which after recrystallization from benzene–hexane gave adduct 7 as white prisms: mp 217–218° (0.18 g, 7%); nmr ($CDCl_3$) τ 2.4–2.9 (16 H, m), 5.5 and 5.7 (2 H, AB, $J \cong 7$ Hz); mass spectrum m/e (rel intensity) 350 (34, P), 317 (20), 239, (27), 198 (19), 152 (100), and 78 (55). *Anal.* Calcd for $C_{25}H_{18}S$: C, 85.74; H, 5.15. Found: C, 85.56; H, 5.31.

Acknowledgments. I am deeply grateful to the following individuals at the National Institutes of Health: Dr. Hermann Ziffer for 220-MHz nmr spectra; Dr. Herman Yeh for decoupling experiments; and Mr. Bill Landis for the mass spectra of the compounds reported.

Registry No.—1, 1450-31-3; 2, 49746-16-9; 4, 49746-17-0; 5, 49746-18-1; 6, 49746-19-2; 7, 49746-20-5; cyclooctatetraene, 629-20-9; 6,6-diphenylfulvene, 2175-90-8; acenaphthylene, 208-96-8.

References and Notes

(1) A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *J. Amer. Chem. Soc.*, **91**, 5038 (1969), and references cited therein.
(2) (a) H. Gotthardt, *Tetrahedron Lett.*, 2345 (1971); (b) A. Ohno, T. Koizumi, Y. Ohnishi, and G. Tsuchihashi, *ibid.*, 2025 (1970).
(3) K. Yamada, M. Yoshioka, and N. Sugiyama, *J. Org. Chem.*, **33**, 1240 (1968).
(4) E. J. Gardner, R. H. Squire, R. C. Elder, and R. M. Wilson, *J. Amer. Chem. Soc.*, **95**, 1693 (1973).
(5) D. Bryce-Smith, A. Gilbert, and M. G. Johnson, *J. Chem. Soc. C*, 383 (1967).
(6) In these experiments irradiation of the entire vinyl multiplet of **2** and of **4** caused collapse of the two methine hydrogen signals to broadened singlets ($W_{1/2} < 2$ Hz) in each case.
(7) λ_{max} 290 nm (ϵ 20,000): J. L. Kice and F. M. Parham, *J. Amer. Chem. Soc.*, **80**, 3792 (1958).
(8) R. E. Harmon, W. D. Barta, S. K. Gupta, and G. Slomp, *Chem. Commun.*, 935 (1970).
(9) (a) J. L. Kice, *J. Amer. Chem. Soc.*, **80**, 348 (1958); (b) T. S. Cantrell, *J. Org. Chem.*, **32**, 911 (1967); (c) H. Shechter, J. J. Gardikes, T. S. Cantrell, and G. V. Tiers, *J. Amer. Chem. Soc.*, **89**, 3300 (1967).
(10) (a) J. L. Kice and T. S. Cantrell, *J. Amer. Chem. Soc.*, **85**, 2298 (1963); (b) T. S. Cantrell, *J. Org. Chem.*, **32**, 911 (1967).

Preparation of Benzoate Esters of Tertiary Alcohols by Transesterification[1]

Roberto A. Rossi* and Rita Hoyos de Rossi

Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Argentina

Received September 24, 1973

Standard procedures for esterification are usually not adequate for the synthesis of esters of tertiary alcohols.[2] Although several methods have been developed, they either suffer from lack of generality or present new disadvantages.[3] For example, procedures utilizing such intermediates as acid chlorides[4] or trialkyloxonium salts[5] require additional synthetic and purification steps, with consequent decreases in yield.

The finding that phenyl benzoate readily reacts with potassium 2-propoxide in liquid ammonia to give 2-propyl benzoate in high yield[6] prompted us to investigate the generality of the reaction. It offered promise as a method for the preparation of benzoate esters of tertiary alcohols. Accordingly we did a few experiments, now reported, which demonstrate the practicability of the method.

