other data for representative syntheses are given in Table II. The BH_3OH^- concentration of a solution was determined by measurement of the hydrogen evolved upon heating at 60 °C for 30 min or longer. The BH_4^- content was then determined from the hydrogen evolved upon addition of excess HCl. The percent yield of BH_3OH^- was calculated from the BH_3OH^- analysis and the boron analysis of a completely hydrolyzed sample. The boron-11 NMR spectrum of a 0.35 M solution of BH_3OH^- was recorded at 0 °C on a Varian HA-100 spectrometer using a carbon-13 probe and by lowering the magnetic field to resonate for boron-11 at 25.15 MHz.

Esters. An ice-cold solution (35 mL) containing 10 mmol of BH_3OH^- was adjusted to pH 11.9 by the addition of approximately 10 mL of a diethylamine–diethylammonium chloride solution. A solution of 1 mmol of ethyl benzoate in 3 mL of cold acetonitrile was added, and the mixture was stirred at 0 °C for 17 h before quenching the reaction by adding excess 1 M HCl. After quenching, 1 mmol of octyl alcohol (internal standard) was added; the mixture was extracted with three 15-mL portions of diethyl ether, and the combined extracts were analyzed by GLC. A 10-ft long, ⅛ in. o.d. column, packed with 5% Carbowax 20M on acid-washed Chromosorb W support, was used.

Benzonitrile. The pH of an ice-cold solution containing 20 mmol of BH_3OH^- was adjusted to 12.5 with ice-cold diethylamine–diethylammonium chloride solution, and a solution of 1.96 mmol of benzonitrile in 5 mL of methanol was added. The reaction mixture was held at 25 °C and stirred for 16 h. The mixture was then quenched with 1 M HCl; 1 mmol of valeronitrile was added as an internal standard, and the solution was again made alkaline with NaOH before extracting with three 15-mL portions of diethyl ether. The ether extracts were washed with a known amount of acid, and the yield of benzylamine was determined by titration with standard NaOH solution. To check the titration results, the solution was made approximately 1 M in OH^-, a small excess of benzoyl chloride was added, and the precipitated benzyl benzamide was filtered, dried, and weighed. The calculated yields agreed within 2%. Unconsumed benzonitrile was determined by GLC of the ether extracts using a column of 5% FFAP on Chromosorb G.

Nitrobenzene. Two millimoles of nitrobenzenes in 5 mL of methanol was added to an ice-cold solution containing 20 mmol of BH_3OH^-. The pH of the solution was adjusted to 11.7, and the reaction mixture was stirred for 5 h at 6 °C. Then the pH was adjusted to approximately 7 by adding a solution of oxalic acid. One millimole of valeronitrile (internal standard) was added; the mixture was extracted with three 15-mL portions of diethyl ether, and the extracts were analyzed by GLC utilizing the same column used to analyze for benzylamine.

Ketones. An ice-cold solution (25 mL) containing 10 mmol of BH_3OH^- was added to an ice-cold solution of 5 mmol of benzophenone in 35 mL of methanol, and the mixture was stirred. After 15 min, a white precipitate of diphenylmethanol had formed, and the reaction was stopped by adding 1 M HCl. The product was filtered, dried, and weighed: yield, 0.924 g, 84% of theory. After recrystallization from ligroin, the melting point was 67–69 °C (lit.[9] 69 °C). Diglyme and tetrahydrofuran were used as cosolvents for some of the ketones, with no significant changes in the yields. In the case of cyclopentanone and 2-methylcyclohexanone, the products were liquids, and yields were determined by GLC using a column packed with 5% SE-30 on acid-washed Chromasorb W support.

Alkyl Halides. A solution of the halide and decane (internal standard) in ice-cold methanol was mixed with ice-cold BH_3OH^- solution. After 5 or 48 h (depending on whether the pH was ca. 11.6 or ca. 12.6, respectively), an aliquot of the reaction mixture was quenched with 1 M HCl and extracted with three 15-mL portions of diethyl ether. No octane was found in the extracts by GLC.

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A Convenient Synthesis of Methacrylates

Allen R. Banks,* Richard F. Fibiger, and Ted Jones

AMC Cancer Research Center and Hospital, Lakewood, Colorado 80214

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Previous syntheses of acrylate and methacrylate esters have generally proved tedious and have often produced the desired esters in only fair yields.[1-4] The usual methods of synthesis have utilized the reaction of methacryloyl chloride and an alcohol in the presence of triethylamine or a transesterification employing methyl methacrylate, the desired alcohol, and a trace of acid catalyst.[5,6] Competing polymerization of the reactive α,β-unsaturated esters caused by traces of free acid which are inevitably present during such reactions is often a primary cause of the low yields reported. Difficult separations of closely boiling liquids and further polymerization of the product during distillation can cause additional reductions in the overall yields. Our interest in a large variety of methacrylate esters prompted us to investigate other methods of preparing these compounds.

