# High Purity Tertiary-Amyl Acetate

## Synthesis and Properties

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**High purity *tert*-amyl acetate is prepared by reacting *tert*-amyl alcohol with acetic anhydride in the presence of HCl. The reaction is rapid and high yields were obtained. The properties of *tert*-amyl acetate have been compared with those given in the literature and spectral data analyzed.**

REPORTED METHODS of preparation of *tert*-amyl acetate were cumbersome (*6*), uneconomical of yield (*12, 5*), or resulted in a product of low purity (*12, 5, 7, 1*). An acetic anhydride method described below has been entirely satisfactory.

### PROCEDURE

The reaction of acetic anhydride with *tert*-amyl alcohol was quantitative and rapid using an acid catalyst:

$$CH_3CH_2C(CH_3)_2OH + (CH_3CO)_2O \xrightarrow{HCl} CH_3CH_2C(CH_3)_2OOCCH_3 + CH_3COOH \quad (1)$$

The reaction proceeded readily under reflux to yield a high-purity product. To a 300-ml. flask equipped with a 20-cm. Vigreaux column, reflux condenser, drying tube, and take-off adapter, were added 100 ml. of acetic anhydride (Matheson, Coleman, and Bell) and 110 ml. of *tert*-amyl alcohol (Matheson, Coleman, and Bell) and 4 drops of concentrated HCl. The mixture was heated and maintained at gentle reflux for 3 hours (100° C. to a maximum of 112° C.). The product was distilled and the 120° to 125° C. fraction was collected. The crude product was washed with 10% $K_2CO_3$ until neutral to litmus, and then dried over $CaSO_4$ and CaH. Fractional distillation over potassium metal resulted in an 80% yield of the *tert*-amyl acetate. B.p. 123°–124° C. Anal. Calcd. for $C_7H_{14}O_2$: C, 64.6; H, 10.8. Found: C, 64.6, 64.7; H, 10.9, 10.9. M.W. (in benzene): 131, 137 (Theoretical 130.18 for monomer).

No impurities were detectable by gas chromatography on a column using diethylene glycol succinate as the liquid phase. In one distillate product, 0.18% chloride contamination was found. Generally, chloride is absent unless larger amounts than specified of concentrated HCl are used as catalyst. Spectral and physical property data listed in the next section are consistent expected results and are believed to be the best available for the compound.

The infrared spectra were obtained using a capillary film, NaCl and CsBr cells, and Perkin Elmer Model 521 and 221 Double Beam Spectrophotometers.

The use of larger amounts of HCl or longer reflux times to increase the yield of the product results in the reaction of *tert*-amyl acetate with HCl to produce *tert*-amyl chloride and acetic acid. *tert*-Amyl acetate decomposed gradually above 125° C. to 2-methyl-butene and acetic acid (*4*). Consequently, close temperature control on distillation to avoid overheating is required.

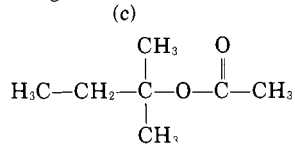
### RESULTS AND DISCUSSION

Property data obtained for *tert*-amyl acetate prepared by the described method are given in Table I. Some applicable literature values have been listed for comparison. The substantial variance in reported boiling point for the compound compared by different methods indicates considerable differences in purity. The nuclear magnetic resonance spectrum is consistent with the expected structure (*10*) including a significant shift ($\Delta\delta$ % 0.52) where $\Delta\delta$ is the difference in chemical shift in parts per million for the methyl protons represented by (c) and (d) in Table I in the methyl group protons adjacent to the carbonyl groups. This agrees exactly with the results reported for *tert*-butyl acetate

