Polymer-Bound Sulfonylhydrazine Functionality. Preparation, Characterization, and Reactions of Copoly(styrene–divinylbenzenesulfonylhydrazine)

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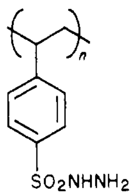
A resin has been prepared which consists of a porous highly cross-linked polystyrene–divinylbenzene matrix functionalized with sulfonylhydrazine groups in the range of 0.8–5.2 mmol/g. The quantity of functional group can be determined by measuring the amount of nitrogen evolved when the resin is treated with sodium hypochlorite. The resin reacts with aldehydes, ketones, and glucose presumably to form the sulfonylhydrazone derivatives. The extent of reaction with ketones is sensitive to the bulk of the ketone, ranging from >90% with acetone to <2% with camphor. Both ketones and aldehydes can be displaced from the resin by pyruvic acid. On heating, the resin evolves diimide which hydrogenates the carbon–carbon double bond in alkenes additionally functionalized by a sulfide group, a carboxyl group, or a carbonyl group. Deuteration of the double bond occurs when the reaction is carried out in the presence of deuterium oxide or polymer with deuterated hydrazine groups as shown by the formation of benzyl 2,3-dideuteriopropyl sulfide from allyl benzyl sulfide and *threo*-2,3-dideuterio-3-phenylpropanoic acid from *trans*-cinnamic acid. Monodeuterated products were also formed. Spent polymer which has been used for diimide generation can be recycled to regenerate resin in the sulfonylhydrazine form.

The preparation of a poly(styrenesulfonylhydrazine) (I)



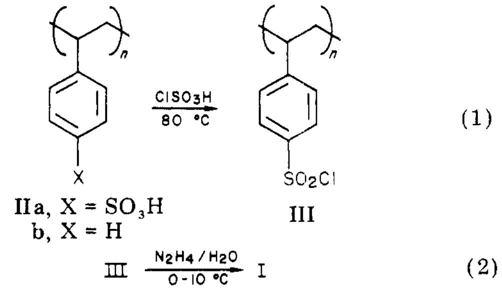
I

and its reaction with acetone in 0.1% concentration in water has been reported.[1] Our interest was to explore the potential of I as a possible source of diimide[2] and to examine in some detail the reaction of I with aldehydes and ketones.

Results and Discussion

The polymers employed as starting reagents for this investigation were the commercially available, macroreticular, sulfonic acid ion-exchange resin Amberlyst-15[3a] and a 20% cross-linked styrene–divinylbenzene copolymer. Either material (II) is readily converted by chlorosulfonic acid at 80 °C to the intermediate poly(styrene–divinylbenzenesulfonyl chloride) (III),[3b,c] and thence by the action of hydrazine–water solutions to I (Scheme I).

Scheme I



The products I were characterized in two ways: (1) a total exchange capacity measurement[4] to determine acidic protons in I, and (2) estimation of the sulfonylhydrazine functional group by gasometric determination of the nitrogen produced when I is treated with excess sodium hypochlorite. The results of several preparations are shown in Table I. In general, it was observed that a high loading of sulfonyl chloride groups in III is favored by a high mole ratio (10:1) of chlorosulfonic acid to II,[3c] that the amount of sulfonylhydrazine function incorporated in I is not sensitive to the water–hydrazine ratio, that it is unnecessary to use THF as a diluent[1] for the hydrazine–water mixtures, that I can be prepared from recycled polymer (see below), and that it is important to add III to the water–hydrazine mixtures slowly to avoid overheating of the reaction mixture. Elemental analysis gives good agreement of nitrogen content but indicates somewhat more sulfur than can be accounted for by the sulfonylhydrazine groups and groups having exchangeable hydrogens.

The reaction of I with aldehydes and ketones (reaction 3) produced varied results. Portions of I were dried in vacuo to constant weight and then treated with solutions of various aldehydes and ketones in dioxane or benzene. The amount of carbonyl compound combining with I was calculated from the increase in weight of the resin after washing and again drying the resin in vacuo to constant weight. It was established that samples of I did not show a significant weight gain when treated with dioxane or benzene alone in the absence of the carbonyl compound. The results are shown in Table II. It is evident that not all of the functional groups of I react with a carbonyl compound even in the presence of a large excess of the latter, which suggests that some of the sulfonylhydrazine groups are in an environment too crowded to accommodate the hydrocarbon residues of bulky ketones. The trends observed, e.g., >90% of the functional groups of I react

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[1] S. Sevcik, J. Stamberg, and A. Story, Czechoslovakian Patent 120 156 (1966); *Chem. Abstr.*, **68**, 68699 (1968).

[2] (a) F. Raschig, *Angew. Chem.*, **23**, 972 (1910); (b) R. S. Dewey and E. E. van Tamelen, *J. Am. Chem. Soc.*, **83**, 3729 (1961); (c) S. Hünig, H.-R. Müller, and W. Thier, *Tetrahedron Lett.*, 353 (1961); (d) S. Hünig, H.-R. Müller, and W. Thier, *Angew. Chem., Int. Ed. Engl.*, **4**, 271 (1965), and references cited therein; (e) C. E. Miller, *J. Chem. Educ.*, **42**, 254 (1965), and references cited therein. (f) While this manuscript was under editorial consideration, the generation of diimide from a similar polymer was reported: F. Gavina, P. Gil, and B. Palazón, *Tetrahedron Lett.*, 1333 (1979).

[3] (a) R. Kunin, E. Meitzner, and N. Bortnick, *J. Am. Chem. Soc.*, **84**, 305 (1962); (b) W. R. Roush, D. Feitler, and J. Rebek, *Tetrahedron Lett.*, 1391 (1974); (c) D. W. Emerson and E. M. Sorensen, *Ind. Eng. Chem. Prod. Res. Dev.*, **17**, 269 (1978), and references cited therein.

[4] R. Kunin, "Ion Exchange Resins", 2nd ed., Wiley, New York, N.Y., 1958, p 341ff.

