amounting to about 4% at the greatest. Because of uncertainty in the value of m for this particular instrument, the calculated viscosities are probably reliable to only 1%.

The results obtained are given in Table I.

TABLE I

VISCOSITIES OF COMPOUNDS IN MILLIPOISES

	15°	25°	35°
Dimethylamine			
Viscosity	2.07	1.86	1.67
KE Corr.	− .06	− .06	− .07
Trimethylamine			
Viscosity	1.94	1.77	1.61
KE Corr.	− .06	− .06	− .07

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The Use of Trimethyl Phosphate as a Methylating Agent

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The commercial availability of trialkyl phosphates has created considerable interest regarding their use as alkylating agents. Noller and Dutton[1] have shown that they may be used to alkylate phenols, and more recently Billman, Radike and Mundy[2] have applied them successfully to the alkylation of amines.

The present paper reports the methylation of aliphatic alcohols with trimethyl phosphate.

The reaction proceeds readily on heating, but the yield of methyl ether is only 50–60% based on the alcohol used, and not all of the available methyl groups of the phosphate ester are utilized. A fraction of the alcohol is converted into olefins and another part appears in the form of mixed alkyl acid phosphates. By employing an excess of the alkylating agent the yield of methyl ether may be increased.

With the procedures used the method is limited to alcohols boiling above 160°, because with lower boiling compounds the reaction proceeds too slowly.

(1) Noller and Dutton, THIS JOURNAL, **55**, 424 (1933).
(2) Billman, Radike and Mundy, *ibid.*, **64**, 2977 (1942).

TABLE I

ALKYL METHYL ETHERS

Alcohol used	Moles phosphate per mole alc.[a]	Method	Time, hr.	Yield, %	B. p., °C. (uncor.)	Ref.
2-Ethyl-	0.350	I	23	56.6	159–160	*b*
hexanol-1	.350	II	5	57.8	159–160	
	.500	II	4.5	62.0	159–160	
	.667	II	6.0	68.0	159–160	
Octanol-1	.667	II	2.0	69.5	173–174	*c*
Octanol-2	.350	I	27	56.7	159–160	*d*
Heptanol-2	.600	I	20	54.3	139–140	*e*
Hexanol-1	.350	II	9	52.7	124–125	*f*
Ethylene						
glycol	.333	I	5.3	37.2	122–123	*g*

[a] One and one-half moles of alcohol used in all cases. [b] Calcd. for $C_9H_{20}O$: C, 75.0; H, 13.9. Found: C, 74.4; H, 13.6. [c] Dobriner, *Ann.*, **243**, 3 (1888). [d] Cerchez, *Bull. soc. chim.*, [4] **43**, 767 (1928). [e] Calcd. for $C_8H_{18}O$: C, 73.8; H, 13.85. Found: C, 73.6; H, 14.0. [f] Lespieau, *Bull. soc. chim.*, [4] **43**, 1190 (1928). [g] The compound obtained is ethylene glycol monomethyl ether: Palomaa, *Ber.*, **35**, 3300 (1902).

Experimental Part

Two general procedures were followed, both employing commercial grade trimethyl phosphate.

Method I.—The alcohol and the trimethyl phosphate were boiled under reflux until the temperature of the liquid phase reached a constant minimum. The volatile components were distilled, the last portions being removed under reduced pressure, and the desired methyl ether was isolated by careful fractionation of the distillate. The time required for the reaction was twenty to thirty hours.

Method II.—The reactants were boiled in a Claisen flask connected to a water-cooled receiver, and the temperature of both the liquid and the vapor phase was measured. After one hour the temperature of the liquid was 15–20° below the initial temperature. More heat was applied, so that the ether distilled as it was formed, and the temperature of the liquid phase was maintained 3–10° below the initial temperature. The reaction was complete when distillation ceased or when the residue began to decompose. The last traces of volatile material were removed by distillation under reduced pressure and the product was isolated as above.

The results of runs with various alcohols are listed in the table. Analyses were by Mr. Russell Bell of this Laboratory.

Among the volatile by-products, small amounts of olefins, methyl alcohol and unchanged starting material were found. The non-volatile residue was an alkali-soluble mixture of alkyl acid phosphates resembling those obtained by the action of phosphorus pentoxide on alcohols.[3]

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(3) Adler and Woodstock, *Chem. Industries*, **51**, 516 (1942).