Table I. Some Properties of High Purity *tert*-Amyl Acetate

| Property | This Method | | | | Prior Method, Ref. |
|---|---|---|---|---|---|
| B.P., ° C. | 123–4 | | | | 124 (*4*)<br>124–124.5(*1*)<br>124–125 (*6, 12*)<br>123–124 (*5*)<br>119–121 (*7*) |
| Specific Gravity | 0.8725 @ 24.7° C. | | | | 0.8738 @ 19° C.(*1, 4*) |
| Refractive Index | $1.3969_7$ @ 24.5° C. | | | | 1.392 @ 20° C.(*4*) |
| N.M.R. Data (TMS std.) | | | | | |
| Chemical Shift, p.p.m. | 0.85 | 1.80 | 1.38 | 1.90 | |
| Peak Type | Triplet | Quadruplet | Singlet | Singlet | |
| No. of Protons | 3 | 2 | 6 | 3 | |
| Assignment | (a) | (b) | (c) | (d) | |

(c)



(a) (b) (c) (d)

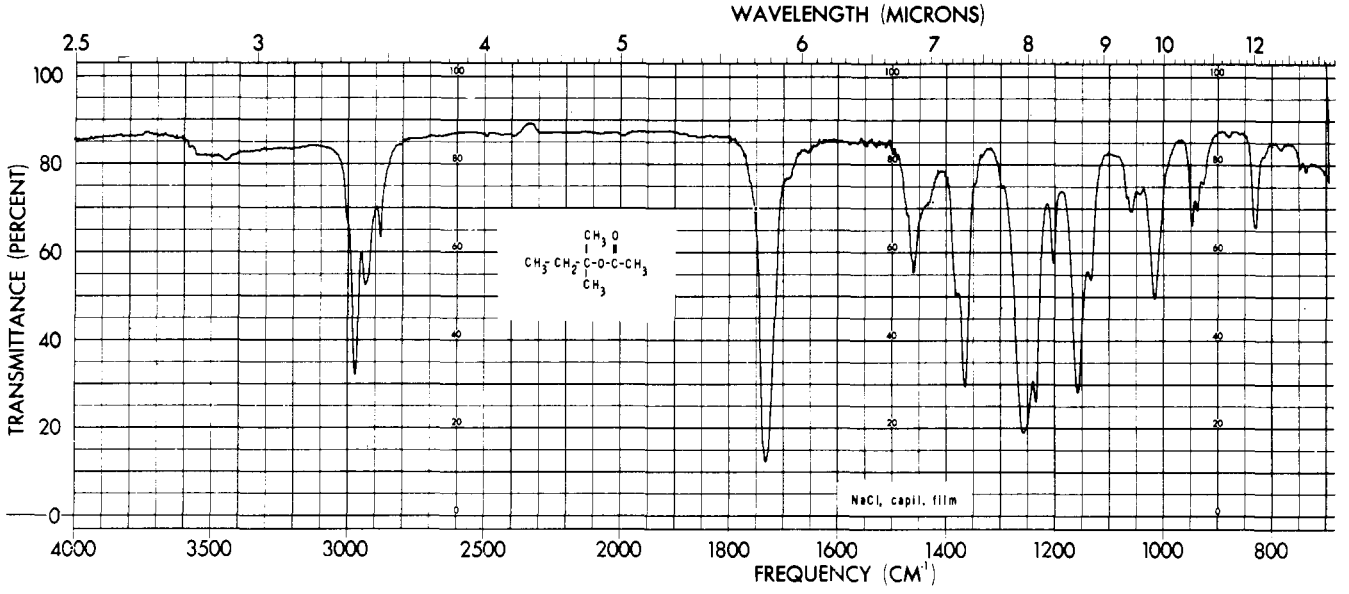



Figure 1. Infrared spectrum of tertiary amyl acetate

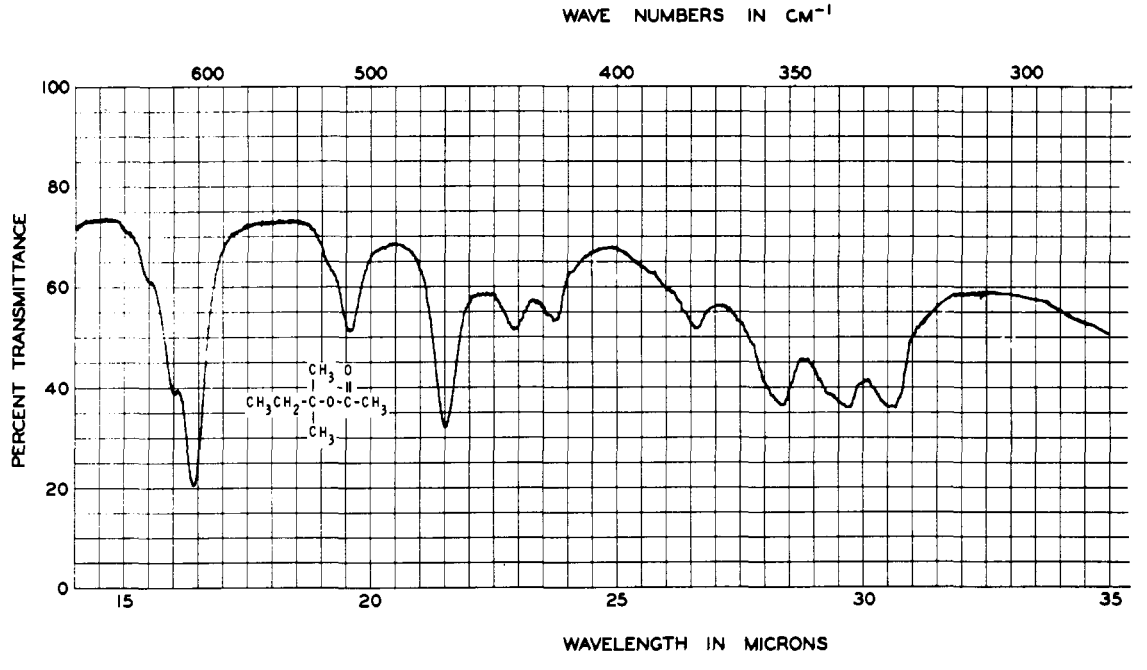



Figure 2. Medium infrared spectrum of tertiary amyl acetate

for the methyl group adjacent to the carbonyl group *(3)*. The infrared spectrum of this compound is given in Figures 1 and 2 for the region from 5000 to 285 cm.$^{-1}$

In the region from 4000 to 700 cm.$^{-1}$, the characteristic carbonyl stretch vibration for esters is found at 1733 cm.$^{-1}$. A methylene deformation vibration is observed at 1459 cm.$^{-1}$ which is typical of an acetate group *(2)*. Based on the work of Zeiss and Tsutsui *(13)*, the 1157-cm.