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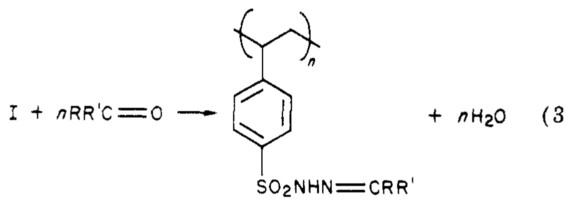


(3)

IV

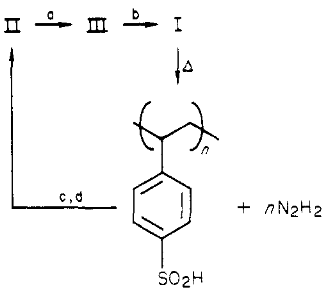
with acetone but <2% react with camphor, strongly suggest the operation of a steric effect with the smaller and/or "flatter" carbonyl compounds reacting with a higher proportion of the sulfonylhydrazine groups. Increasing the loading of functional group on I did not result in an increased weight uptake of 2-pentanone or cyclopentanone (items 8, 9, 12, and 15, Table II) at the same ketone to sulfonylhydrazine mole ratio. Using a tenfold molar excess of cyclopentanone did not result in a very different uptake of cyclopentanone compared with the experiment in which equimolar amounts were used (items 12 and 13, Table II). It was found that glucose reacts with I to a modest extent, a result anticipated by analogy with the reactions of *p*-toluenesulfonylhydrazine with sugars[5] (items 20–24, Table II). Interestingly, treatment of I with glucose followed by treatment with cyclohexanone reduced the ability of I to combine with cyclohexanone by about two-thirds even though >80% of the sulfonylhydrazine functional groups of I must have remained intact during the glucose treatment (items 18 and 19, Table II).

It was found in the few cases attempted that aldehydes and ketones which had combined with I, presumably to form IV, could be recovered by treatment of IV with pyruvic acid, a procedure which is useful with tosylhydrazones.[6] Cyclopentanone was recovered in 72% yield from the corresponding IV and butyraldehyde in 17% yield. In the case of butyraldehyde its low boiling point was probably a factor in the low recovery and no attempt was made to optimize the yield.

It was expected that I would serve as a source of diimide by analogy with nonpolymeric arenesulfonylhydrazines.[2] The polymeric diimide source, I, should offer distinct advantages in product workup inasmuch as somewhat soluble arenesulfinic acids and arenesulfinic acid decomposition products would be avoided.[2b] These expectations were amply justified. The hydrogenation of allyl benzyl sulfide to benzyl *n*-propyl sulfide (V) was accomplished in 99% yield (Table III) when the substrate in dioxane containing *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) was refluxed with I.

The inability of I to react extensively to bind bulky ketones as the sulfonylhydrazones (IV) prompted us to attempt the hydrogenation of the carbon–carbon double bond of unsaturated ketones. The most exposed functional groups of I were blocked by reaction with glucose and then the modified I was used to generate diimide for the hydrogenation of 2-acetyl-5-norbornene (Table III). A nearly quantitative yield of 2-acetylnorbornane was obtained. Without prior glucose treatment of I the yield was 51%. The α,β-unsaturated ketones 2-cyclohexenone and 3-methylene-2-norbornanone were hydrogenated at the carbon–carbon double bond, but the amounts of saturated ketones recovered were very low.[7] 6-Methyl-5-hepten-2-one was hydrogenated. The material which was recovered by a normal workup (see Experimental Section) was estimated by NMR and GLC analysis to be 42% 6-methyl-2-heptanone. A very small amount of additional material displaced from the spent resin by pyruvic acid was shown by GLC analysis to contain equal quantities of starting material and 6-methyl-2-heptanone and some more volatile unidentified material. The resistance of the triply substituted ethylenic double bond to hydrogenation by diimide was anticipated from a previous report.[8]

Scheme II[a]



[a] a, $ClSO_3H$, 80 °C; b, N_2H_4/H_2O, 0–10 °C; c, NaOCl; d, H^+.

Deuteration of double bonds was attempted by treating I with deuterium oxide, drying it, and conducting the hydrogenation in anhydrous dioxane or by conducting the hydrogenation in the presence of deuterium oxide. Deuteration of double bonds has been accomplished by dideuteriodiimide generated by the action of acids on dipotassium diazodicarboxylate in deuterium oxide[8] or oxidation of perdeuteriohydrazine.[8,9] Allyl benzyl sulfide in a mixture of dioxane and deuterium oxide was converted to *dl*-benzyl 2,3-dideuteriopropyl sulfide (VI) in 41% yield and 19% of a mixture of monodeuterated benzyl *n*-propyl sulfides (VII), 2% V, and 16% starting material. Pretreatment of I with deuterium oxide followed by drying yielded 38% VI, 30% VII, 6.6% V, and 2.7% starting material. Treatment of *trans*-cinnamic acid with I in deuterium oxide yielded 25% *dl*-*threo*-2,3-dideuterio-3-phenylpropanoic acid,[10] 7% of a mixture of *dl*-2-[11a] and/or *dl*-3-(deuteriophenyl)propanoic acids, and 0.5% hydrocinnamic acid.

Recycling of the polymer is feasible (Scheme II). Polymer which had been used for the generation of diimide in a variety of different runs was oxidized by sodium hypochlorite to the sulfonic acid form, chlorosulfonated again, and converted to I. Some results are shown in Table I. Because the functional groups are immobilized on insoluble beads, the several regeneration steps in Scheme II, which might prove to be prohibitively tedious with soluble compounds, are conveniently carried out.

Experimental Section

All melting points and boiling points are uncorrected.

Copoly(styrene–divinylbenzenesulfonyl chloride) (III). Method A. Amberlyst-15[3a] (50 g) was placed in a 500-mL suction flask and 150 mL (264 g, 2.28 mol) of technical grade chlorosulfonic acid was added. The mixture was stirred gently for 1 h at 80 °C.

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[5] (a) K. Freudenberg and F. Blümmel, *Justus Liebigs Ann. Chem.*, **440**, 45 (1924); (b) K. Freudenberg and K. Raschig, *Ber. Dtsch. Chem. Ges.*, **62**, 373 (1929); (c) D. G. Easterby, L. Hough, and J. K. N. Jones, *J. Chem. Soc.*, 3416 (1951); (d) K. Freudenberg and K. von Oertzen, *Justus Liebigs Ann. Chem.*, **574**, 37 (1951); (e) J. C. Snowden and A. S. Spriggs, *J. Am. Chem. Soc.*, **78**, 2503 (1956).

[6] E. B. Hershberg, *J. Org. Chem.*, **13**, 542 (1948).

