Trityl Esters. I. Synthesis and Structure Determination[1]

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An improved procedure for the general synthesis and purification of trityl esters has been developed which involves the heterogeneous condensation of trityl bromide with salts of carboxylic acids in hydrocarbon solvents. A mechanism is suggested for the esterification in which trityl ion attacks the carbonyl oxygen atom of the salt. Structural confirmation for trityl propionate was accomplished *via* methanolysis to give trityl methyl ether and propionic acid. Saponification data are included as support for the structures of four new esters, and infrared spectra have been recorded for all of the compounds.

Triphenylmethyl (trityl) esters of carboxylic acids are of current interest in the elucidation of the over-all behavior pattern of the trityl group, particularly in solvolysis reactions.[2, 3l, 3m] Actually few esters have been prepared and often yields have been modest or completely omitted in previous documents.[2,3] The procedure has involved a heterogeneous condensation of trityl chloride with the silver salt of the acid over extended time intervals. For example, the method used in the preparation of trityl *p*-toluate involved a condensation of trityl chloride with silver *p*-toluate in benzene. A product was isolated after two days in unspecified yield and was identified by elemental analysis only.[3f] The hygroscopic nature of trityl chloride[4] is a serious detriment to the process since tritanol, the hydrolysis product, proves a difficult contaminent to remove by recrystallization techniques. We have found that trityl bromide offers several advantages in the general synthesis of trityl esters.[5] The halide is much less hygroscopic, silver, sodium, or potassium salts can be used, and only a slight excess of the salt is required to give high yields. Moreover, the reactions are complete within a few hours, which is indicative of the increased reactivity of the bromide. The general scheme is outlined:

$$\mathrm{RCO_2M + (C_6H_5)_3CBr \longrightarrow RCO_2C(C_6H_5)_3 + MBr}$$

M = Ag, K, Na
R = CH_3, C_2H_5, $(CH_3)_3C$, $C_6H_5CH_2CH_2$, C_6H_5, *o*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, $C_6H_5CH{=}CH$

Anhydrous benzene (or cyclohexane) proved a satisfactory solvent, and filtration of the reaction mixture removed the insoluble metal bromide and excess salt. Concentration of the solution left a solid of high purity which could be analytically purified, usually by one recrystallization from methyl ethyl ketone or from low-boiling hydrocarbons such as heptane. Early attempts with chromatography of the reaction mixture on alumina resulted in some absorption.[6] Like trityl acetate,[7] the corresponding propionate is also unstable as evidenced by the odor of propionic acid in a stored sample of ester. However, all of the examples in this study could be preserved indefinitely in a vacuum desiccator. The physical constants for the esters and the reaction conditions are found in Table I.

In order to minimize the amount of residual base, the various alkali metal salts were conveniently prepared by adjustment of an aqueous or alcoholic solution of the respective acid to about pH 7.5. Careful drying of the salts was essential to remove traces of moisture. As expected, silver propionate was light-sensitive[8] and was used within twenty-four hours as extensive decomposition occurred at longer time intervals.

Hydrolysis of trityl benzoate, trityl *o*-toluate, trityl cinnamate, and trityl hydrocinnamate with aqueous sodium hydroxide resulted in quantitative conversions to the tritanol and the sodium salts of the respective acids. Reminiscent of the attempted saponification of *t*-butyl acetate with 28% aqueous sodium hydroxide,[9] trityl pivalate was recovered nearly unchanged (90%) after twenty-four hours at reflux in excess 10% aqueous sodium hydroxide. Bunton and Konasiewicz have demonstrated by isotopic studies with trityl acetate in 80% aqueous dioxane that alkyl-oxygen fission occurs predominately in basic hydrolysis.[7]

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[1] We gratefully acknowledge the support of the National Science Foundation, Grant G-19733. Partial support by the Oklahoma State University Research Foundation is also acknowledged.

[2] See pertinent references in: L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **83**, 3708 (1961).

[3] (a) R. Anschutz, *Ann.*, **359**, 196 (1908); (b) M. Gomberg, *J. Am. Chem. Soc.*, **35**, 200 (1913); (c) C. S. Schoepfle, *ibid.*, **47**, 1469 (1925); (d) S. T. Bowden, *J. Chem. Soc.*, 310 (1939); (e) S. T. Bowden and T. F. Watkins, *ibid.*, 1333 (1940); (f) H. Weiland and A. Meyers, *Ann.*, **551**, 249 (1942); (g) A. Perret and R. Perrot, *Helv. Chim. Acta*, **28**, 558 (1945); (h) C. R. Hauser, P. O. Saperstein, and J. C. Shivers, *J. Am. Chem. Soc.*, **70**, 606 (1948); (i) S. V. Khuravlev, *Zh. Prihl. Khim.*, **23**, 1100 (1950); *Chem. Abstr.*, **46**, 10107 (1952); (j) W. Theilacker and M. L. Wessel, *Ann.*, **594**, 229 (1955); (k) D. W. A. Sharp and N. Sheppard, *J. Chem. Soc.*, 674 (1957); (l) C. G. Swain, T. E. C. Knee, and A. MacLachlan, *J. Am. Chem. Soc.*, **82**, 6101 (1960); (m) R. M. Keefer and L. J. Andrews, *ibid.*, **84**, 941 (1962) and references therein.

