Experimental Section

Compounds **3** and **4** were purchased from Matheson Coleman and Bell. Compounds **1**,[14] **2**,[15] **5**,[16] **6**,[17] **7**,[6] and **8**[17] were prepared by known procedures. All starting materials were purified by distillation or recrystallization prior to use. Melting points were taken on a Fisher-Johns melting point apparatus and all melting and boiling points are uncorrected. Pmr spectra were taken on a Varian T-60 spectrometer using TMS as an internal standard. Ir spectra were determined in a Perkin-Elmer Model 21 spectrophotometer; mass spectra in a Finnegan 1015 mass spectrometer. In most cases, product verification and quantitation was accomplished by gas–liquid chromatography using an F & M Model 402 gas chromatograph equipped with columns made from 5% Carbowax 20 n on Gas-Chrom Q, 1800 mesh (system A), and 1.5% OV-3 on Gas-Chrom Q, 80/100 mesh (system B), at a flow rate of 60 ml of carrier gas (nitrogen) per minute. Retention times of the products from the reaction between the various *N*-haloamides and phosphates are given in Table IV.

TABLE IV
RETENTION TIMES (MIN) AT FLOW RATE OF 60 ML/MIN

Compd	Column	Temp, °C	Retention time
$(EtO)_2P(O)Cl$	A[a]	108	2.20
	A	116	1.62
	B[b]	115	0.50
$(EtO)_2P(O)H$	A	108	2.75
	A	116	1.75
	B	115	0.68
$(EtO)_2P(O)Br$	A	108	2.45
	B	116	0.60
C_6H_5CN	A	116	2.40
$(EtO)_3PO$	A	116	2.88
	B	115	1.12
$(EtO)_2P(O)NHPr$	B	115	5.49
	B	171	0.51

[a] Column A, 5% Carbowax 20 n on Gas-Chrom Q, 1800 mesh. [b] Column B, 1.5% OV-3, on Gas-Chrom Q, 80/100 mesh.

All organophosphorus compounds were detectable at the nanogram level. Diethyl halophosphates also were identified and quantitated by converting them to *O,O*-diethyl *N*-propylphosphoramidates by reaction with excess propylamine and subsequent analysis by glc. This reaction was shown to be quantitative in control experiments. Benzonitrile also was quantitated from the nitrile absorption peak at 2250 cm^{-1}. Tlc systems used were silica/ether–petroleum ether (bp 30–60°) (1:1), silica/chloroform, alumina/chloroform, alumina/ether, and cellulose/benzene.

Reaction of Triethyl Phosphite and *N*-Bromoacetamide.—To a vigorously stirred suspension of 6.9 g (0.05 mol) of *N*-bromoacetamide in 30 ml of toluene at room temperature was added rapidly 16.6 g (0.1 mol) of triethyl phosphite. The reaction was exothermic and, after cooling, the mixture was distilled through a Vigreux column at atmospheric pressure to give 4.88 g (90%) of ethyl bromide, bp 40–41°, and 1.90 g (93%) of acetonitrile, bp 82–84°. Toluene was removed under reduced pressure and distillation of the residue gave 5.05 g (73%) of diethyl hydrogen phosphite, bp 66–74° (8.0–8.5 mm), $n^{25}D$ 1.4068 [lit.[18] bp 75° (15 mm), $n^{26}D$ 1.4080], and 7.6 g (83%) of triethyl phosphate, bp 94–96° (8.0 mm), $n^{25}D$ 1.4040 [lit.[19] bp 90° (10 mm), $n^{25}D$ 1.4039]. Products also were verified by tlc and ir.

Reaction of Triethyl Phosphite and *N*-Chlorobenzamide.—*N*-Chlorobenzamide (1.55 g, 0.01 mol) was added in small portions over 15 min to a stirred suspension of 3.32 g (0.02 mol) of triethyl phosphite in 10 ml of carbon tetrachloride under a nitrogen atmosphere. Ethyl chloride was removed under reduced pressure and identified by pmr. The reaction mixture was cooled and benzamide, mp 128–130°, was collected. Diethyl phosphorochloridate, diethyl hydrogen phosphite, benzonitrile, and triethyl phosphate were identified and quantitated by glc.

