The monoblocking of symmetrical diketones on insoluble polymer supports[1,2]

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A 1% crosslinked divinylbenzene–styrene copolymer, incorporating vicinal diol groups or their isopropylidene precursors, was used to form the monoacetals of the symmetrical diketones, *p*-diacetylbenzene, 1,2-cyclohexanedione, 1,3-cyclohexanedione, 1,4-cyclohexanedione, and 2,5-hexanedione. The free ketone groups reacted with phenylmagnesium bromide to give, in high yield, after acid hydrolysis from the polymer, the expected products such as 3-phenyl-2-cyclohexen-1-one from 1,3-cyclohexanedione. The ^{13}C nmr spectra of some polymer-bound substrates and simple analogs are described.

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On a utilisé un copolymère de divinylbenzène–styrène réticulé à 1%, incorporant un groupe diol vicinal ou son précurseur isopropylidène pour former le monoacétal des dicétones symétriques, *p*-diacétylbenzène, cyclohexanedione-1,2, cyclohexanedione-1,3, cyclohexanedione-1,4 et hexanedione-2,5. Les groupes cétone libres réagissent avec le bromure de phénylmagnésium pour donner avec un fort rendement, les produits attendus tels: la phényl-3 cyclohexen-2 one-1 à partir de la cyclohexanedione-1,3 après clivage de la résine par hydrolyse acide. On décrit les spectres de rmn du ^{13}C de quelques substrats fixés sur le polymère ainsi que ceux des analogues simples.

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Acetal formation of ketones represents one of the most common uses of blocking groups in organic synthesis (4). A wide variety of symmetrical diketones have the potential of being used as inexpensive starting materials in the synthesis of complex organic structures, but first it would be necessary to monoprotect *one* of the two identical ketone groups. In fact, the monoprotection of symmetrical diketones has been addressed many times. For example, 1,4-cyclohexanedione ethylene monoacetal (5, 6), other 1,4-dione monoacetals (7), and 1,3-cyclohexanedione ethylene monoacetal (8) have been prepared, but only by circuitous routes or in low yield. Although the most common synthons derived from 1,3-cyclohexanedione are 3-ethoxy-2-cyclohexen-1-one (9, 10) and the 3-halo-2-cyclohexen-1-ones (11, 12), reactions on the former have sometimes proved difficult to perform (13). Monoacetals of *aromatic* 1,2-diketones have been prepared by alkylation procedures (14), but this method cannot be generalized to include all classes of symmetrical diketones.

Insoluble polymer supports (15, 16) can be used to monoblock symmetrical diols (17, 18), aromatic dials (19–21),[4] dihydroxyaromatic compounds (22), diamines (23), and diacid chlorides (24). A solid phase resin incorporating an appropriate functional group can react with a large excess of symmetrical difunctional compound to give the monoprotected derivative, which can be removed from the excess symmetrical difunctional compound by simple filtration. This "fishhook" principle (17, 23, 25) does *not* depend on site-isolation (26) of the polymer-bound functional groups, as these groups are likely to react with only one molecule each of large excesses of the symmetrical difunctional compounds in the solution phase.