[7] E. E. van Tamelen, M. Davis, and M. F. Deem, *Chem. Commun.*, 71 (1965).

[8] E. J. Corey, D. J. Pasto, and W. L. Mock, *J. Am. Chem. Soc.*, **83**, 2957 (1961).

[9] U. Eppenberger, M. E. Warren, and H. Rappaport, *Helv. Chim. Acta*, **51**, 381 (1968).

[10] N. A. Dunham and M. C. Baird, *J. Chem. Soc., Dalton Trans.*, 774 (1975); and private communication from M.C.B.

[11] (a) D. J. G. Ives and M. R. Nettleton, *J. Chem. Soc.*, 1085 (1948); (b) F. A. Hochstein and W. G. Brown, *J. Am. Chem. Soc.*, **70**, 3484 (1948).

Table I. Preparation and Properties of Copoly(styrene-divinylbenzenesulfonylhydrazines) (I)

item	starting material[a]	hydrazinolysis		sulfonylhydrazine, mmol/g	total exchange capacity, mequiv H^+/g
		N_2H_4/g of III	$[H_2O]/[N_2H_4]$		
1	A	0.66	0.6	1.4	1.1
2	B	1.2	unknown	2.8	0.81
3	B[b]	0.95	1.8	4.2	0.64
4	B[c]	0.89	1.8	5.2	*h*
5	B	1.0	1.8	4.8	1.0
6	B[d]	1.0	1.9	4.0	0.5
7	B[e]	0.95	2.1	2.3	1.6
8	C[f]	1.0	1.8	3.0	0.61
9	C[f]	0.51	62.4	3.0	0.98
10	C[f]	1.6	2.7	3.1	*h*
11	C[f]	1.6	11	3.1	*h*
12	C[f]	1.6	22	3.0	*h*
13	*g*	1.0	1.8	3.5	0.65
14	B	1.0	3.0	4.0	0.49

[a] Starting material was the sulfonyl chloride form of the resin, ref 3c. A. Macroreticular polystyrene-DVB copolymer containing 20% DVB. Biobeads SM-2, Bio-Rad Laboratories. B. Amberlyst-15, macroreticular, sulfonated, styrene-DVB copolymer containing not less than 15% DVB. Rohm and Haas Chemical Co. C. Amberlyst-15 recycled from the sulfonylhydrazine form. See Scheme II. [b] Sulfonyl chloride stored for 36 days. [c] Same batch of sulfonyl chloride as item 3, stored 60 days. [d] Same batch of sulfonyl chloride as item 5, stored 77 days. [e] Same batch of sulfonyl chloride as item 5, stored 42 days. Resin was added to the hydrazine-water mixture fast enough that the reaction mixture became hot. [f] All from the same batch of resin C. [g] Amberlyst-15 recycled from sulfonamide and chlorosulfonated. [h] Not determined.

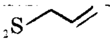
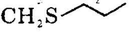
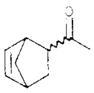
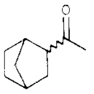
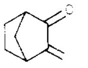
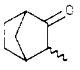
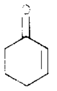
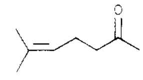
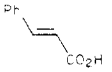
Table II. Reaction of Aldehydes and Ketones with Copoly(styrene-divinylbenzenesulfonylhydrazine)

	aldehyde or ketone	resin[a]/solvent[b]/mmol of $SO_2N_2H_3$ per g	reaction product			reactn condns, mol of $RR^1C=O$/mol of resin
			wt gain, g/g of resin	mmol/g of resin	mol/mol of resin	
1	none	A/1/2.3	−0.007			0
2	none	A/2/2.3	+0.014			0
3	acetone	B/1/2.8	0.109	2.73	0.93	10
4	2-butanone	B/1/2.8	0.113	2.09	0.72	10
5	butanal	B/1/2.8	0.142	2.63	0.91	10
6	butanal	G/1/4.0	0.176	3.13	0.78	10
7	2-methylpropanal	B/1/2.8	0.116	2.15	0.74	10
8	2-pentanone	B/1/2.8	0.128	1.88	0.66	10
9	2-pentanone	E/1/4.8	0.118	1.65	0.36	10
10	2-pentanone	E/1/4.8	0.076	1.09	0.23	0.5
11	3-pentanone	B/1/2.8	0.113	1.66	0.58	10
12	cyclopentanone	B/1/2.8	0.125	1.89	0.66	10
13	cyclopentanone	F/1/5.2	0.122	1.85	0.35	0.9
14	cyclopentanone	E/1/4.8	0.048	0.73	0.15	0.5
15	cyclopentanone	E/1/4.8	0.119	1.81	0.38	10
16	cyclohexanone	B/1/2.8	0.046	0.58	0.20	10
17	cyclohexanone	C/1/4.2	0.095	1.19	0.25	10
18	cyclohexanone	D/1/4.2	0.030	0.38	0.08	10
19	cyclohexanone	D/1/4.2	0.028	0.36	0.07	1
20	glucose	C/3/4.2	0.130	0.80	0.17	1.1
21	glucose	C/3/4.2	0.088	0.54	0.11	1.1
22	glucose	C/3/4.2	0.138	0.85	0.18	10
23	glucose	C/3/4.2	0.111	0.69	0.14	0.46
24	3,3-dimethyl-2-butanone	B/1/2.8	0.062	0.76	0.26	10
25	2-methylcyclohexanone	B/1/2.8	0.040	0.43	0.15	10
26	camphor	B/1/2.8	0.005	0.04	0.013	10
27	benzaldehyde	B/1/2.8	0.210	2.39	0.84	10
28	acetophenone	B/1/2.8	0.041	0.40	0.14	10
29	1,3-diphenyl-2-propanone	B/1/2.8	0.030	0.016	0.055	10
30	2-acetyl-5-norbornene	E/2/4.2	0.131	1.11	0.23	1.4
31	2-acetyl-5-norbornene	D/2/4.8	0.034	0.29	0.06	10
32	2-cyclohexen-1-one	E/2/4.8	0.132	1.69	0.35	2
33	2-cyclohexen-1-one	D/2/4.2	0.028	0.36	0.08	10
34	3-methylene-2-norbornanone	E/2/4.8	0.094	0.90	0.19	1.4
35	3-methylene-2-norbornanone	D/2/4.2	0.039	0.38	0.08	10
36	*l*-carvone	C/2/4.2	0.076	0.57	0.12	10
37	*l*-carvone	D/2/4.3	0.045	0.34	0.07	10

[a] The resins used were as follows: A, resin 6, Table I; B, resin 2, Table I, sodium sulfonate salt form; C, resin 3, Table I; D, resin C pretreated with an aqueous glucose solution; E, resin 5, Table I; F, resin 4, Table I; G, resin 6, Table I, sodium sulfonate salt form; H, resin 7, Table I. [b] Solvent: 1 = benzene, 2 = dioxane, 3 = water.