Molecular sieves are widely used as drying agents for organic solvents and in a few instances have been used to trap water generated during a reaction.[7-11] The ability of molecular sieves to scavenge other small molecules such as hydrogen chloride has been exploited in only a few cases.[12,13] The capacity of molecular sieves to absorb the hydrogen chloride liberated from the reaction of methacryloyl chloride and an alcohol was predicted to favor product formation as well as to prevent any polymerization. It was found that powdered 3 Å molecular sieves in refluxing carbon tetrachloride or ethylene chloride rapidly absorb the hydrogen chloride produced by the reaction of methacryloyl chloride (**1**) with a number of primary, secondary, tertiary, benzylic alcohols (**2a–d**), and phenols (**2e–j**) to form the esters **3** in good to excellent yields (Table I).

$$\underset{\mathbf{1}}{CH_2{=}C(CH_3)COCl} + \underset{\mathbf{2}}{ROH} \xrightarrow{3\ \text{Å molecular sieves}} \underset{\mathbf{3}}{CH_2{=}C(CH_3)COOR}$$

The solvents of choice for these reactions are carbon tetrachloride for ordinary alcohols and ethylene chloride or acetonitrile for alcohols which are not soluble in carbon tetrachloride. Oxygen-containing solvents such as tetrahydrofuran and ethyl acetate were found to interfere with the trapping of hydrogen chloride by the molecular sieves. The capacity of the molecular sieves to prevent polymerization of the reactants allows reaction times (refluxing solvent) of at least 200 h with no evidence of polymer formation. Product isolation requires only separation of the molecular sieves by filtration of the cooled reaction mixture followed by evaporation of the solvent and any excess methacryloyl chloride under reduced pressure. Final purification of the ester is accomplished by simple vacuum distillation. Some of the higher molecular weight

Table I. Preparation of Methacrylate Esters $H_2C=C(CH_3)CO_2R$ 3

Alcohols 2	Registry no.	R	Isolated yield 3, %	Reaction time, h	Solvent	Registry no.
a	71-36-3	$CH_3(CH_2)_3$	91	13	CCl_4	97-88-1 (3a)
b	96-41-3	Cyclopentyl	95	20	CCl_4	16868-14-7 (3b)
c	77-74-7	$(CH_3CH_2)_2CH_3C$	50 (100)[a]	185[b]	CCl_4	63715-93-5 (3c)
d	100-51-6	$C_6H_5CH_2$	85	12	CCl_4	2495-37-6 (3d)
e	108-95-2	C_6H_5	98	39	CCl_4	2177-70-0 (3e)
f	108-39-4	m-$CH_3C_6H_4$	93	50	CCl_4	14908-64-6 (3f)
g	100-02-7	p-$NO_2C_6H_4$	74	56	$ClCH_2CH_2Cl$	16522-41-1 (3g)
h	106-48-9	p-ClC_6H_4	94	56	CCl_4	16522-37-5 (3h)
i	108-43-0	m-ClC_6H_4	87	60	CCl_4	30322-45-3 (3i)
j	95-57-8	o-ClC_6H_4	93	160	CCl_4	18967-23-2 (3j)

[a] Yield based on reacted alcohol. [b] Time required for the reaction to proceed to 50% completion.

esters were found to polymerize if distillation temperatures in excess of 100 °C were employed. In these cases purification by short-path distillation or recrystallization prevented decomposition of the product. The purified methacryloyl chloride and any esters synthesized are best stored at −20 °C over molecular sieves. This procedure minimizes any polymerization from prolonged storage and unlike most stabilizers the molecular sieves allow immediate access to the pure compounds.

It is apparent, from inspection of Table I, that the reaction times for primary, secondary, and benzylic alcohols are convenient for general synthetic applications. Phenols require at most 60 h of refluxing, but this relatively long reaction time is justified by the high yields obtained from this procedure. Esters derived from tertiary or highly hindered alcohols are notoriously difficult to prepare. The use of powdered molecular sieves to prevent polymerization allows one to successfully employ the long reaction time necessary to prepare these elusive hindered esters in reasonable yields.

We feel that the use of molecular sieves as a stabilizer for acid-sensitive compounds such as 3 may find numerous synthetic applications.

Experimental Section

Melting points were determined on Fisher–Johns apparatus and are not corrected. Elemental analyses were performed by Atlantic Microlab, Atlanta, Ga. IR spectra were recorded on a Beckmann IR-4. NMR and mass spectra were obtained on Varian EM-360 and MAT CH5 spectrometer, respectively.

General Procedure. To 4 g of powdered 3 Å molecular sieves (Davison Chemical, dried under vacuum) and 20 mmol of the desired alcohol in a stirred solution of 40 mL of carbon tetrachloride was added 25 mmol of methacryloyl chloride. The reaction mixture was heated to reflux and when no starting material was evident by NMR the reaction mixture was cooled to room temperature and filtered. The solvent and excess methacryloyl chloride were removed under reduced pressure to yield the crude product. Recrystallization of solids or distillation of liquids under reduced pressure gave high yields of the esters listed in Table I.