In earlier work we have used polymer-bound 1-*O*-benzyl-2,3-*O*-isopropylideneglycerol (**1**) to prepare polymer-bound 3-benzyloxypropan-1,2-diol (**2**). Subsequent use of **2** as a monoacetalization reagent of aromatic dialdehydes has been reported (19–21), but the use of **2** and related polymer-bound 1,3-diols as monoblocking agents for *symmetrical diones* either failed or exhibited low loading capacities for the diones (20).[5] We have recently shown (27) that ^{13}C nmr spectroscopy can be used to characterize polymer-bound substrates and hence we prepared (19) new samples of **1** and **2** for possible use as monoacetalization agents. The ^{13}C nmr of **1** and **2** exhibited the normal broad absorptions due to the aliphatic and aromatic carbons of the cross-linked polystyrene and, for **1**, distinct absorptions for the 2,3-*O*-isopropylideneglyceryl appendage (Table 1). Much to our surprise, the ^{13}C nmr of polymer **2** showed that polymer **2** contained a major amount of polymer **1** resulting from incomplete acid hydrolysis of **1** to **2**. Thus our early work on the use of polymer **2** for the monoacetylation of symmetrical aromatic dials involved the use of a mixture of mostly **1**, admixed with some of **2**, and hence we had done a *transacetalization* as opposed to an *acetalization*.[6] Indeed, reaction of terephthalaldehyde with **1** (instead of **2**) *or* new pure **2**, prepared by hydrolysis of **1** under more vigorous conditions (Experimental), gave us results identical to those previously reported (19). The ^{13}C nmr of pure **2** (Table 1), as prepared herein, did not exhibit the characteristic absorptions of the isopropylidene group in **1**.

The assignments of the ^{13}C absorption peaks in Table 1 are based on coupled and decoupled (Table 1) spectra of **1**, **2**, 1-*O*-benzyl-2,3-*O*-isopropylidene glycerol (**2***a*) (28), and L-1-*O*-benzylglycerol (**2***b*) (Sigma Chem. Co.) (Fig. 1). Polymers **1** and **2** exhibited low intensity peaks for C-1, medium

[1]The use of polymer supports in organic synthesis, Part XXVIII. For parts XXVII to XXV, see refs. 1–3 respectively.

[2]Presented in part at the International Symposium on Polymer Supported Reagents in Organic Chemistry, Lyons, France, June–July, 1982.

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[4]A non-polystyrene based polymer has been used recently (37) in the preparation of monoblocked symmetrical aromatic dialdehydes but extensive double-binding occurred, undoubtedly due to their much higher capacities and the nature of the polymer. This polymer was not used to monoblock symmetrical diketones.

[5]At a recent symposium a report has appeared on using polymer-bound diols as blocking agents of symmetrical diones (38).

[6]Only 5–10 mg of the original samples were still available but 500 mg of sample is required for the ^{13}C nmr of these polymers and hence old polymer **2**, prepared by the old method, yielded **2** containing significant amounts of residual **1** as shown by ^{13}C nmr.

TABLE 1. ^{13}C chemical shifts of some polymer-bound substrates and their monomeric analogs

	Carbon		Position[a]				
Compound	1	2	3[b]	4[b]	5	6, 7	Aromatic
1	73.12	70.62	74.38	66.90	108.8	26.40,25.01	Broad
2	73.56	71.78	70.87	64.21			Broad
2*a*	73.51	71.15	74.78	66.91	109.36	26.79,25.41	138.1 128.4 127.7
2*b*	73.34	71.53	70.95	63.87			137.9 128.4,127.8

[a] Aliphatic carbons numbered from the phenyl group, δ ppm with respect to TMS.
[b] ^{13}C chemical shifts of glycerol, δ 62.95 and 72.30 ppm for C-1 and C-2 respectively (DMSO), and 2,3-*O*-isopropylidene glycerol (2,2-dimethyl-1,3-dioxolane-4-methanol), δ 63.11, 76.44, 66.07, 109.41 and 26.74, 26.05 ppm respectively, for the C-1 to C-7 carbons numbered from the alcohol end were used in assigning the absorption peaks.

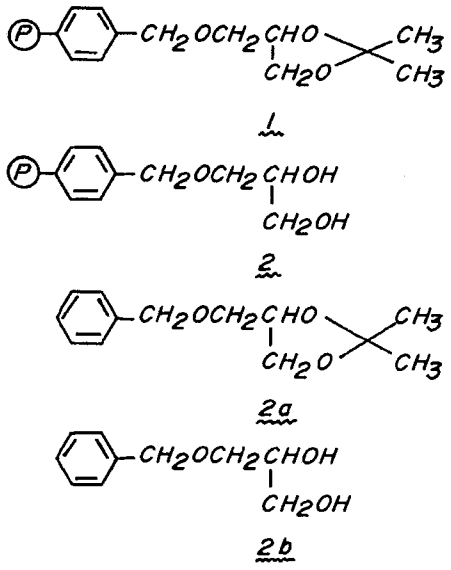


FIG. 1

intensity peaks for C-2, and sharp, high intensity peaks for other carbons, consistent with our earlier observations (27) of reduced mobility of carbons close to the polymer backbone.