The mixture was filtered on a frit. The filter flask was changed and the resin was washed successively with two 100-mL portions of dichloromethane. The filter flask was replaced again and the resin was washed with two 100-mL portions of 4:1 v/v dichloromethane–THF, one 100-mL portion of 3:2 v/v dichloromethane–THF, 60 mL of THF, and 60 mL of dichloromethane.

Table III. Hydrogenations by Diimide Generated from I

item	substrate	conditions[h]	products (% yield)
1	PhCH$_2$S	dioxane, 3, TMEDA	PhCH$_2$S (99)
2	same	dioxane + D$_2$O, 3, TMEDA	dl-PhCH$_2$S-CH$_2$CHDCH$_2$D[a] (41) $\left.\begin{array}{l}dl\text{-PhCH}_2\text{SCH}_2\text{CHDCH}_3\\ \text{PhCH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{D}\end{array}\right]$ (19) PhCH$_2$S (2) starting material (16)
3	same	dioxane (I-d_3), 6, TMEDA	dl-PhCH$_2$SCH$_2$CHDCH$_2$D[a] (43) $\left.\begin{array}{l}dl\text{-PhCH}_2\text{SCH}_2\text{CHDCH}_3\\ \text{PhCH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{D}\end{array}\right]$ (32) PhCH$_2$S (6)
4		dioxane, 4, TMEDA	 (51)[b,c]
5	same	dioxane, 4, TMEDA, glucose	same (99)
6		dioxane, 4, TMEDA	 (10)[d]
7	same	dioxane, 4.7, TMEDA, glucose	same (4)
8		dioxane, 6.2, TMEDA	cyclohexanone (22)
9		dioxane, 3, TMEDA	6-methyl-2-heptanone (42[e]) starting material (58) 6-methyl-2-heptanone[f] starting material
10		D$_2$O, 5, CuBr$_2$	dl-*threo*-PhCHDCHDCO$_2$H[g] (25) $\left.\begin{array}{l}dl\text{-PhCHDCH}_2\text{CO}_2\text{H (7)}\\ dl\text{-PhCH}_2\text{CHDCO}_2\text{H}\end{array}\right]$ PhCH$_2$CH$_2$CO$_2$H (0.5)

[a] NMR spectrum (CCl$_4$-Me$_4$Si) showed δ 0.96 (d, 2 H), 1.50 (m, 1 H), 2.39 (d, 2 H), 3.74 (s, 2 H), 7.43 (s, 5 H). [b] Endo/exo ratio not determined. [c] NMR spectrum was clean below δ 3.0 and the CH$_3$C=O signal was a doublet at δ 2.09 and 2.12.[13] [d] NMR spectrum (CCl$_4$-Me$_4$Si) was clean below δ 2.85 and displayed a doublet at δ 1.01 (CH$_3$). [e] Material recovered from solution. Composition of mixture determined by GLC analysis (CCl$_4$-Me$_4$Si). NMR spectrum: δ 0.9 (d). [f] Material displaced from spent resin by pyruvic acid. GLC analysis showed other material but equal amounts of product and starting material. [g] The NMR spectrum (CDCl$_3$-Me$_4$Si) showed a downfield doublet (benzylic CHD) at δ 3.01 and a coupling constant of 6.5 Hz characteristic of the threo isomer.[10] [h] Solvent, mol I/mol substrate, catalyst, additive.

The resin was placed in a round-bottom flask and was dried to constant weight: yield, 51.3 g.

Method B. To 20 g of macroporous styrene–divinylbenzene copolymer (20% DVB, Bio Beads SM-2, Bio-Rad Laboratories) was added 107 g (0.93 mol) of technical grade chlorosulfonic acid. The mixture was kept at 60–80 °C for 1 h with occasional stirring. The product was filtered on a frit and was washed successively with two portions of dichloromethane, two portions of dichloromethane–THF mixture, two portions of THF, and a final wash with dichloromethane. A small portion of the product was lost due to a rapid pressure buildup in the suction flask. The vacuum-dried polymer weighed 20.0 g.

Copoly(styrene–divinylbenzenesulfonyl chloride) from Regenerated Amberlyst-15. Several batches of spent copoly(styrene–divinylbenzenesulfonylhydrazine) which had been used for the generation of diimide were combined and treated with 5.25% sodium hypochlorite. The resin was then filtered and washed with water, 20% sulfuric acid, and water again, and the resulting product was dried in vacuo to a constant weight of 44.6 g. A 2.50-g sample of this material was subjected to a total exchange capacity measurement[4] and had 3.33 mequiv/g of "strong acid" replaceable hydrogens. A 44.6-g sample of this material was subjected to chlorosulfonation as described above in method A: yield, 49.5 g. Copoly(styrene–divinylbenzenesulfonamide), which had been used for a number of purposes,[3c] was treated with dilute hydrochloric acid and a solution of 0.5 mol of sodium nitrite added in portions over a 2-h period. The resin was then washed with distilled water, 500 mL of dilute nitric acid, 500 mL of 15% sulfuric acid, 1.5 L of distilled water, two portions of methanol, and two portions of dichloromethane. The resin was air dried and then washed with 200 mL of 4 N nitric acid followed by distilled water until the effluent from the filter was at pH > 4. The resin was dried in vacuo to yield 42.8 g of product. A total exchange capacity measurement[4] was performed showing 3.4 mequiv of H$^+$/g of dry resin. The resin was chlorosulfonated in the usual manner.

Safety note: THF undergoes an exothermic reaction with chlorosulfonic acid;[15] hence it is advisable to use a dry suction flask when the washing solvent contains THF.