Operationally, the method involves two steps. First, phenol is converted to the desired benzoic ester through reaction with an appropiate benzoic acid in toluene, catalyzed by boric–sulfuric acid[7] (eq 1). This reaction gives good yields with all the acids so far studied (70–90%).

$$ArCO_2H + PhOH \longrightarrow ArCO_2Ph + H_2O \quad (1)$$

Second, the phenyl benzoate so obtained reacts with the potassium salt of the desired tertiary alcohol in liquid ammonia, giving an alkyl benzoate and potassium phenoxide (eq 2).

$$ArCO_2Ph + RO^- \longrightarrow ArCO_2R + PhO^- \quad (2)$$

Table I
Transesterification of Phenyl Benzoates by Alkoxide Ions in Liquid Ammonia

$ArCO_2Ph$		RO^-K^+		$ArCO_2R$ yield,
Ar	Mmol	R	Mmol	%
C_6H_5	41	*tert*-Butyl	42	91[a]
	35	Isopropyl	39	92[a]
	85	*tert*-Amyl	88	62[a]
	13	*tert*-Amyl	26	86[a]
	75	Isobutyl	90	89[a]
	5	*n*-Butyl[b]	9	90[c]
o-$CH_3OC_6H_4$	5	*tert*-Butyl	10	76[c]
	9	*tert*-Amyl	30	83[c]
3,5-$(NO_2)_2C_6H_3$	6	*tert*-Butyl	13	0[a]
m-ClC_6H_4	8.5	*tert*-Butyl	25	80[c]

[a] Determined by glpc. [b] Potassium *tert*-butoxide (9 mmol) also was present. No *tert*-butyl benzoate was found. [c] Isolated and weighed.

Potassium alkoxides are readily formed *in situ* by the iron-catalyzed reaction of potassium metal with tertiary alcohols in liquid ammonia.[8]

The second step is quite fast, and the conversion is complete in about 45 min. As expected, with primary alcohols the transesterification is even faster, as was demonstrated by an experiment in which equal amounts of primary and tertiary alkoxides were allowed to compete with phenyl benzoate. No tertiary ester was found, but *ca.* 90% of the primary ester was formed. In the cases we have examined the yields of the second step are 80–90%. Results obtained are summarized in Table I.

In the second step, two main factors cause the reaction to proceed in the desired direction. First, the phenoxide anion is a better leaving group (lower pK_a) that any aliphatic alkoxide. Second, potassium phenoxide appears to be less soluble in the reaction medium; we observed that at the end of the reaction a white precipitate is present, presumably potassium phenoxide.

Among others, this method has the advantage that the two operational steps are easy to perform, quickly, and since the solvent is ammonia the product is easily isolated from the reaction mixture. Small-scale preparations are feasible with this method because the reaction is very clean and the corresponding benzamide (2–10%) is the only contaminating product. This impurity is very easy to remove (see Experimental Section).

Substituents such as alkoxy and halogen in the aromatic moiety survive, as probably would also alkyl, aryl, and aryloxy groups. Also, alcohols sensitive to heat or acids would survive under our reaction conditions.

When an attempt was made to utilize phenyl 3,5-dinitrobenzoate in this synthesis, a deep red color was formed immediately after mixing the reagents, probably due to σ-complex formation,[9] and no transesterification product was found.

Experimental Section

Phenyl benzoates were prepared by the method of Lawrence.[7] The structures of the esters were established by melting point, nmr, ir, and agreement of physical constants with published data. Benzoic acids were all commercially available materials. Boiling and melting points are uncorrected. Infrared spectra were recorded on a Beckman IR-8 spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian T-60 spectrometer, using carbon tetrachloride as solvent and TMS as internal standard. Gas chromatographic analyses were performed on an F

& M Biomedical Gas Chromatograph Model 400, and yields were obtained using biphenyl as internal standard with appropiate corrections being made for relative response factors. A 4 ft × 3/16 in. column packed with 4% silicon rubber SE-30 on 60/80 Chromosorb P was used.

Transesterification of Phenyl Benzoates with Alkoxides. A procedure for transesterification of phenyl benzoate with potassium *tert*-butoxide is representative. Dried liquid ammonia from a commercial cylinder was condensed in a three-necked, round-bottomed flask (1 l.) fitted with a cold-finger condenser containing solid CO_2 in methyl alcohol and a magnetic stirrer and was constantly swept by a slow stream of dry N_2. Potassium metal (0.042 mol) was added, and the *tert*-butyl alcohol (0.042 mol) was added dropwise followed by the addition of a small amount (2–5 mg) of solid ferric chloride to catalyze the formation of potassium *tert*-butoxide. (*Caution:* very little catalyst should be used because the reaction can become violent.) Without ferric chloride the formation of potassium *tert*-butoxide is remarkably slow; 2–3 hr are necessary for completion. Solid phenyl benzoate (0.041 mol) was then added at once with stirring, and after 50 min the reaction solution was quenched by the addition of ammonium chloride. The ammonia was then allowed to evaporate. Water and ether were added and the two layers were separated. The aqueous phase was extracted with ether and the combined ether extracts were washed with 10% sodium hydroxide solution to remove phenol. This was further washed with water until neutral and dried over anhydrous sodium sulfate. A small portion of the ether extract was examined by glpc, and *tert*-butyl benzoate (91%) together with unreacted phenyl benzoate (3%) were identified. The ether was removed and the residue was distilled *in vacuo*, yielding 6.52 g (77%) of *tert*-butyl benzoate, bp 108–110° (20 mm), 97% pure by glpc, and the structure was confirmed by nmr and ir. The residue after distillation was washed with pentane, and the remaining white precipitate was identified as benzamide (3% yield) by its melting point (126–128°), nmr, and ir compared with those of an authentic sample. In small-scale preparations (5–8 mmol) the procedure was the same but the crude product was dissolved in pentane and the undissolved benzamide was removed before glpc analysis.