***N*-(Diethylphosphinyl)-2-pyrrolidinone.**—To a stirred suspension of *N*-bromo-2-pyrrolidinone (6.6 g) in 10 ml of benzene was added over 30 min triethyl phosphite (6.65 g) in 6 ml of benzene. The ratio of ethyl bromide to total ethoxy protons was shown to be 1:2 by pmr spectroscopy. Rapid chromatography (alumina/$CHCl_3$) gave 8.4 g (94%) of *N*-(diethylphosphinyl)-2-pyrrolidinone, *m/e* 221, unstable to distillation: pmr (CCl_4) τ 8.87–8.49 (m, 6), 8.24–7.55 (m, 4), 7.14–6.52 (m, 2), 6.31–5.47 (m, 4).

Reaction of Triethyl Phosphite with *N*-Chlorosuccinimide in the Presence of Water.—To a stirred suspension of 6.65 g of *N*-chlorosuccinimide in a mixture of 10 ml of ether, 2 ml of acetone, and 2 ml of water was added 8.4 g of triethyl phosphite over 20 min at room temperature. The solvent was removed under reduced pressure and the residue was washed with cold ether and filtered to give 4.75 g (96%) of succinimide, mp 118.5–119.5°. The etheral filtrate was distilled to yield 4.33 g (57%) of diethylphosphoric acid, bp 130–135° (0.025 mm), $n^{25}D$ 1.4143 (lit.[20] $n^{25}D$ 1.4148).

Reaction of Trimethyl Phosphite with *N*-Bromobenzamide in the Presence of Methanol.—To a stirred suspension of 10 g of *N*-bromobenzamide in 10 ml of benzene and 5 ml of methanol was added 6.2 g of trimethyl phosphite over 30 min. The resulting solution was concentrated under reduced pressure and diluted with petroleum ether. Benzamide (4.95 g, 82%), mp 127–129°, was removed by filtration and the filtrate was distilled to give 5.9 g (84%) of trimethyl phosphate, bp 73–75° (10 mm), $n^{25}D$ 1.3954 [lit.[19] bp 73° (10 mm), $n^{25}D$ 1.3950].

Reaction of *N*-Chlorobenzamide and Trimethyl Phosphorothioite.—To a stirred suspension of *N*-chlorobenzamide (0.77 g) in benzene (10 ml) was added at room temperature trimethyl phosphorothioite (0.70 g) in benzene (5 ml). Methyl chloride (1.5×10^{-3} mol) was removed in a stream of nitrogen and identified by pmr. The reaction mixture was concentrated and filtered to give benzamide (0.21 g, 1.7×10^{-3} mol). Benzonitrile (1.6×10^{-3} mol) was identified by ir.

Registry No.—**1**, 79-15-2; **2**, 1821-34-7; **3**, 128-09-6; **4**, 128-08-5; **5**, 2401-40-3; **6**, 598-49-2; **7**, 5014-39-1; **8**, 19964-97-7; triethyl phosphite, 122-52-1; ethyl bromide, 74-96-4; acetonitrile, 75-05-8; *N*-(diethylphosphinyl)-2-pyrrolidinone, 36614-67-2; diethyl phosphoric acid, 598-02-7; trimethyl phosphite, 121-45-9; trimethyl phosphorothioite, 36614-68-3.

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Reaction of *N*-Iodosuccinimide with Tertiary Alcohols

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The reaction of secondary alcohols with *N*-iodosuccinimide (NIS) has been shown to produce ketones or cyclic ethers. Secondary alcohols in steroid systems with the hydroxy group in the axial position on carbon 6 produce the cyclic ethers,[1] while oxidation of 1-phenylethanol with NIS gives the ketone.[2] The formation of a cyclic ether from an alcohol and NIS indicates that