Copoly(styrene–divinylbenzenesulfonylhydrazine) (I). To an ice cold mixture of 30 g of hydrazine hydrate (0.60 mol of hydrazine) and 22.6 mL of water (1.80 mol total) externally cooled in an ice bath was added, in small portions, 20 g of III derived from Amberlyst-15. The reaction mixture was allowed to stand for 3 h in an ice bath. The resin was filtered off, washed with 200 mL of 3 N hydrochloric acid, and rinsed with distilled water until the pH > 5. Sodium sulfate (1 L, 4%) was passed over the resin and collected and the resin was rinsed with distilled water and allowed to dry. It was transferred to a round-bottom flask and was dried to constant weight at <1 torr: yield, 18.0 g. Many other batches of this material were prepared using minor variations of this procedure. The highest content of functional group was obtained when temperatures were kept low. The water–hydrazine mole ratio had little effect on the product; see Table I.

Analysis of I. A total exchange capacity measurement by the flow method[4] was performed. Three 50.0-mL aliquots of the 1.000 L of 4% sodium sulfate eluate were titrated to the phenolphthalein end point. The aliquots required 4.11, 4.10, and 4.10 mL of 0.1073

N NaOH. The total exchange capacity was 0.49 mequiv of H^+/g.

Sulfonylhydrazine Groups. A 0.1308-g portion of resin was placed in a 25-mL suction flask. The top of the flask was fitted with a septum and the sidearm was connected to a gas collecting buret. A 5.00-mL portion of 5.25% sodium hypochlorite solution was injected into the flask. After 3.5 h the water level in the buret was matched with that in the water reservoir (a sidearm test tube with a dip tube in the top connected to the delivery tube of the buret and sidearm connected to the reaction flask) and the buret was read. The ambient temperature was 22 °C and atmospheric pressure was 740 torr. A net 13.12 mL of gas was collected, over water, indicating the presence of 4.03 mmol of sulfonylhydrazine/g of I. A second determination with 0.1279 g of resin and 5.00 mL of sodium hypochlorite yielded, after 4.5 h, 13.20 mL of gas over water at 24 °C and 747 torr, indicating 4.04 mmol of sulfonylhydrazine/g of I. The underlying assumption in this method is that 1 mol of gas is equivalent to 1 mol of sulfonylhydrazine functional group. This assumption was checked by using *p*-toluenesulfonylhydrazine prepared by a standard method.[12] Using this material, a gas recovery of 95.6 ± 2.7% was obtained. A sample of I was placed in an Erlenmeyer flask with water and an azobenzene solution in 2,2,4-trimethylpentane (isooctane) was floated on the water layer. Bleach was injected into the lower layer and the resulting gas bubbled through the isooctane layer. There was no change in the concentration of the azobenzene solution. Thus, diimide, formed by the action of bleach on I, does not survive to escape the aqueous layer. Azobenzene is an efficient substrate for diimide[13] and a decrease in the azobenzene as measured by colorimetry would have been expected if diimide had passed into the isooctane layer. Elemental analysis of a sample of I (Spang Microanalytical Laboratory, Eagle Harbor, Mich.). Calcd: N, 11.30; S, 12.93 (basis sulfonylhydrazine groups only). Found: C, 49.33; H, 5.12; N, 11.46; S, 15.70.

Imbibition of Solvent by Copoly(styrene–divinylbenzenesulfonylhydrazine) (I). To 0.9019 g of I (item 7, Table I) was added 10 mL of benzene and the mixture was allowed to stand for 3 days. The resin was filtered off, washed with 15 mL of dichloromethane, and dried in vacuo to a constant weight of 0.8958 g: weight loss, 0.7%. A 1.1664-g sample of the same batch of resin was treated with 10 mL of dioxane for 3 days. The resin was filtered off and washed with 15 mL of dichloromethane, and the resin was dried in vacuo to a constant weight of 1.1817 g: weight gain, 1.5%.

Formation of Copoly(styrene–divinylbenzenesulfonylhydrazones) (IV). To 0.723 g of vacuum-dried I (3.0 mmol of $SO_2N_2H_3$) was added a solution of 2.88 g of cyclohexanone (2.94 mmol) in 10 mL of dioxane. The mixture was allowed to stand for 3 days. The resin was filtered off, washed with 40 mL of dichloromethane, and dried in vacuo to constant weight: yield, 0.792 g; weight gain, 0.069 g, or 1.19 mmol of cyclohexanone/g of I. The general procedure for conducting the experiments leading to the data in Table II was similar.

Reaction of I with Glucose. To 7.98 g of vacuum-dried I (33.5 mmol of $SO_2N_2H_3$) was added a solution of 60 g (333 mmol) of glucose in 120 mL of distilled water. The mixture was allowed to stand for 3.5 days, after which the resin was filtered off and washed with 1.5 L of distilled water. The resin was dried at <1 torr to a constant weight of 9.08 g. The weight gain of 1.10 g corresponds to an uptake of 0.85 mmol of glucose/g of I. Other preparations of glucose-treated I were done in an analogous manner.

Recovery of Cyclopentanone and Butyraldehyde as Their DNP Derivatives from Copoly(*N*-alkylidenestyrene–divinylbenzenesulfonylhydrazone). To 0.70 g of copoly(*N*-cyclopentylidenestyrene–divinylbenzenesulfonylhydrazine) (item 13, Table II, 1.15 mmol) were added 0.5 mL of water, 0.44 g of pyruvic acid (5 mmol), and enough dichloromethane to cover the resin. The mixture was refluxed for 1 h. Additional dichloromethane was added through the condenser and the resin was filtered off. The filtrate was extracted with aqueous sodium bicarbonate, dried over sodium sulfate, and concentrated on the rotary evaporator. The residue was treated with 2,4-dinitrophenylhydrazine reagent and 0.22 g of product, mp 141–142 °C, was obtained, corresponding to a 72% recovery of cyclopentanone. The corresponding procedure was applied to copoly(*N*-butylidenestyrene–divinylbenzenesulfonylhydrazone) to obtain 0.78 g of IV (item 5, Table II, 1.73 mmol). The evaporation of dichloromethane was omitted. The yield of twice recrystallized (ethanol, methanol) dinitrophenylhydrazone derivative, mp 120–121 °C (lit.[16] 120–122 °C), was 0.076 g, corresponding to a 17% recovery.