Monoprotection of p-*diacetylbenzene (3) and its reaction with Grignard reagent*

Treatment of the polymer-bound isopropylidene derivative (**1**) or the polymer-bound 1,2-diol (**2**) with excess *p*-diacetylbenzene (**3**) gave the polymer-bound *p*-diacetylbenzene monoacetal (**4**) in high yield using *p*-toluenesulfonic acid and triethylorthoformate as a catalyst (29). Standard conditions (30) or the use of the boron trifluoride – ether complex (31) as catalysts afforded **4** in lower yield. The loading capacities of various preparations of **4** were determined by acid hydrolysis of **4** and recovery of the starting dione **3** (Table 2).

The infrared (ir) spectrum of **4** exhibited a characteristic carbonyl absorption at 1690 cm^{-1}. When **4** (prepared from **2**) reacted with phenylmagnesium bromide (**5**) in tetrahydrofuran (THF) polymer **6** was obtained. Polymer **6** no longer exhibited absorptions at 1690 cm^{-1} and a strong O—H absorption at 3400 cm^{-1} indicated that reaction had occurred and was essentially complete. Acid cleavage of **6** liberated 1-(4′-acetylphenyl)-1-phenylethene (**7**), the expected product in 99% yield resulting from the Grignard reaction and dehydration of the labile tertiary benzylic alcohol present in **6** (Scheme 1).

Monoprotection of 1,2-cyclohexanedione (8), 1-3-cyclohexanedione (9), and 1,4-cyclohexanedione (10) and their reactions with phenylmagnesium bromide (5)

Treatment of **1** or **2** with **8**, **9**, or **10** as above yielded the polymer-bound monoblocked acetals **11**, **12**, and **13** respectively. Polymers **11**–**13** exhibited strong absorptions at 1720 cm^{-1} supporting the assigned structures. The ^{13}C nmr spectrum of **12** exhibited a characteristic absorption at 110.7 ppm due to the quaternary carbon of the 5-membered ring acetal. This can be compared to similar absorption peaks for **1** and **2***a* (Table 1). The loading capacities of **11**–**13** prepared under various conditions were determined as for **4** above (Table 2). When the polymer-bound monacetals **12** and **13** were treated with phenylmagnesium bromide (**5**) as before, the polymer-bound tertiary alcohols **14** and **15** were obtained. The ir spectra of **14** and **15** exhibited broad peaks at 3400 cm^{-1}, typical of O—H vibrations, and the carbonyl absorptions had disappeared. Acid hydrolysis of **15** gave the expected 3-phenyl-2-cyclohexen-1-one (**16**) in 90% yield based on the amount of **9** bound to **12**. Similarly, **15** gave a mixture of 4-phenyl-3-cyclohexen-1-one (**17***a*) and 4-phenyl-2-cyclohexen-1-one (**17***b*) in 79% yield. Predictably, the acid cleavage conditions caused elimination of the tertiary alcohol groups and some isomerization to the α,β-unsaturated ketone (**17***b*) (Scheme 2).[7]

Acyclic diketones such as 2,5-hexanedione (**18**) can be monoblocked by the above methods using **2** to give the polymer-bound monacetal (**19**) (Table 2) (Fig. 2). Treatment of other ketones such as 2,3-butanedione (**20**), acetophenone (**21**), and cyclododecanone (**22**) gave the polymer-bound acetals (**23**–**25**) respectively. Only *p*-benzoquinone (**26**) proved unreactive to **2** under the standard conditions.