Spectral Data for Esters 3. 3a: bp 66 °C (17 mm Hg); IR (neat) 2960, 2930, 1715, 1635, 1455, 1335, 1170, 1065, and 1015 cm^{-1}; NMR ($CDCl_3$) δ 0.95 (m, 3 H), 1.57 (m, 4 H), 1.93 (m, 3 H), 4.15 (t, J = 6 Hz, 2 H), 5.53 (m, 1 H), and 6.10 ppm (m, 1 H); MS m/e 142 (M^+, 1%) and 69 (100%). Anal. ($C_8H_{14}O_2$) C, H.

3b: bp 79–80 °C (7 mm Hg); IR (neat) 2960, 2870, 1710, 1630, 1450, and 1180 cm^{-1}; NMR ($CDCl_3$) δ 1.80 (m, 8 H) 1.98 (m, 3 H), 5.25 (m, 1 H), 5.50 (m, 1 H), and 6.05 ppm (m, 1 H); MS m/e 154 (M^+, 1%) and 69 (100%). Anal. ($C_9H_{14}O_2$) C, H.

3c: bp 165–168 °C (640 mm Hg); IR (neat) 2969, 2930, 1710, 1630, 1460, 1380, 1185, and 1130 cm^{-1}; NMR ($CDCl_3$) δ 1.00 (m, 6 H), 1.41 (s, 3 H), 1.80 (m, 7 H), 5.49 (m, 1 H), and 6.08 ppm (m, 1 H); MS m/e 170 (M^+, <1%) and 69 (100%). Anal. ($C_{10}H_{18}O_2$) C, H.

3d: bp 56 °C (0.15 mm Hg); IR (neat) 3095–3040, 2937, 2900, 1717, 1637, 1455, 1165, 1020, 760, 745, and 708 cm^{-1}; NMR ($CDCl_3$) δ 1.97 (m, 3 H), 5.18 (s, 2 H), 5.58 (m, 1 H), 6.15 (m, 1 H), and 7.33 ppm (s, 5 H); MS m/e 176 (M^+, 35%), 91 (100%), and 69 (63%). Anal. ($C_{11}H_{12}O_2$) C, H.

3e: bp 40 °C (0.15 mm Hg); IR (neat) 3060–3030, 2975–2920, 1725, 1630, 1200, 1160, 1130, 750, and 690 cm^{-1}; NMR ($CDCl_3$) δ 2.03 (m, 3 H), 5.72 (m, 1 H), 6.32 (m, 1 H), and 7.23 ppm (m, 5 H); MS m/e 162 (M^+, 34%) and 69 (100%). Anal. ($C_{10}H_{10}O_2$) C, H.

3f: bp 55–57 °C (0.1 mm Hg); IR (neat) 1730, 1635, 1610, 1585, 1490, and 1155 cm^{-1}; NMR ($CDCl_3$) δ 2.00 (m, 3 H), 2.30 (s, 3 H), 5.67 (m, 1 H), 6.31 (m, 1 H), and 7.00 ppm (m, 4 H); MS m/e 176 (M^+, 18%) and 69 (100%). Anal. ($C_{11}H_{12}O_2$) C, H.

3g: mp 93.5–94.5 °C; IR (KBr) 3080, 1730, 1625, 1605, 1585, 1515, 1350, and 1215 cm^{-1}; NMR ($CDCl_3$) δ 2.00 (m, 3 H), 5.80 (m, 1 H), 6.35 (m, 1 H), 7.28 (AA', 2 H), and 8.27 ppm (BB', 2 H); MS m/e 207 (M^+, 7%) and 69 (100%). Anal. ($C_{10}H_9NO_4$) C, H.

3h: bp 61 °C (0.08 mm Hg); IR (neat) 3090, 1735, 1632, 1585, 1205, 1165, 1130, 1095, and 810 cm^{-1}; NMR ($CDCl_3$) δ 2.03 (m, 3 H), 5.70 (m, 1 H), 6.33 (m, 1 H), and 7.20 ppm (AA'BB', 4 H); MS m/e 198 (M^+, 4%), 196 (M^+, 11%), and 69 (100%). Anal. ($C_{10}H_9ClO_2$) C, H.

3i: bp 65 °C (0.1 mm Hg); IR (neat) 3065, 1725, 1630, 1585, 1205, 1125, and 680 cm^{-1}; NMR ($CDCl_3$) δ 2.00 (m, 3 H), 5.73 (m, 1 H), 6.33 (m, 1 H), and 7.15 ppm (m, 4 H); MS m/e 198 (M^+, 4%), 196 (M^+, 11%), and 69 (100%). Anal. ($C_{10}H_9ClO_2$) C, H.

3j: bp 55 °C (0.07 mm Hg); IR (neat) 3070, 1740, 1635, 1585, 1220, 1135, 1125, 1065, and 758 cm^{-1}; NMR ($CDCl_3$) δ 2.02 (m, 3 H); 5.70 (m, 1 H), 6.35 (m, 1 H), and 7.20 ppm (m, 4 H); MS m/e 198 (M^+, 5%), 196 (M^+, 16%), and 69 (100%). Anal. ($C_{10}H_9ClO_2$) C, H.

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