Hydrogenation of Allyl Benzyl Sulfide by Diimide Generated from I. In a round-bottom flask were placed 2.0 g of I in the sodium salt form (7.58 mmol), 0.44 g (2.68 mmol) of allyl benzyl sulfide, 0.46 g (3.97 mmol) of *N,N,N',N'*-tetramethylethylenediamine (TMEDA), and 10 mL of dioxane. The flask was connected to an apparatus which measured gas evolution by displacement of water. The mixture was refluxed for 7 h, and produced 6.78 mmol of gas. The inside of the condenser was rinsed with dichloromethane and the resin was filtered off and rinsed with three small portions of dichloromethane. The filtrate was extracted with dilute hydrochloric acid. The resin was washed with four portions of petroleum ether, 50 mL in all, which was then used in two portions to extract the hydrochloric acid layer. The combined organic layer was extracted with 20% brine and dried over sodium sulfate. The extract was concentrated on the rotary evaporator and the residue was subjected to a Kugelrohr distillation at 97 °C at approximately 10 torr. The product, benzyl *n*-propyl sulfide, weighed 0.44 g (yield 99%). The product was subjected to GLC analysis [12% Carbowax 20M on Chromosorb W (AW, HMDS treated), column 10 ft × $^1/_4$ in., 180 °C, 40 mL/min He flow, thermal conductivity detector]. There was no detectable unreacted allyl benzyl sulfide. NMR spectrum, δ 0.97 (t, 3 H), 1.55 (m, 2 H), 2.38 (t, 3 H), 3.72 (s, 5 H). Mass spectrum[17] (rel intensity) 168 (0.25), 167 (0.63), 166 (5.71), 165 (0.29), 123 (3.04), 122 (12.62), 121 (2.51), 92 (14.67), 91 (100.00), 73 (19.85), 65 (12.59), 59 (22.09), 45 (75.33).

Deuteration of Allyl Benzyl Sulfide by Dideuterodiimide. Procedure A. A round-bottom flask was charged with 1.86 g (8.9 mmol) of I (item 5, Table I) and 7.5 g of deuterium oxide (99.7 atom %). The flask was stoppered and allowed to stand for 16 h. With a pipet, 4.8 g of the deuterium oxide was removed and 3 mL of dioxane (passed through an alumina column immediately before use) was added and mixed. With a pipet, 2.8 mL of the liquid was removed from the flask and the following were added: 10 mL of dioxane, 1.0 mL of deuterium oxide, 0.42 g (2.56 mmol) of allyl benzyl sulfide, and 1.16 g (10 mmol) of TMEDA. The apparatus was topped by a drying tube containing calcium chloride and refluxed for 24 h. The product was worked up as in the hydrogenation of allyl benzyl sulfide. The Kugelrohr distillation yielded 0.36 g of material which was estimated by NMR analysis to contain 22% starting material and 78% deuterated and hydrogenated product: NMR of allyl benzyl sulfide, δ 3.02 (d, 2 H), 3.34 (s, 2 H), 4.95–6.4 (m, 3 H), 7.40 (d, 5 H); NMR of product, δ 0.93 (d, 23 units), 1.57 (t, 12 units), 2.37 (d, 21 units), 3.03 (d, 6 units), 3.68 (d, 27 units), 4.95–6.4 (m, 6 units), 7.40 (s, 64 units). The IR spectrum had a band at 2190 cm^{-1} not found in either starting material or benzyl *n*-propyl sulfide. Mass spectrum[17] (rel intensity) 170 (1.61), 169 (4.39), 168 (33.00), 167 (13.90), 166 (1.52), 125 (0.81), 124 (2.03), 123 (6.67), 122 (1.15), 121 (4.23), 92 (40.27), 91 (100.00), 79 (2.11), 78 (2.74), 77 (9.19), 76 (3.36), 75 (1.92), 74 (0.86), 73 (0.67), 66 (2.06), 65 (33.53), 59 (1.59), 45 (34.49).

Procedure B. A 3.1-g portion of I (item 5, Table I, 14.9 mmol) was soaked for 16 h in 12 mL of deuterium oxide in a closed flask. The bulk of the deuterium oxide was removed by pipet and the resin was dried in vacuo at room temperature. The procedure was repeated. To the flask were added 12.5 mL of dioxane (filtered through alumina just before use), 0.41 g (2.5 mmol) of allyl benzyl

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[17] Obtained using a Finnigan 4023 GC-MS and INCOS DATASYSTEM.

sulfide, and 1.74 g (15 mmol) of TMEDA. The apparatus was attached via a drying tube to a gas collector and the mixture was refluxed for 8 h, producing 9.7 mmol of gas. The product was worked up as before and yielded, after Kugelrohr distillation, 0.34 g, 81%: NMR (CCl_4) δ 0.96 (messy d), 1.53 (messy t), 2.38 (messy d), 3.70 (s), 7.42 (s); GLC analysis revealed 96.5% hydrogenated and deuterated product and 3.5% starting material; mass spectrum[17] (rel intensity) 170 (1.37), 169 (4.20), 168 (28.47), 167 (23.16), 166 (5.07), 125 (0.84), 124 (2.33), 123 (7.28), 122 (1.23), 121 (4.47), 92 (40.61), 91 (100.00), 79 (2.35), 78 (2.85), 77 (9.30), 76 (3.56), 75 (2.51), 74 (1.15), 73 (0.54), 66 (2.09), 65 (34.39), 59 (1.34), 45 (32.91). Another experiment run in the same way gave substantially similar results. The relative intensities of masses 168, 167, and 166 indicate that the product is 51% *dl*-benzyl 2,3-dideuteriopropyl sulfide and 40% of a combination of *dl*-benzyl 2-deuteriopropyl sulfide and benzyl 3-deuteriopropyl sulfide.