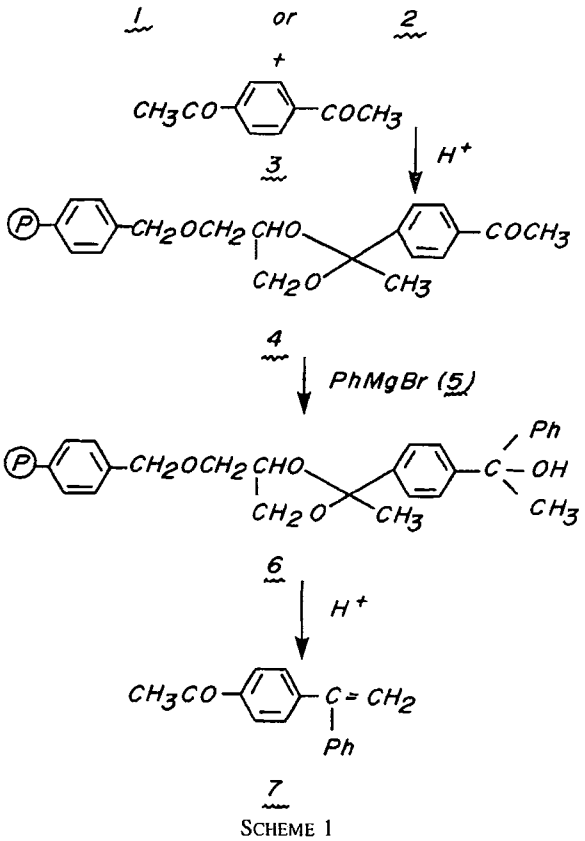
As shown in Table 2, a used polymer **2** showed no diminution in its capacity to prepare 3-phenyl-2-cyclohexen-1-one (**16**) (32). As mentioned recently, 4-substituted-2-cyclohexen-

[7] The high yields of the Grignard adducts show that double-binding of the symmetrical diones to the polymers is not significant at these capacities.

TABLE 2. The quantity of ketones attached to polymers **1** or **2**

Polymer	Ketone	Reaction conditions[a]	Product	Amount of bound ketone,[b] mmol/g	Ratio of dione to polymer-bound diol or acetal groups	Unreacted[d] polymer-bound diol groups, mmol/g
1	**3**	A	**4**	0.39	2.1	0.53
1	**3**	B	**4**	0.63	2.4	0.29
1	**3**	C	**4**	0.32	2.5	0.60
2	**3**	A	**4**	0.44	0.7	0.48
2	**3**	B	**4**	0.65	2.5	0.27
2	**3**	C	**4**	0.35	2.7	0.57
2	**8**	A	**11**	0.29	1.5	0.63
2	**9**	A	**12**	0.65[c]	2.3	0.27
2	**9**	A	**12**	0.65	3.1	0.27
1	**10**	B	**13**	0.45	1.9	0.47
2	**10**	A	**13**	0.39	2.5	0.53
2	**18**	A	**19**	0.42	3.5	0.50
2	**20**	A	**23**	0.72	4.7	0.20
2	**21**	A	**24**	0.66	3.1	0.26
2	**22**	A	**25**	0.19	2.3	0.73
2	**26**	A	—	—		

[a]Reaction conditions; A = *p*-toluenesulfonic acid, 80°C, 48 h; B = *p*-toluenesulfonic acid, triethylorthoformate, 80°C, 48 h; C = boron trifluoride – ether complex, room temperature, 24 h.
[b]Determined by liberation from the polymer with 4 *M* HCl at 80°C and purification by preparative tlc.
[c]This value was obtained indirectly from *used* polymer **2**. At least 0.62 mmol/g of **16** was obtained using recycled **2**. This yield is greater than using fresh **2** and hence recycled **2** shows no reduced capacity.
[d]By analysis of residual chloride in **1**, polymers **1** and **2** contain 0.92 mmol/g of vicinal diol moieties and hence the percentage of *reactive* polymer-bound diol groups can be recorded.