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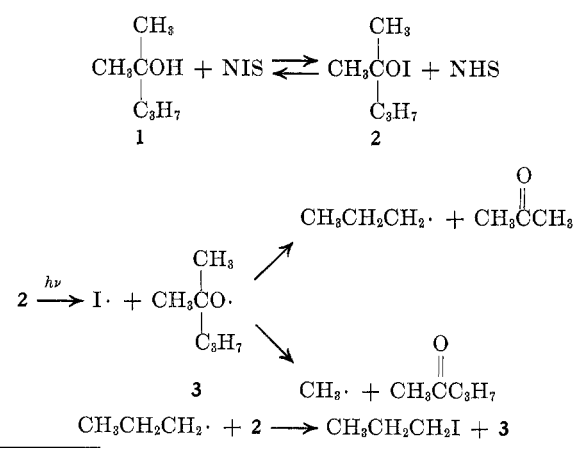
an intermediate hypoiodite is probably formed, while the production of a ketone allows for either hypohalite formation or for succinimidyl radical oxidation of the alcohol. To study the possibility that alkyl hypoiodites might be a general product when NIS and alcohols are heated together, we decided to investigate the reaction of *tert*-alkyl alcohols with *N*-iodosuccinimide.

This paper describes the successful conversion of several tertiary alcohols by NIS to alkyl iodides and ketones. Reported here are the reactions of four tertiary alcohols with NIS: *tert*-butyl alcohol, 3-ethyl-3-pentanol, 3-methyl-3-pentanol, and 2-methyl-2-pentanol (**1**). Two of the alcohols, *tert*-butyl alcohol and 3-ethyl-3-pentanol, are symmetrical alcohols and the proposed hypoiodite intermediates that are formed can give only one ketone and one alkyl iodide product. *tert*-Butyl alcohol in benzene with NIS gave 54–57% yields of acetone and 47–60% yields of methyl iodide when the mixtures were irradiated. The irradiation of a mixture of NIS and 3-ethyl-3-pentanol in benzene gave yields of 95–99% of 3-pentanone and 91–100% of ethyl iodide. Succinimide was recovered in 73–80% yields.

The products formed from the reaction of *N*-iodosuccinimide with 3-methyl-3-pentanol and 2-methyl-2-pentanol give more evidence that an alkyl hypoiodite is an intermediate when tertiary alcohols react with NIS. The alkyl iodides and ketones formed follow the β-scission order found by Walling and Padwa[3] in the decomposition of *tert*-alkyl hypochlorites. 3-Methyl-3-pentanol with NIS produced 85–91% yields of ethyl iodide. (The 2-butanone peak could not be separated from the benzene solvent peak on the glc and was not determined.) The reaction of 2-methyl-2-pentanol in benzene with NIS gave 40–52% of acetone and 52–58% of *n*-propyl iodide. The formation of acetone and *n*- propyl iodide is believed to occur by the following pathway. The formation of the intermediate *tert*-hypoiodite **2** is very likely an equilibrium step, as Barton and coworkers[4] have prepared *N*-iodoamides with *tert*-butyl hypoiodite. The decomposition of the *tert*-hypoiodite **2** follows the expected light-induced cleavage of the O–I bond producing an iodine atom and *tert*-alkoxy radical **3**, which decomposes to produce the *n*-propyl radical and acetone. The *n*-propyl radical then forms *n*-propyl iodide by abstracting an iodine atom from **2**. We had expected that the major product of the decomposition of the hypoiodite **2** might be 2,2-dimethyltetrahydrofuran, which would require an intramolecular hydrogen-abstracting step[3] by the *tert*-alkoxy radical **3**. The gas chromatographic analysis of the products showed only one small unidentified peak which could not account for more than 10–20% of the starting NIS. The major products formed under our reaction conditions came from C–C bond cleavage of the intermediate alkoxy radical **3** and not from intramolecular hydrogen abstraction.