Deuteration of Cinnamic Acid. To 3.13 g of I (item 5, Table I, 15.0 mmol) were added 0.44 g (3.3 mmol) of cinnamic acid, 0.05 g of copper(II) bromide, 12.5 mL of deuterium oxide (99.7 atom %), and 0.75 g of sodium carbonate (7.07 mmol). The mixture was attached via a drying tube to a gas collector and was refluxed for 8 h, producing 12.9 mmol of gas. The resin was filtered off and the flask and resin were rinsed with 20 mL of hot 1 N sodium hydroxide. The filtrate was acidified with concentrated hydrochloric acid and the product was crystallized. It was recrystallized from water, yielding 0.15 g of product: mp 42.0–42.5 °C; yield 33%; NMR ($CDCl_3$) δ 2.75 (d), 3.01 (d, J = 6.5 Hz), 7.50 (s); mass spectrum[18] (rel intensity) of hydrocinnamic acid, 151 (3.8), 150 (37.7), 105 (15.8), 104 (41.2), 103 (67), 92 (7.9), 91 (100.0), 79 (6.8), 78 (11.5), 77 (11.9); mass spectrum of product[17] (rel intensity) 153 (3.01), 152 (30.15), 151 (8.30), 150 (0.58), 107 (13.06), 106 (37.46), 105 (27.89), 104 (7.58), 103 (1.72), 94 (0.49), 93 (8.98), 92 (100.0), 91 (29.59), 81 (3.10), 80 (6.18), 79 (11.97), 78 (15.93), 77 (8.26). Comparison of masses 152, 151, and 150 of the reference spectrum[18] and the product indicates that the product consists of 1.5% hydrocinnamic acid, 21% of a mixture of *dl*-3-deuterio-3-phenylpropanoic acid[11a] and *dl*-2-deuterio-3-phenylpropanoic acid,[11b] and 77% *dl-threo*-2,3-dideuterio-3-phenylpropanoic acid.[10]

Hydrogenation of 2-Acetyl-5-norbornene. To 2.31 g of I (item 13, Table I, 8.2 mmol) were added 0.46 g (4 mmol) of TMEDA, 0.27 g (2 mmol) of 2-acetyl-5-norbornene (Aldrich), and 10 mL of dioxane which was passed through an alumina column prior to use. The flask was connected to a gas collector and the mixture was refluxed until gas evolution ceased, at which point 7 mmol of gas had been produced. The condenser was rinsed with dichloromethane and the resin was filtered and washed with three portions of dichloromethane. The filtrate was extracted with 50 mL of dilute hydrochloric acid. The resin was washed with four 25-mL portions of petroleum ether, which was then used in two portions to extract the hydrochloric acid layer. The combined organic layer was extracted with 20% brine and dried over sodium sulfate. The layer was concentrated on a rotary evaporator and the residue was subjected to a Kugelrohr distillation at 98 °C and aspirator pressure, affording 0.14 g, 51% of product. The IR spectrum showed a strong band at 1708 cm^{-1} and the bands 3090 and 710 cm^{-1} present in the starting material were not present. In the NMR spectrum (CCl_4) the multiplets at δ 5.5–6.4 present in the starting material were totally absent. The CH_3CO doublet (exo and endo isomers) found at δ 2.10 and 2.20 in the starting material were at δ 2.09 and 2.12 in the product.

Hydrogenation of 2-Acetyl-5-norbornene with Diimide from Glucose-Treated I. To 0.28 g (2.06 mmol) of *endo,exo*-2-acetyl-5-norbornene (Aldrich) were added 2.63 g of I pretreated with glucose as already described, 0.52 g (4.5 mmol) of TMEDA, and 10 mL of dioxane. The reaction was conducted and the product worked up as described above (yield, 0.28 g, 98%). The IR spectrum of this product was identical with that from the previous run.

Hydrogenation of 3-Methylene-2-norbornanone by Diimide Generated from I. To 2.32 g of I (item 13, Table I, 8.2 mmol) were added 0.25 g (2.0 mmol) of 3-methylene-2-norbornanone, 0.46 g of TMEDA (4.0 mmol), and 10 mL of dioxane. The flask was attached to a gas collector and the mixture was refluxed until the rate of gas evolution was negligible, at which time 6.4 mmol of gas had been produced. The product was worked up as in the case of 2-acetyl-5-norbornane (yield, 0.03 g, 10%). The IR spectrum, showed a strong band at 1746 cm^{-1} and the bands at 1655 and 780 cm^{-1} in the starting material were absent in the spectrum for the product. The NMR spectrum (CCl_4) was clean in the $C{=}CH_2$ region and a doublet appeared at δ 1.01 (J = 3.8 Hz).

Hydrogenation of 3-Methylene-2-norbornanone by Diimide Generated from Glucose-Treated I. To 2.59 g of glucose-treated I (item 3, Table I, before glucose treatment) were added 0.26 g (2.1 mmol) of 3-methylene-2-norbornane (Aldrich), 0.46 g (4.0 mmol) of TMEDA, and 10 mL of dioxane. The reaction was conducted and the product was worked up as before. The gas yield after 16 h was 4.8 mmol. The product yield was 0.01 g (4%). There was insufficient product for an IR spectrum and the NMR spectrum (CCl_4) showed the same features as before.

Hydrogenation of 2-Cyclohexen-1-one by Diimide Generated from Glucose-Treated I. To I (item 3, Table II) which had been treated with 4.80 g of glucose were added 0.28 g (2.9 mmol) of 2-cyclohexen-1-one (Aldrich), 0.70 g (6.0 mmol) of TMEDA, and 10 mL of dioxane. The reaction was conducted as before, 9.3 mmol of gas being produced. The resin was extracted as before and the organic extract was concentrated to 0.15 g on a rotary evaporator. An IR spectrum was obtained on this concentrate which showed a strong band at 1708 cm^{-1} and the bands of the starting material at 3060, 1690, 1395, 945, and 738 cm^{-1} were missing. The concentrate was treated with 2,4-dinitrophenylhydrazine derivatizing reagent and 0.18 g of product was obtained: mp 156–157 °C; yield of cyclohexanone, 22%.