[4] W. E. Bachmann, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, 1955, p. 841.

[5] Ref. 3c contains a brief report on the synthesis of trityl acetate from trityl bromide and ammonium acetate.

[6] A similar result was observed with trityl acetate by E. Meitz, F. Schmidt, and J. Singer, *Z. Electrochem.*, **46**, 222 (1940).

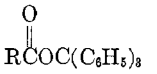
[7] C. A. Bunton and A. Konasiewicz, *J. Chem. Soc.*, 1354 (1955).

[8] S. Peterson, J. L. Jones, J. M. Schmitt, and L. H. Knabeschuh, *J. Phys. Chem.*, **56**, 491 (1952).

[9] C. D. Hurd and F. H. Blunck, *J. Am. Chem. Soc.*, **60**, 2419 (1938).

TABLE I

PREPARATION AND PROPERTIES OF TRITYL ESTERS



$$\overset{O}{\overset{\|}{RC}}OC(C_6H_5)_3$$

R	M	Solvent	Moles RCO₂M / Moles (C₆H₅)₃CBr	Reaction time, hr.	Yield, %	Recryst. solvent	M.p., °C.	Calcd. C	Calcd. H	Found C	Found H
CH_3	Ag	C_6H_6	1.02	4	90	C_6H_{12}	82–84[d]				
C_2H_5	Ag	C_6H_{12}	1.14	3	86	C_6H_{12}	81–83[e]				
$C_6H_5CH_2CH_2$	Na	C_6H_6	1.07	5.5	94	IE[b]	108–110	85.68	6.16	85.24	6.26
$C_6H_5CH_2CH_2$	K	C_6H_6	1.05	6	94	IE					
$(CH_3)_3C$	Na	C_6H_6	2.00	6	87	C_7H_{16}	91–93	83.10	7.20	83.00	6.97
$(CH_3)_3C$	K	C_6H_6	1.21	5	94	C_7H_{16}					
C_6H_5	Na	C_3H_6O[a]	1.02	4	60	MEK[c]	168–170[f]				
C_6H_5	K	C_6H_6	1.20	4	92	MEK					
o-$CH_3C_6H_4$	Na	C_6H_6	1.20	5	84	MEK	140–142	85.68	5.81	84.87	5.80
p-$CH_3OC_6H_4$	Na	C_6H_6	1.01	4	73	MEK	156–157[g]	82.21	5.58	82.35	5.87
$C_6H_5CH{=}CH$	K	C_6H_6	1.01	2.5	83	IE	128–129	86.12	5.69	86.46	5.83

[a] Acetone. [b] Isopropyl ether. [c] Methyl ethyl ketone—it is to be noted that trityl benzoate has been prepared in only 40% yield using trityl chloride and a 7-hr. reaction time.[12] The highest yield (55%) has been reported using silver benzoate and trityl chloride in anhydrous dioxane for an unspecified time.[3j] [d] Reported m.p. 84°, ref. 31. [e] Reported m.p. 80–82°, ref. 2. [f] Reported m.p. 168–169°, ref. 12. [g] Reported m.p. 164°, ref. 3f. The synthesis required 1.5 days and no yield was given for trityl *p*-anisate. The melting point is near that reported for tritanol and therefore the structure previously reported may be in doubt.

Ionization of the ester was postulated as the rate-determining step. With trityl pivalate, the low solubility of the ester in water may greatly retard the ionization process. Treatment of trityl acetate with the methyl[10] or *t*-butyl[11] Grignard reagents resulted in good yields of 1,1,1-triphenylethane and 1,1,1-triphenyl-2,2-dimethylpropane, respectively. The fact that these hydrocarbons were obtained suggests the existence of trityl ion although the classical prediction would involve acyl-oxygen bond fission to give tritanol. Molecular models do suggest, however, that the backside of the carbonyl group in the pivalate is extremely hindered to attack by the hydroxyl nucleophile.