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Experimental Section

Analyses were carried out using a Perkin-Elmer 810 glc and a Varian Aerograph Model 700 glc. Infrared analyses were done using a Perkin-Elmer 337 grating infrared spectrophotometer. Circulation of ice water through the condensers was accomplished by means of a Cole-Parmer water pump, Model 7020-C with Masterflex SCR controller. Irradiation of the reaction mixtures was effected with a G. E. Projector Spot 150-W, 130-V tungsten lamp. The NIS was purchased from K & K Laboratories and was not recrystallized. The alcohols, ketones, and internal standards were purchased from Matheson Scientific and were fractionally distilled. Analyses of the *tert*-butyl alcohol and 2-methyl-2-pentanol reactions were performed using a 6-ft column of 15% SE-30–5% Carbowax 20M adsorbed on 60–80 mesh base-washed Chromosorb P, while the 3-ethyl-3-pentanol and 3-methyl-3-pentanol reactions were analyzed using a 6-ft column of 20% Carbowax 20M adsorbed on 60–80 mesh base-washed Chromosorb P. All reactions were run at reflux. A description of the oxidation of 3-ethyl-3-pentanol with NIS (Table I) is given in detail. The oxidations of *tert*-butyl alcohol, 3-methyl-3-pentanol, and 2-methyl-2-pentanol with NIS were run under identical conditions and the results of these oxidations are given in Tables II, III, and IV.

TABLE I

OXIDATION OF 3-ETHYL-3-PENTANOL WITH NIS

Conditions (Solvent, irradiation, time)	Yield of products, % 3-Pentanone	Ethyl iodide
Benzene, $h\nu$, 1 hr	99	100
Benzene, $h\nu$, 0.5 hr	95	91
Benzene, dark, 2.5 hr	31	26
p-Dioxane, $h\nu$, 0.5 hr	95	86
Pentane, $h\nu$, 10 hr	64	70
Diethyl ether, $h\nu$, 3 hr	70	80

TABLE II

OXIDATION OF *tert*-BUTYL ALCOHOL WITH NIS

Conditions (Solvent, irradiation, time)	Yield of products, % Acetone	Methyl iodide
Benzene, $h\nu$, 5 hr	54	60
Benzene, $h\nu$, 6 hr	57	50
Benzene, $h\nu$, 5 hr	54	60
Benzene, $h\nu$, 5 hr	54	47
tert-Butyl alcohol, $h\nu$, 25 min	54	47
tert-Butyl alcohol, $h\nu$, 2 hr	61	73
Benzene, dark, 9 hr	Trace	Trace

TABLE III

OXIDATION OF 3-METHYL-3-PENTANOL WITH NIS[a]

Conditions (Solvent, irradiation, time)	Yield of product, % Ethyl iodide
Benzene, $h\nu$, 20 min	85
Benzene, $h\nu$, 30 min	91
Benzene, dark, 3 hr	20
Benzene, dark, 20 hr	44

[a] The 2-butanone peak was not separated on the glc from the benzene peak and its per cent yield was not determined. Only trace amounts of methyl iodide and 3-pentanone were found.

TABLE IV

OXIDATION OF 2-METHYL-2-PENTANOL WITH NIS[a]

Conditions (Solvent, irradiation, time)	Yield of products, % Acetone	n-Propyl iodide
Benzene, *hν*, 2 hr	40	52
Benzene, *hν*, 1.5 hr	52	58

[a] Only trace amounts of methyl iodide and 2-pentanone could be found. An unknown glc peak, 10–20% of the starting NIS, appeared between the benzene and *n*-propyl iodide peaks and was believed to be 2,2-dimethyltetrahydrofuran. No identification of the peak was attempted.

Oxidation of 3-Ethyl-3-pentanol with NIS.—Five milliliters of a solution of 0.516 *M* 3-ethyl-3-pentanol (2.58 mmol) and 0.596 *M* chlorobenzene (2.88 mmol) in dry benzene were added to 302 mg (1.34 mmol) of NIS. The mixtue was irradiated and heated to reflux for 1 hr. Glc analysis indicated yields of 101% ethyl iodide and 99% 3-pentanone. Water extractions of the reaction mixture produced 97 mg (0.98 mmol) of succinimide. Identification was made by mixture melting point and ir comparison with known succinimide. The results of all reactions of NIS with 3-ethyl-3-pentanol are given in Table I.

Registry No.—NIS, 516-12-1; *tert*-butyl alcohol, 75-65-0; 3-ethyl-3-pentanol, 597-49-9; 3-methyl-3-pentanol, 77-74-7; 2-methyl-2-pentanol, 590-36-3.

