetroxide in a stainless steel autoclave cooled in an ice bath. The resulting mixture was sealed and heated to about 100° for about 1 hr.

Method B.—A tenfold excess of the acid anhydride at room temperature was treated with 90% nitric acid at such a rate as to maintain the temperature at about 20°. The resulting mixture was dripped through the vapor phase nitrator.

Method C.—Dinitrogen pentoxide was generated by confluent mixing of streams of ozone and dinitrogen tetroxide and passed into a tenfold excess of the acid anhydride at 0° until the desired increase in weight was observed.

Method D.—Dinitrogen tetroxide was bubbled through a fivefold excess of cold acetyl peroxide prepared by Price's method.[12] When this mixture was introduced into the vapor phase nitrator, decomposition was not as smooth as in other nitrations because of the rapid decomposition of the excess acetyl peroxide.

Model E.—Equimolar amounts of silver nitrate and acyl halide were slowly mixed in acetonitrile solvent at 0° with stirring. The precipitate or silver halide was filtered off after 2 hr and before introducing the acyl nitrate solution into the nitrator.

Method F.—The carboxylic acid was dissolved in at least a twofold excess of acetic anhydride, cooled to 0°, and treated with nitric acid dropwise. With no further treatment the mixture was introduced into the nitrator.

Decarboxylative Nitration.—The liquid mixture, prepared as indicated above in methods B–F, was placed in a dropping funnel and dropped at a constant rate, approximately 3×10^{-4} mol of acyl nitrate/min, through a 2 × 20 cm glass tube packed with glass helices and heated to about 290°. The effluent vapors were condensed and analyzed by vpc or fractionally distilled (under vacuum if necessary).

In a typical experiment (method B) 0.008 mol of valeroyl nitrate was found to afford 0.0045 mol (56.5%) of 1-nitrobutane. In addition, 0.0016 mol (20.0%) of 1-butanol and 0.0008 mol (20.0%) of *n*-butyl valerate were obtained.

A temperature dependence study revealed that 135° was the lowest temperature to obtain nitromethane at a reasonable rate. An optimum temperature of 290° produced nitromethane in 54% conversion based on eq 1. Higher temperatures resulted in lower conversions to nitromethane, and at 350° considerable carbonization occurred in the pyrolysis tube.

Preparation of 2-Nitrobutane from Optically Active 2-Methylbutyric Acid.—2-Methyl-1-butanol ($[\alpha]^{26.5}D$ −8.1°) was oxidized to 2-methylbutyric acid ($[\alpha]^{26.5}D$ +19.7°) in 66% yield by the method of Marckwald[13] and converted to 2-methylbutanoyl chloride ($[\alpha]^{26.5}D$ +14.7°) in 81% yield with thionyl chloride by the method of Bartlett and Stauffer.[14] The chloride (5 ml, 0.041 mol) was added slowly to 7.65 g (0.045 mol) of silver nitrate dissolved in 17.5 ml of acetonitrile at 0°. The mixture was stirred 0.5 hr, filtered, and pyrolyzed at 260°. The condensate was fractionally distilled to obtain optically inactive 2-nitrobutane, bp 139–141°, yield 1.8 g (42.6%).

Registry No.—Nitromethane, 75-52-5; nitroethane, 79-24-3; 1-nitrobutane, 627-05-4; 1-nitroheptane, 693-39-0; nitrocyclohexane, 1122-60-7; 2-nitrobutane, 600-24-8; *tert*-nitrobutane, 594-70-7; *tert*-nitropentane, 595-42-6; 2,2-dinitropropane, 595-49-3; 3-chloro-1-nitropropane, 16694-52-3; nitrobenzene, 98-95-3; *p*-nitrotoluene, 99-99-0.

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Derivatives of Fluorene. XXXIII. Synthesis and Reactions of Hydrazofluorenes and Related Compounds[1a–c]

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In a preliminary study of the synthesis of 2,2′-hydrazofluorene (**1a**) and 2,2′-azofluorene (**3a**), possible metabolites of the carcinogen *N*-(2-fluorenyl)acetamide, we reported[1c] that quantitative disproportionation occurs when **1a** is heated in alcoholic hydrochloric acid. Aware that "clean" (or 100%) disproportionation has been found with relatively few hydrazo compounds, we thought it of interest to prepare a few 7,7′-symmetrically substituted hydrazo- and azofluorenes and related compounds for comparison.[1d]

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