$^{-1}$ band would be assigned to a C—O stretch vibration. However, this is a difficult assignment to make unequivocally *(11)*. Recent work with transition metal alkoxides compounds *(9)*, in which the C—O stretch has been influenced by the attached heavy metal, has shown that the C—O stretch vibration is near 1000 cm.$^{-1}$ for tertiary alcohols. The C—C stretch vibration intensity is stronger than the C—O stretch vibration in this region. Based on these results and a consideration of alkane spectra in general *(2)*, the 1018 cm.$^{-1}$ peak is assigned to the C—O vibration and the 1255, 1202, 1157, 1059, 948, and 829-cm.$^{-1}$ absorptions arise from skeletal vibrations of the *tert*-amyl group.

The characterization of saturated aliphatic esters is facilitated by use of the medium infrared spectra from 650 to 285 cm.$^{-1}$ *(8)*. The strong band at 610 cm.$^{-1}$ is characteristic of acetates of secondary and tertiary alcohols, as is the 615-cm.$^{-1}$ band which is stronger for *tert*-butyl acetate and other lower molecular weight acetates *(8)*. The 510-cm.$^{-1}$ peak is a skeletal vibration found for esters where at least three carbon atoms are in a straight chain attached to the acetate—e.g., *n*-propl, *n*-butyl, isobutyl, *neo*-pentyl.