Although reported recently in unspecified yield,[2] no structure confirmation was given for trityl propionate. The ester underwent methanolysis[12] to yield propionic acid and trityl methyl ether. Both products were isolated in nearly quantitative amounts and were identified by comparison with authentic samples.

$$C_2H_5CO_2C(C_6H_5)_3 + CH_3OH \longrightarrow C_2H_5CO_2H + (C_6H_5)_3COCH_3$$

The infrared spectra of the esters contain strong absorption for the carbonyl functional group at 1739 cm.$^{-1}$ in the trityl aliphatic compounds and near 1724 cm.$^{-1}$ for the aromatic derivatives and the cinnamate ester, as anticipated from the conjugation effect.[13] One example, trityl *p*-anisate, had a carbonyl peak at 1709 cm.$^{-1}$ apparently indicative of the ground state resonance influence by the methoxy group on the carbonyl frequency.[14] The carbonyl absorption has been reported for trityl trifluoroacetate at 1785 cm.$^{-1}$,[3k] a considerably higher frequency than in our examples. The powerful inductive effect of the trifluoromethyl group would be expected to increase the force constant of the carbonyl function. The spectra contained a strong band at 700 cm.$^{-1}$ for the monosubstituted phenyl group and were in general agreement with the postulated structures.

It is immediately evident that the heterogeneous condensation of trityl bromide with salts of carboxylic acids may occur either in solution or at a surface. Ionization of trityl bromide in benzene has been postulated,[15] and it seems reasonable that trityl carbonium ion may be present in our solutions since the reactions are quite sensitive to moisture. In contrast trityl radicals are apparently absent since trityl peroxide[16] could not be isolated from the condensation of trityl bromide with sodium hydrocinnamate when a dry oxygen stream was conducted through the mixture.

Limited solubility of the acids salts in the hydrocarbon solvents would offer opportunity for a

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(10) L. F. Fieser and H. Heymann, *J. Am. Chem. Soc.*, **64**, 376 (1942).

(11) R. C. Fuson and D. E. Brasure, *ibid.*, **77**, 3131 (1955).

(12) A kinetic study of the alcoholysis of trityl benzoate has been reported; see ref. 7 and G. S. Hammond and J. T. Rudesill, *ibid.*, **72**, 2769 (1950).

(13) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, 1958, Chap. 11.

(14) Steroid benzoates are reported to absorb in the range 1719–1724 cm.$^{-1}$ [see R. N. Jones, P. Humphries, and K. Dobriner, *J. Am. Chem. Soc.*, **71**, 241 (1949)] while several *o*-, *m*-, and *p*-nitrobenzoates show a carbonyl frequency at 1733 cm.$^{-1}$ [see R. S. Rasmussen and R. R. Brittain, *ibid.*, **71**, 1073 (1949)] which was explained as the result of an inductive effect operative through the ring. The high dipole moment of ethyl anisate has been rationalized *via* a large charge separation in the ground state of the molecule due to a resonance effect involving the methoxy function and the carbonyl group [see M. T. Rogers, *ibid.*, **77**, 3681 (1955)].

(15) P. B. D. De LaMare and E. D. Hughes, *J. Chem. Soc.*, 845 (1956).

(16) Trityl radical is known to react rapidly with air to give trityl peroxide at room temperature; see L. Horner and W. Naumann, *Ann.*, **587**, 93 (1959), who studied the ultraviolet-catalyzed decomposition of trityl azobenzene in benzene. If moisture was not excluded from our reaction, tritanol was isolated in abundance.

parallel, classical carbonium ion esterification involving either attack of the trityl ion on the carboxylate anion or on the salt.[17] However, the results of Meyer and co-workers may be pertinent with respect to this type of esterification.[18] Although certain hindered acids were difficult to esterify by the usual methods, it was discovered that the corresponding silver salts react with methyl iodide with marked facility. It was recently postulated that the carbonyl oxygen atom may be involved in the initial phase of the reaction.[19] Such a step could also be operative in the trityl esterifications. Noteworthy is that acetic acid and pivalic acid were converted to the trityl esters in good yields under comparable conditions. Acetic acid is esterified with methanol nearly thirty times faster than pivalic acid by the usual acid-catalyzed process.[20]

Experimental[21]

Trityl Bromide.—Preparation of the halide was similar to that given for trityl chloride in "Organic Syntheses."[22] A typical run included 220.8 g. (0.84 mole) of trityl carbinol, 122.9 g. (1.0 mole) of acetyl bromide, and 100 ml. of anhydrous benzene; m.p. 153–154°, yield 90%.

Silver Acetate.—Purchased from W. H. Curtin and Co.

Silver Propionate.—The recorded procedure for this compound did not afford the pure salt in high yield.[8] A modification of the "Organic Syntheses" preparation for silver adipate[23] gave nearly quantitative results.

To a solution of 56.0 g. (1.0 mole) of potassium hydroxide in 250 ml. of water was added 74.0 g. (1.0 mole) of propionic acid. With constant stirring and in near total darkness was added a solution of 171.0 g. (1.0 mole) of silver nitrate in 200 ml. of water. When the addition was complete, the mixture was stirred 0.5 hr. and filtered. After washing with water and dry methanol, the white silver propionate was stored in a dark bottle and used within 24 hr.; yield, nearly quantitative based upon the synthesis of trityl propionate.