SCHEME 1

1-ones and -3-enones have great synthetic potential (33) and the procedure outlined herein represents the first general method of monoprotecting symmetrical diketones. The free ketone group can be used for synthetic elaboration in multistep synthesis of polycyclic and acyclic compounds.

Experimental

Nuclear magnetic resonance (nmr) spectra for carbon were recorded on a Varian FT-80A spectrometer at 20 MHz using deuterochloroform ($CDCl_3$) as solvent and tetramethylsilane as the internal standard. Parameters used for polymers swollen in $CDCl_3$ were similar to those previously described.[27] Mass spectra (ms) were recorded at 70 eV on a VG Micromass 16F mass spectrometer in the EI mode. Microanalyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ont. All other instrumentation and general procedures were the same as described previously (34).

Preparation of polymer-bound 1-O-benzyl-2,3-isopropylidene glycerol (1)

A Merrifield resin (Sigma Chemical Col.) containing 1.04 mmol of $-CH_2Cl$ groups per g of resin was treated as previously described (19), except that the mixture was stirred for *48 h instead of 24 h*, to give polymer **1**. A modified Volhard analysis (35) of **1** prepared after 24 h stirring showed 0.33 mmol of residual chloride per g of polymer, while stirring for 48 h or longer resulted in analyses showing only 0.12 mmol of residual chloride. The ^{13}C nmr spectrum of **1** is described in Table 1.

Preparation of polymer-bound 3-benzyloxypropan-1,2-diol (2)

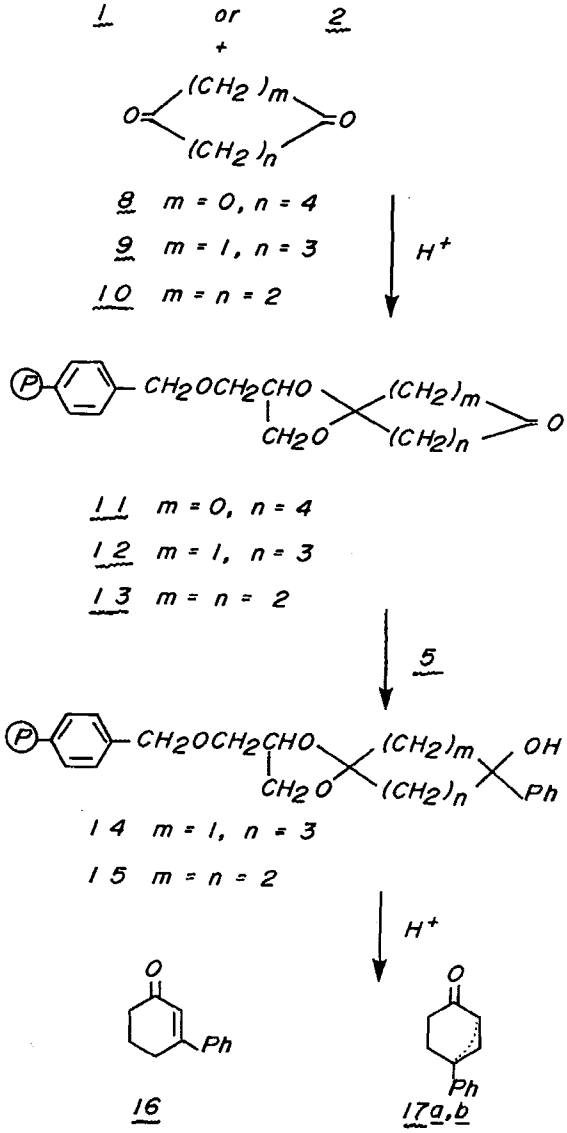
Polymer **1** was treated as previously described (19), except that the mixture of 1.5 *M* aqueous HCl in dioxane (1 : 1) or 1 *M* H_2SO_4 in dioxane (1 : 1) was stirred *at 80°C for 72 h* to give polymer **2**. Hydrolysis of the ketal group of **1** was shown to be complete by examination of the ^{13}C nmr of **2** (Table 1).