The 466, 352, and 337 cm.$^{-1}$ are characteristic of esters of tertiary alcohols and the 327-cm.$^{-1}$ band is found for all tertiary acetates.

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# Cocatalysts for the Polymerization of ϵ-Caprolactam

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**The preparation, characterization, and properties of several new caprolactam anionic polymerization cocatalysts are described. An improved method for the preparation of some of the compounds is discussed. The specific compounds reported are: *N*-*n*-valeryl-, *N*-*n*-hexanoyl-, *N*-*n*-heptanoyl-, *N*-*n*-octanoyl-, *N*-*n*-nonanoyl-, *N*-*n*-decanoyl-, *N*-*n*-undecanoyl-, *N*-lauryl-, *N*-*n*-tridecanoyl-, *N*-myristoyl-, *N*-4-methoxybenzoyl-, *N*-4-chlorobenzoyl-, *N*-4-bromobenzoyl-, and *N*-4-iodobenzoylcaprolactams.**

IN A previous publication (*3*), the preparation of several new *N*-acyl caprolactam derivatives was reported. These compounds were prepared in order to study steric and electronic effects in the catalysis of the fast anionic polymerization of caprolactam (*2*). To round out the kinetic studies, a larger number of homologous and analogous catalysts were prepared (see Table I). In addition, a more reliable method for the preparation of *N*-4-methoxybenzoylcaprolactam was desired.

In previous work (*3*)two general types of reaction systems for acylating caprolactam were employed. In one, the lactam was dissolved in dry pyridine and the appropriate acyl chloride was added to the solution. The other method involved treating the sodium salt of caprolactam with the requisite acid chloride. Of the two procedures reported (*3*), the pyridine method was superior. However, when it was employed to prepare para-substituted *N*-benzoylcaprolactams, the yields of the desired products were low when the substituent was electropositive with respect to the benzene nucleus, and where the substituent was methoxy, the reaction was very erratic; often, none of the desired product was obtained. Indeed, the authors have found that the product reported previously was not pure *N*-4-methoxybenzoyl caprolactam, but a mixture of the acyl lactam and 4-methoxybenzoic acid anhydride (*3*). Thompson (*6*) reported similar results upon attempting to acylate amides. Furthermore, the addition of solutions of acyl halides in pyridine to water yields anhydrides (*4*). Adkins and Thompson (*1*) have isolated pyridine–acyl halide adducts. Since our product isolation procedure involved addition of the reaction mixture to water (*3*), it is not suprising that the major products were anhydrides, if the assumption is made that the pyridine–acyl halide adduct is stable enough so that its rate of reaction with caprolactam is slow. On the other hand, when 4-nitrobenzoyl chloride was employed in an otherwise identical reaction system (*3*), no anhydride was isolated, and the yield of *N*-4-nitrobenzoylcaprolactam was 90%. Thus, it is possible, by comparing resonance structures of the pyridinium adducts, to assume that the electron-withdrawing nitro group decreased the stability of the adduct.

In view of the preceding assumption, any change in the reaction system which would make the intermediate adduct less stable might favor the desired reaction and suppress anhydride formation. If a Dreiding model of a para-substituted benzoyl pyridinum adduct is fashioned and compared with the model of the analogous adduct, using triethylamine in place of pyridine, it is readily apparent that the triethylamine analog might be less stable because of steric effects which are not present in the pyridinium adduct. As a result, if triethylamine were used in place of pyridine for the preparation of *N*-4-methoxybenzoylcaprolactam, the yield of the *N*-acyllactam might be significantly improved, and the reaction might be easily reproducible. In actual experimentation, this proved to be the case (see Table I).

All *N*-acylcaprolactams prepared were screened for antimalarial activity (*5*), but none was found.

The *N*-acylcaprolactams reported all function as cocatalysts for the anionic polymerization of caprolactam.