

THE PREPARATION AND PROPERTIES OF SOME
tert-ALKYL FORMATES

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Several years ago (1) we were interested in the preparation and properties of *tert*-alkyl formates. In view of the recent work of Knight, Koos, and Swern (2) on the addition of formic acid to monoolefinic compounds the information collected in that study should be published since the preparations involved the addition of formic acid to *tert*-alkenes.

Information concerning *tert*-alkyl formates is very meager and a study of their preparation and some of their properties was considered advisable. Obviously *tert*-alkyl formates cannot be made by the usual method of making esters though Kailan and his co-workers (3) have studied the rate of reaction of *tert*-butyl alcohol with formic acid, using both the alcohol and acid as solvents, but did not isolate the ester. Taylor (4) appears to have been the first to isolate *tert*-butyl formate using the reaction of *tert*-butyl chloride with formic acid in the presence of calcium formate. The yield was very poor and he reports a saponification equivalent of 113.7 when the calculated equivalent is 102.13. His carbon and hydrogen analysis however, checked with the theoretical. *tert*-Amyl formate was prepared by Kondakoff (5) by adding formic acid to trimethylethylene using zinc chloride as a catalyst. The addition of formic acid to cracking oils, using concentrated sulfuric acid as a catalyst, is also reported by Sucharda and Mazon-ski (6). A careful translation of this Polish article revealed that only crude mixtures of alkenes from cracking oils were used and no pure esters were ever isolated. No other references to *tert*-alkyl formates could be found.

The use of an ester interchange between an ester and aluminum alkoxide reported by Baker (7) appeared to offer a possible method of synthesis of *tert*-butyl formate and, by using an ester boiling higher than *tert*-butyl formate, the reaction could be forced towards completion. This was found to be the case and *tert*-butyl formate in fair yields was obtained. This method is not practical for other alkyl formates since the corresponding aluminum *tert*-alkoxides are difficult to prepare.

The addition of formic acid to the correct alkene appears to be the most promising synthesis and Kondakoff (5) has prepared *tert*-amyl formate in this manner using zinc chloride as a catalyst. This method was thoroughly investigated but the esters were always contaminated with *tert*-alkyl chlorides. The use of concentrated sulfuric acid as a catalyst in the addition of acids other than formic to alkenes has been reported (8, 9). After this work was completed, Altschul (10) published a study of the action of several acids with isobutylene but did not include formic acid.

Preliminary quantitative runs were made by adding formic acid to various alkenes using concentrated sulfuric acid as a catalyst. Using this data, fairly

large scale runs were made and several new *tert*-alkyl formates were obtained in a pure state and some of their properties were determined.

EXPERIMENTAL

Preparation of tert-butyl formate by the reaction of aluminum tert-butoxide with n-butyl formate. In a 3-l. flask was placed 325 g. (1.34 moles) of aluminum *tert*-butoxide, which had been carefully freed of benzene, and 1000 ml. of *n*-butyl formate. The ester was used both as a reactant as well as a solvent. The mixture was heated at 60° and slowly distilled through a 10-in. Widmer column at a pressure of 130 mm. The vapors were condensed by a spiral glass condenser surrounded with ice-water. The distillation required 36 hours and 620 g. of product was obtained, the last 150 g. of which was pure *n*-butyl formate as determined by its index of refraction.

The combined distillates were diluted with 250 ml. of ether, washed ten times with 250 ml. of ice-water, and then dried over freshly heated magnesium sulfate. The mixture was carefully filtered from the drying agent and distilled through a 10-plate column collecting very small fractions and following the separation by the index of refraction of each fraction. After removing the ether, 260 g. of a fairly pure material distilled. After this amount had been removed the distillate became acid and the distillation was discontinued. The combined distillates were again washed with water, thoroughly dried with Drierite, and again fractionated. After 162 g. of constant index of refraction material had distilled the distillate again became acid and was discarded. The ester is a colorless liquid. Sap. Equiv. Calc'd: 102.13. Found: 102.2; n_D^{25} 1.3783, b.p. 81.07° (735 mm.) (11). The yield was 45.7% based on aluminum *tert*-butoxide. Apparently *tert*-butyl formate when slightly impure is very easily decomposed into isobutylene and formic acid on heating. This unpredictable decomposition was never eliminated when the ester was made by this method and accounts for the relatively low yield.