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The Solvolysis and Rearrangement of 2-Phenylethyl Tosylate in Trifluoroethanol[1]

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2,2,2-Trifluoroethanol (TFE) was first introduced as a solvent for the study of solvolytic reactions by Scott.[3] Subsequently, Trahanovsky and Doyle[4] pointed out that the low nucleophilicity of TFE promotes the formation of cyclized products from 5-hexenyl arenesulfonates. In a comprehensive study, Shiner, *et al.*,[5] have evaluated many of the desirable properties and characteristics of TFE for solvolysis studies. Bentley and Lacadie[6] have shown that TFE accentuates differences in reactivity of diverse benzyl chlorides more than does ethanol, aqueous dioxane, or acetic acid.

We have investigated the utility of TFE for the study of the solvolytic rearrangement of β-arylethyl tosylates. Our results indicate that TFE has considerable potential in this regard.

Solvolysis of 2-phenylethyl tosylate (**1**) in TFE is substantially *more rapid* than that for a model compound, ethyl tosylate (**2**). Electron-donating substituents in the aromatic moiety cause a marked further increase in the observed rates (Table I). From 2-(*p*-methylphenyl)ethyl tosylate (**3**) and 2-(*p*-methoxyphenyl)ethyl tosylate (**4**) a ρ of -2.5 (using σ^+) is obtained. This value is comparable to that observed for similar solvolytic rearrangements in acetic acid.[7]

TABLE I

RATE CONSTANTS FOR THE SOLVOLYSIS OF ARYLETHYL TOSYLATES IN TRIFLUOROETHANOL

Compound solvolyzed[a]	T, °C	$k_t \times 10^6$, sec^{-1}	Added salt
1	75.0	4.83 ± 0.05	
	100.0	37.5 ± 0.6	
	75.0	5.35 ± 0.1	NaOAc[b]
	74.8	64.9[c]	
	75.0	67.7[c]	NaOAc[b]
2	75.0	3.87 ± 0.04[c]	
	90.0	12.5 ± 0.2[c]	
	109.6	5.38 ± 0.06	
	109.6	...[d]	NaOAc[b]
3	75.0	53.1 ± 1	
4	75.0	339 ± 5	
5	75.0	3.98 ± 0.05	
6	75.0	...[e]	
	75.0	13.1	NaOAc[b]

[a] Kinetic solutions were 0.02 *M* in sulfonate. [b] Sodium acetate, 0.03 *M*. [c] *p*-Nitrobenzenesulfonate rather than tolysate solvolyzed. [d] Non-first-order kinetics; apparent "first-order rate constant" from initial rate data, 26.6×10^{-6} sec^{-1}. [e] Decomposition occurs.

Isotopically substituted **1**, 2-phenyl-*1,1-d*$_2$-ethyl tosylate (**5**) shows essentially complete scrambling in the products of solvolysis. Furthermore, the secondary deuterium isotope effect upon the rate is large, k_H/k_D = 1.21, which is apparently near maximum, and is as large as the ratios observed in the formolysis of activated β-arylethyl systems.[8] This high k_H/k_D is evidence for the dominance of the participating pathway, k_Δ, over the k_s pathway in the trifluoroethanolysis of **1** and supports an unsymmetrical partially bridged transition state.

A final point of interest, which is germane to present mechanistic discussions regarding the role of the phenonium ion in these solvolyses is the sharp *qualitative* difference in behavior between **1** and **2** when solvolyses are carried out in TFE with the addition of sodium acetate. The rate constant for **1** increases, and the magnitude of the increase is typical of normal salt effects. **2**, on the other hand, gives non-first-order behavior under these conditions, suggestive of bimolecular reaction between **2** and acetate ion.

A further study had been carried out examining the solvolysis of 2-(2-furyl)ethyl tosylate (**6**) in TFE buffered with sodium acetate.[9] This reaction is clean kinetically, in contrast to preliminary results with **6** in formic acid and sodium formate. In formic acid **6** shows appreciable extraneous decomposition and severe darkening of the kinetic solution before the apparent first half-period is complete.

Thus TFE shows promise for the study of β-arylethyl sulfonates. It accentuates the participating

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