Polymer-bound p*-diacetylbenzene monoacetal (4)*

As shown in Table 2, the preparation of **4** occurred almost equally as well from polymer **1** as polymer **2** in all three methods, A, B, or C. The procedures are identical using **1** or **2** and hence we describe the preparation of **4** using **1** or **2** as representative.

Method A. Using p*-toluenesulfonic acid*

To 15.91 g of polymer **1** in 100 mL of dry benzene was added 3.07 g of *p*-diacetylbenzene (**3**), 0.20 g of *p*-toluenesulfonic acid, and 9.47 g of anhydrous sodium sulphate. The mixture was heated for 48 h at 80°C. The mixture was filtered, washed twice with pyridine, twice with pyridine–water (1 : 1), ten times with water, three times



SCHEME 2

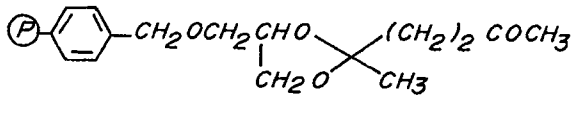


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FIG. 2

with ethanol, and three times with dry ether, and dried under vacuum to give 16.8 g of polymer (**4**). In general, higher loadings are obtained with greater excesses of symmetrical difunctional compounds (16).

The loading capacity of polymer **4** for **3** was determined as follows. A mixture of 4.50 g of **4** in 10 mL of dioxane and 10 mL of 4 *M* aqueous HCl was stirred at 80°C for at least 48 h. The mixture was filtered and recovered **1** was washed six times with water, once with acetone, three times with ethanol, and three times with ether. The aqueous filtrate was extracted three times with ether. The combined ether extracts were dried over Na_2SO_4, filtered, and evaporated to crude **3**. Purification of **3** by column chromatography or silica yielded 0.176 g of pure **3** in the ether–hexane (1:1) fractions, showing that **4** contained at least 0.39 mmol per g of **3** (Table 2).

Method B. Using p-toluenesulfonic acid and triethyl orthoformate

To 2.68 g of polymer **2** in 30 mL of dry benzene was added 1.02 g of **3**, 0.12 g of *p*-toluenesulfonic acid, 0.5 mL of triethyl orthoformate, and 4.1 g of anhydrous sodium sulphate. The mixture was stirred at 80°C for 48 h and worked up as described for method A to give 2.8 g of **4**. The loading capacity (Table 2) of this polymer **4** was determined as for method A.

Method C. Use of boron trifluoride – ether complex

To 2.66 g of **2** in 30 mL of dry benzene was added 1.07 g of **3**, 1.0 mL of boron trifluoride – diethyl ether, and 3.44 g of anhydrous sodium sulphate. The mixture was stirred at room temperature for 24 h and worked up as described for method A to give 2.8 g of **4**. The loading capacity (Table 2) of this polymer **4** was determined as for method A.

The ir spectra of **4** from methods A, B, and C all showed significant C=O stretching vibrations, at 1690 cm^{-1}, of varying intensities depending on the loading capacities (Table 2).

Preparation of the polymer-bound Grignard adduct 6

To 6.2 g of **4** (containing 0.39 mmol of **3** per g of **4**) in 70 mL of dry THF was added 0.1 mol of phenylmagnesium bromide (**5**) in 50 mL of dry THF. The mixture was stirred at room temperature for 43 h and at 80°C for 2 h. The mixture was filtered and washed three times each with dry THF, anhydrous ethanol, and dry ether to give 7.0 g of polymer **6**. Polymer **6** showed a broad absorption band at 3400 cm^{-1} and no absorption band at 1690 cm^{-1} in the ir spectrum.