Properties of Alkyl Benzoic Esters. 2-propyl benzoate had bp 93–96° (19 mm), nmr δ 1.28 (d, J = 6.3 Hz, 6 H), 5.12 (septet, J = 6.3 Hz, 1 H), 7.2 (m, 3 H), and 7.9 (m, 2 H). *tert*-Butyl benzoate had bp 108–110° (20 mm), nmr δ 1.56 (s, 9 H), 7.4 (m, 3 H), and 8.0 (m, 2 H). *tert*-Amyl benzoate had bp 120–122° (20 mm), nmr δ 0.97 (t, J = 7 Hz, 3 H), 1.53 (s, 6 H), 1.91 (q, J = 7 Hz, 2 H), 7.4 (m, 3 H), and 8.0 (m, 2 H). Isobutyl benzoate had bp 114–117° (20 mm), nmr δ 0.97 (d, J = 6.7 Hz, 6 H), 2.02 (m, 1 H), 4.10 (d, J = 6.7 Hz, 2 H), 7.4 (m, 3 H), 8.0 (m, 2 H). *n*-Butyl benzoate had nmr δ 0.93 (m, 3 H), 1.2–1.8 (m, 4 H), 4.24 ("t", 2 H), 7.4 (m, 3 H), and 8.0 (m, 2 H). *tert*-Butyl 2-methoxybenzoate had nmr δ 1.90 (s, 9 H), 3.72 (s, 3 H), 6.8–7.8 (m, 4 H). *tert*-Amyl 2-methoxybenzoate had nmr 0.97 (t, J = 7 Hz, 3 H), 1.52 (s, 6 H), 1.89 (q, J = 7 Hz, 2 H), 3.74 (s, 3 H), 6.8–7.8 (m, 4 H). *tert*-Butyl *m*-chlorobenzoate had bp 123–125° (18 mm), nmr δ 1.58 (s, 9 H), 7.2–8.0 (m, 4 H).

Acknowledgment. We thank Professor Joseph F. Bunnett for helpful suggestions and critical reading of the manuscript. The gas chromatograph made available to us by Dr. R. Caputto is greatly appreciated.

Registry No.—2-Propyl benzoate, 939-48-0; *tert*-butyl benzoate, 774-65-2; *tert*-amyl benzoate, 3581-70-2; isobutyl benzoate, 120-50-3; *n*-butyl benzoate, 136-60-7; *tert*-butyl 2-methoxybenzoate, 16537-20-5; *tert*-amyl 2-methoxybenzoate, 50507-00-1; *tert*-butyl *m*-chlorobenzoate, 16537-17-0.

References and Notes

(1) Research supported in part by the Consejo Nacional de Investigaciones Cientificas y Técnicas, Argentina.
(2) *Cf.* J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill, New York, N. Y., 1968 p 320.
(3) R. C. Parish and L. M. Stock, *J. Org. Chem.*, **30**, 927 (1965); M. S. Newman, *J. Amer. Chem. Soc.*, **63**, 2431 (1941); S. B. Lippincott, U. S. Patent 2,476,052 (July 12, 1949); *Chem. Abstr.*, **43**, 7951e (1949).
(4) J. F. Norris and G. W. Rigby, *J. Amer. Chem. Soc.*, **54**, 2088 (1932); E. M. Kaiser and R. H. Woodruff, *J. Org. Chem.*, **35**, 1198 (1970).
(5) J. Raber and D. Gariano, *Tetrahedron Lett.*, 4741 (1971).
(6) R. A. Rossi and J. F. Bunnett, *J. Amer. Chem. Soc.*, submitted for publication.
(7) W. W. Lawrence, Jr., *Tetrahedron Lett.*, 3453 (1971).
(8) It is remarkable that formation of potassium alkoxides from the alcohol and potassium metal in liquid ammonia is very slow in the absence of catalyst, but it is achieved in a few minutes in the presence of small amounts of ferric chloride.
(9) M. Strauss, *Chem. Rev.*, **70**, 667 (1970).