Trityl Aliphatic Esters.—The four esters were prepared in similar fashion and a typical procedure is illustrated with trityl propionate.

Trityl Propionate.—A mixture of trityl bromide (11.2 g., 0.03 mole), silver propionate (7.5 g., 0.04 mole), and 100 ml. of anhydrous cyclohexane was heated at reflux with rapid stirring near 1200 r.p.m. under nitrogen for 3 hr. Filtration removed excess salt and silver bromide, and concentration of the filtrate *in vacuo* afforded a viscous oil which crystallized upon standing in a vacuum desiccator, m.p. 81–83°.[2] Confirmation of structure for the ester resulted from a methanolysis reaction. Trityl methyl ether, m.p. 82–84° (recorded m.p. 83.5°)[7], was isolated in 94% yield. Authentication was completed by comparison of the infrared spectrum with a pure sample of the ether. Propionic acid was isolated in near quantitative yield; neut. equiv., 74; found: 74.

Alkali Metal Salts.—The potassium and sodium salts were prepared in a similar manner; the sodium *o*-toluate synthesis is typical.

Sodium *o*-Toluate.—Reagent sodium hydroxide (20.0 g., 0.5 mole) was dissolved in about 20 ml. of absolute ethanol. To this solution was added an equivalent amount of *o*-toluic acid (68.0 g., 0.5 mole) dissolved in 70 ml. of ethanol. After 1 hr., a clear solution was observed whose pH was determined and adjusted to about 7.5. Filtration of the liquid and evaporation of the filtrate gave the white salt which was thoroughly dried in an oven at 110°, m.p. 224–227°; yield, quantitative.

Trityl Aromatic Esters.—The syntheses of trityl *o*-toluate is illustrative of the general method employed with the aromatic derivatives.

Trityl *o*-Toluate.—In a three-neck flask were placed 9.4 g. (0.06 mole) of sodium *o*-toluate and 16.16 g. (0.05 mole) of trityl bromide in 100 ml. of anhydrous benzene. The mixture was heated at reflux with rapid stirring near 1200 r.p.m. under nitrogen for 5 hr. The hot reaction mixture was filtered and concentration of the filtrate left an oil which solidified when allowed to cool. One recrystallization from methyl ethyl ketone afforded analytical crystals, m.p. 140–142°, yield 15.9 g.

Attempt to Trap Trityl Radicals.—A mixture of 4.6 g. (0.014 mole) of trityl bromide and 2.9 g. (0.0146 mole) of potassium hydrocinnamate in anhydrous benzene (50 ml.) was heated at reflux with stirring for 5 hr. During the condensation, a stream of dry oxygen was bubbled continually through the reaction mixture. Normal work-up afforded pure trityl hydrocinnamate in yield greater than 90%. No trace of trityl peroxide was detected when the ester was examined by gas chromatography.

Saponification of Trityl Hydrocinnamate.—In a flask was placed 5.1 g. (0.01 mole) of trityl hydrocinnamate and 50 ml. of 10% aqueous sodium hydroxide. After the mixture had been held at reflux for 24 hr., it was acidified with dilute hydrochloric acid. Extraction of the mixture with ether removed tritanol quantitatively. Purification of the acid was achieved through repeated acidification of a mixture of the sodium salt in ether; yield 70%. Identification of both products was made by infrared analysis and mixed melting point determinations. Likewise, saponification of trityl benzoate,[24] trityl cinnamate, trityl hydrocinnamate, and trityl *o*-toluate gave tritanol and the corresponding salts in high yields. Trityl pivalate was recovered in quantities greater than 90% when subjected to such basic conditions.

Acknowledgment.—We wish to thank Dr. John D. Roberts for a valuable discussion during the course of this problem.

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[17] See E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, 1959, pp. 339–342.

[18] V. Meyer and J. J. Sudborough, *Ber.*, **27**, 1580, 3146 (1894).

[19] For a critical discussion of this reaction see G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, 1960, pp. 498–506.

[20] K. L. Loening, A. B. Garrett, and M. S. Newman, *J. Am. Chem. Soc.*, **74**, 3929 (1952).

[21] All melting points are corrected. The microanalyses were performed by the Midwest Micro Laboratory, Indianapolis, Indiana.

[22] W. E. Bachmann, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, 1955, p. 841.

[23] A. F. H. Allen and C. V. Wilson, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, 1955, p. 578.

[24] Trityl benzoate has been reported to undergo saponification (see 3g, 7, 12), but the work-up and product analysis was not described in its entirety.