Hydrolysis of 6 to give 1-(4'-acetylphenyl)-1-phenylethene (7)

A mixture of 5.56 g of **6** in 60 mL of 4 *M* aqueous HCl in dioxane (1:1) was stirred and heated at 80°C for at least 48 h. The mixture was filtered and washed six times with water, twice with hot water, and three times each with acetone, ethanol, and ether. The aqueous filtrate was extracted three times with ether, washed twice with water, and dried over magnesium sulphate. The combined acetone and ether extracts yielded 0.8 g of a yellow oil. Column chromatography on silica gel yielded, in the 1:1 ether–hexane fractions, 0.48 g of 1-(4'-acetylphenyl)-1-phenylethene (**7**) in 99% yield based on the amount of **3** bound to **4**; mp 44–46°C; ir ($CDCl_3$): 1690, 1608, 1275; ^1H nmr δ: 2.61 (s, 3H), 5.52 (s, 2H), 7.42 (s, 5H), 7.7 (A_2B_2, q, 4H); *m/e*: (M^+) 222 (100), (M^+ – 15) 207 (100), 176 (82). *Anal.* calcd. for $C_{16}H_{14}O$:C 86.44, H 6.36; found: C 86.53, H 6.40.

Preparation of polymer-bound aliphatic symmetrical dione monoacetals (11–13, 19, 23–25)

The preparations of **11–13**, **19**, and **23–25** were identical to those described for **4** above by Method A and in one example by Method B (Table 2). All polymer-bound monoacetals showed strong carbonyl absorption at 1710–1730 cm^{-1} in their ir spectra. The loading capacities (Table 2) were determined as above for **4**.

Preparation of the polymer-bound Grignard adducts 14 and 15

Polymer-bound 1,3-cyclohexanedione monoacetal (**12**) (4.8 g), containing 0.65 mmol of **9** per g, reacted with **5** as described for **6** above to give 5.5 g of the polymer-bound adduct **14**.

Similarly, polymer-bound 1,4-cyclohexanedione monoacetal (**13**) (4.8 g), containing 0.39 mmol of **10** per g of **13**, gave 5.5 g of the polymer-bound adduct **15**.

Hydrolysis of 14 to give 3-phenyl-2-cyclohexen-1-one

A mixture of 4.8 g of **12** was hydrolyzed as described above in the preparation of **7** to give a yellow oil. Chromatography on silica gel using hexane–ether (1:1) gave, in 90% yield, 0.51 g of 3-phenyl-2-cyclohexen-1-one (**16**); mp 62–63°C (lit. (32) mp 64°C); ir: 1668, 1610, 775; ^1H nmr δ: 1.7–2.8 (m, 6H), 6.28 (s, 1H), 7.32 (m, 5H); *m/e*: (M^+) 172 (56), 144 (100), 115 (58).

Hydrolysis of 15 to give a mixture of 4-phenyl-3-cyclohexen-1-one (17a) and 4-phenyl-2-cyclohexen-1-one (17b)

A mixture of 4.8 g of **13** was hydrolyzed as above for the preparation of **7** to give a yellow oil. Purification as for **16** gave, in 79% yield, 0.35 g of a mixture of 4-phenyl-3-cyclohexen-1-one (**17a**) and 4-phenyl-2-cyclohexen-1-one (**17b**) (36); ir: 1720, 1690. Vapor phase

chromatography – mass spectroscopy of the mixture of **17***a* and **17***b* exhibited only two peaks in the ratio of 42:58. The mass spectra of the two peaks were consistent with the assigned structures, the first eluting peak showing *m/e* at (M^+) 172 (62), 144 (20), 130 (100), 129 (48), 115 (55) and the latter at (M^+) 172 (65), 130 (100), 129 (66), 115 (45).

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