Hydrogenation of 6-Methyl-5-hepten-2-one by Diimide Generated from I. A 3.2-g portion of I (12.8 mmol of sulfonylhydrazine) was treated with 20% brine, washed with distilled water, and dried in vacuo. To I were added 10 mL of dioxane (filtered through alumina) and 0.51 g (4.0 mmol) of 6-methyl-5-hepten-2-one [Aldrich, distilled heart cut, bp 170.5 °C (745 torr)]. The mixture was allowed to stand for 7 days. To the mixture was added 1.48 g (12.8 mmol) of TMEDA and the mixture was refluxed for 7 h, during which time 9.2 mmol of gas was collected. The product was worked up as described for 2-acetyl-5-norbornene. Kugelrohr distillation yielded a small amount of distillate and more residue. An infrared spectrum of the residue showed a band at 1640 cm^{-1}, suggesting an azine. (Material with the same band could be produced by refluxing hydrazine and starting material in a 1:2 mol ratio in dioxane in the absence of polymer.) The residue was dissolved in 10 mL of dichloromethane to which were added 0.30 g (3.4 mmol) of pyruvic acid and a few drops of water. The mixture was refluxed for 1 h, extracted with 0.5 N NaOH, dried over anhydrous sodium sulfate, and concentrated on the rotary evaporator. The Kugelrohr distillation was resumed and the material, bp 70 °C (14 torr) was collected: yield 0.25 g. NMR and IR spectra were obtained and the mixture was subjected to GLC analysis (10 ft × $^1/_4$ in. Carbowax 20M on Chromosorb W, HMDS treated, 155 °C, 40 mL/min He, thermal conductivity detector). The mixture consisted of 42 ± 0.8% 6-methyl-2-heptanone and 58 ± 0.8% starting material. A residue weighing 0.03 g was left in the distillation pot. To the resin were added 10 mL of dichloromethane and 1.5 g (16 mmol) of pyruvic acid. The mixture was refluxed for 1 h and filtered. The resin was washed with dichloromethane. The filtrate was extracted with 0.5 N NaOH, dried over sodium sulfate, and concentrated by evaporation to 0.03 g of material. This was diluted with cyclohexane and subjected to GLC analysis. Several peaks emerged at retention times shorter than the product and starting material. Product and starting material were present in equal quantities.

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Registry No. Acetone, 67-64-1; 2-butanone, 78-93-3; butanal,

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123-72-8; 2-methylpropanal, 78-84-2; 2-pentanone, 107-87-9; 3-pentanone, 96-22-0; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; glucose, 50-99-7; 3,3-dimethyl-2-butanone, 75-97-8; 2-methylcyclohexanone, 583-60-8; camphor, 76-22-2; benzaldehyde, 100-52-7; acetophenone, 98-86-2; 1,3-diphenyl-2-propanone, 102-04-5; 2-acetyl-5-norbornene, 5063-03-6; 2-cyclohexen-1-one, 930-68-7; 3-methylene-2-norbornanone, 5597-27-3; *l*-carvone, 99-49-0; (2-propenylthiomethyl)benzene, 6937-97-9; 6-methyl-5-hepten-2-one, 110-93-0; 3-phenyl-2-propenoic acid, 621-82-9; (propylthiomethyl)benzene, 22336-59-0; *dl*-benzyl 2,3-dideuteriopropyl sulfide, 71766-43-3; *dl*-benzyl 2-deuteriopropyl sulfide, 71766-44-4; benzyl 3-deuteriopropyl sulfide, 71766-45-5; *endo*-2-acetylnorbornane, 824-58-8; *exo*-2-acetylnorbornane, 824-59-9; 3-methyl-2-norbornanone, 643-51-6; cyclohexanone, 108-94-1; 6-methyl-2-heptanone, 928-68-7; *dl-threo*-2,3-dideuterio-3-phenylpropanoic acid, 71806-58-1; *dl*-3-deuterio-3-phenylpropanoic acid, 71806-59-2; *dl*-2-deuterio-3-phenylpropanoic acid, 71766-46-6; 3-phenylpropanoic acid, 501-52-0; cyclopentanone dinitrophenylhydrazone derivative, 2057-87-6; butyraldehyde dinitrophenylhydrazone derivative, 1527-98-6; dinitrophenylhydrazine, 119-26-6; cyclohexanone 2,4-dinitrophenylhydrazone, 1589-62-4.

Direct Synthesis of α,β-Unsaturated Nitriles from Acetonitrile and Carbonyl Compounds: Survey, Crown Effects, and Experimental Conditions

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Detailed experimental conditions are presented for the condensation of acetonitrile with a large number of carbonyl compounds. The condensation is found to be most successful with aromatic aldehydes and diaryl ketones, substrates which yield pure α,β-unsaturated nitriles. Dialkyl ketones also condense readily under the conditions described herein but yield mixtures of double bond isomers. Aliphatic aldehydes do not condense satisfactorily, and a number of base-sensitive functional groups are incompatible with this reaction. Potassium hydroxide is found to be the most efficacious base for this reaction, and a detailed study of the condensation between acetonitrile and benzaldehyde reveals that other bases and solvents may be used, but 18-crown-6 polyether is required in some of these. The condensation is also reported for certain sterically biased ketones, and a discussion of the crown effect in these cases is presented.

The introduction of a two-carbon fragment is a cornerstone of synthetic organic chemistry in the form of numerous reactions such as the malonic ester,[1] acetoacetic ester,[2] Perkin,[3] and Doebner–Knoevenagel[4] condensations. Each of these reactions can afford a substituted acetic acid derivative; the latter can yield α,β-unsaturated nitriles under the appropriate conditions.[5] In most circumstances, the formation of α,β-unsaturated nitriles poses far more problems than the preparation of either saturated or unsaturated acetic acid derivatives.

In principle, the $>C{=}CHCN$ unit should be accessible by the condensation of acetonitrile (via the cyanomethide anion) with a carbonyl compound, followed by loss of water, as illustrated in eq 1. Although the metalation of

$$R_2C{=}O + MCH_2CN \rightarrow R_2C(OM)CH_2CN \xrightarrow[-H_2O]{+H^+} R_2C{=}CHCN \quad (1)$$

acetonitrile has been reported[6] and some condensations have proved successful, the reaction has not been general. The most serious problems have been: (1) acetonitrile undergoes numerous base-catalyzed side reactions,[6b,7] (2) the bases required to deprotonate acetonitrile often add to acetonitrile or induce reactions of the electrophiles, and (3) cyanomethide salts are often insoluble in low polarity media.[8] Moreover, such strong bases are usually used in nonpolar solvents like tetrahydrofuran, in which the intermediate β-hydroxynitriles (see eq 1) do not spontaneously dehydrate.[6b] We report here a detailed study of the base-induced reaction of acetonitrile with a variety of carbonyl compounds.[9]

Results and Discussion

Acetonitrile can be deprotonated by alkali metal alkoxides (NaOH, KOH), and the cyanomethide ion can then be condensed with a variety of carbonyl compounds. In excess acetonitrile (solvent), the intermediate β-hydroxynitrile apparently dehydrates spontaneously to afford either the α,β- or β,γ-unsaturated (depending on the sub-

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