Preparation and isolation of the tert-alkyl formates. A weighed amount of a 1% solution by weight of 95.5% sulfuric acid in 99% formic acid was placed in a large glass-stoppered bottle and the equivalent amount of alkene was added. The bottle was placed on a shaking

TABLE I
PHYSICAL CONSTANTS OF *tert*-ALKYL FORMATES^a

Ester	Yield, %	n_D^{25}	d_4^{25}	B.P., °C. (760 mm.)	L	A	B	$\frac{dP}{dT}$	Formula	Analysis			
										Calc'd		Found	
										C	H	C	H
<i>tert</i> -Butyl formate...	64.1	1.3783	0.8718	82.8	7954	1738	7.764	23.49					
<i>tert</i> -Amyl formate...	35.5	1.3951	.8853	112.9	8509	1859	7.700	21.39					
3-Methyl-3-pentanol formate.....	19.2	1.4080	.8926	140.5	9344	2041	7.818	20.46	C ₇ H ₁₄ O ₂	65.34	10.84	65.01	10.99
2-Methyl-2-hexanol formate...	19.1	1.4105	.8981	156.6	9951	2174	7.941	20.17	C ₈ H ₁₆ O ₂	66.62	11.18	66.29	11.40
3-Ethyl-3-pentanol formate...	5.9	1.4168	.9014	162.2	9951	2174	7.877	19.66	C ₈ H ₁₆ O ₂	66.62	11.18	66.31	11.32

^a The vapor pressures were determined by the modified Ramsey-Young method.

machine and shaken for 12 hours. No temperature control was necessary. The contents of the bottle were then transferred to a separatory-funnel, and washed with ice-water, cold dilute sodium bicarbonate solution, and then ice-water. The ester layer was dried by shaking with Drierite for two hours and then was placed in a flask connected with a 20-plate Lecky column being very careful that no dust or drying agent got into the flask. A slow stream of dry nitrogen was passed through the apparatus and a diminished pressure was maintained which was sufficient to distill the ester from a bath whose temperature was never above 80°. By means of a fraction cutter very small fractions were obtained and those having a constant index of refraction were combined and refractionated again combining only those fractions having a constant index of refraction.

Since preliminary runs indicated that at equilibrium only small concentrations of 3-methyl-3-pentanol formate, 2-methyl-2-hexanol formate, and 3-ethyl-3-pentanol formate were present, in preparing these esters the fractional distillation was stopped after the alkene had been stripped off and the alkene so obtained was treated again with formic acid. This was repeated four times before the esters were distilled. *tert*-Butyl formate was made by passing a slow stream of isobutylene, dried by passing through a tower of Drierite, into a fritted glass wash bottle containing the formic acid until no more gas was absorbed. The resulting mixture was worked up in a manner similar to the other esters.

The purity of the esters was determined by their saponification equivalents and these constants checked within 0.5% for the pure esters with the exception of 2-methyl-2-hexanol formate and 3-ethyl-3-pentanol formate. It was found that these two esters hydrolyzed very slowly and, after 72 hours' heating with alcoholic potassium hydroxide, a saponification equivalent within 2% was obtained. The resistance to alkaline hydrolysis of *tert*-butyl benzoate has been reported. Table I gives the yields obtained of the twice fractionated esters of constant index of refraction and some of their properties. The yields are based on the alkenes with the exception of *tert*-butyl formate which was based on formic acid. The repeated distillation of the alkenes at reduced pressure in preparing the last three esters caused considerable loss of alkene with consequent low yields.

SUMMARY

The synthesis of *tert*-butyl formate, *tert*-amyl formate, 3-methyl-3-pentanol formate, 2-methyl-2-hexanol formate, and 3-ethyl-3-pentanol formate, is reported, and some of their physical constants have been determined. The last three esters are new compounds.

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