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Registry No. *trans*-**1a**, 50930-15-9; *trans*-**1b**, 84064-83-5; *trans*-**1c**, 84064-84-6; *trans*-**1d**, 84064-85-7; *trans*-**1e**, 84064-86-8; *trans*-**2**, 84064-87-9; *trans*-**3**, 61608-79-5; *trans*-**4**, 33044-88-1; *trans*-**5**, 84064-93-7; **6a**, 76510-29-7; **6b**, 84064-88-0; **6c**, 1724-45-4; **7a**, 84064-89-1; **7b**, 84064-90-4; **7c**, 84064-91-5; *trans*-**8**, 84064-92-6; *n*-BuLi, 109-72-8; 1-buty-1-vinyl-*trans*-2,3-diphenylcyclopropane, 84064-94-8; 1-bromo-1-methyl-*trans*-2,3-diphenylcyclopropane, 84064-95-9; 1-methyl-*trans*-2,3-diphenylcyclopropane, 84064-96-0.

Wittig Reagents Bound to Cross-Linked Polystyrenes

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Insoluble benzyltriarylphosphonium and methyltriarylphosphonium salts have been prepared on 2% and 8% divinylbenzene cross-linked polystyrene and on 20% divinylbenzene cross-linked macroporous polystyrene. Phosphoranes were generated with sodium methoxide or sodium ethoxide in THF and with the dimethylsulfinyl carbanion in Me$_2$SO from the benzyl- and methylphosphonium salts, respectively. Reactions of the phosphoranes with a variety of aldehydes and ketones provided alkenes in 73–96% yields (by GLC analysis) with the 2% cross-linked polymer, 52–77% yields with the 8% cross-linked polymer, and 72–87% yields with the 20% cross-linked macroporous polymer. The rates of phosphorane generation and alkene formation depend on the polymer, decreasing in the order 2% > 20% macroporous > 8% cross-linked. The fraction of *E* double bond product from the benzylphosphonium salt and either benzaldehyde or cinnamaldehyde is greater with the 20% cross-linked macroporous polymer than with the 2% cross-linked polymer. The byproduct polymer-bound phosphine oxides were reduced to phosphines with trichlorosilane, and the phosphines were reused for Wittig syntheses. A quantitative ^{31}P NMR analysis of phosphine and phosphine oxide residues in polystyrene gels is reported.

Polymer-supported reagents in organic synthesis allow separation of the insoluble polymeric byproduct from the reaction mixture by simple filtration.[1] In some cases the polymeric reagent can be regenerated. The byproduct triphenylphosphine oxide from Wittig reactions in solution is often hard to separate from the product olefin. After use of a polymer-supported Wittig reagent the triarylphosphine oxide can be separated by filtration and can be recycled after reduction to the phosphine. The Wittig reaction is one of the most valuable in synthetic chemistry, for it gives regiospecific introduction of a carbon–carbon double bond.[2]

Earlier papers on polymer-supported Wittig reagents[3-8] reported syntheses of olefins in widely variable yields, depending on the particular reaction conditions and the polymer used. Heitz and Michels[5] found higher yields with a 0.5% cross-linked polystyrene support than with the standard 2% cross-linked polystyrene, which implies that more highly cross-linked polystyrenes would give poor yields of Wittig products. A phase-transfer-catalyzed method of phosphorane generation from the polymer-bound phosphonium salts offers the highest reported yields of olefins from activated benzyl and allyl phosphonium salts.[8] Use of soluble Wittig reagents with polymer-bound aldehydes also has been reported.[9] (Polystyrylmethyl)triphenylphosphonium ions have been used to prepare alkenes bound to the polystyrene.[8b,c,10]

Scheme I

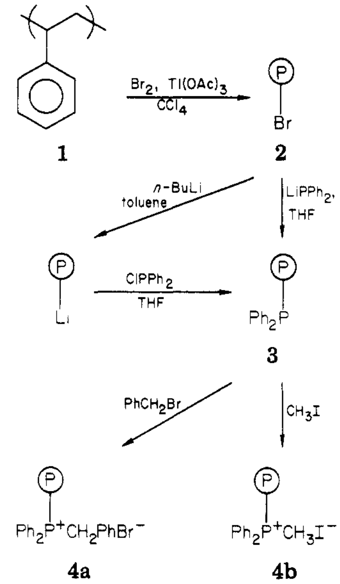

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Table I. Phosphination of Bromopolystyrene

copolymer, % cross-linking	brominated copolymer, mequiv of Br/g [a]	phosphine polymer		% conversion
		mequiv of Br/g [a]	mequiv of P/g [a]	
A. Lithium Diphenylphosphide Method [b]				
2	3.05	0.00	2.09	91
2	3.10	0.00	2.40	100
2	3.05	0.05	2.12	92
8	2.94	0.63	1.60	65
8 [c]	3.00	0.02	2.01	83
20 [c]	3.08	1.63	0.97	35
B. *n*-Butyllithium/Chlorodiphenylphosphine Method [d]				
2	3.10	0.00	1.86	80
20	3.08	0.03	1.13	38

[a] By elemental analysis. [b] A THF solution of 2.5 molar equiv of $LiPPh_2$ was added to the bromopolystyrene in THF at −10 °C, and the mixture was stirred for 48 h at room temperature. [c] The reaction mixture was heated at reflux an additional 6 h. [d] A hexane solution of 3.0 molar equiv of *n*-BuLi was added to the bromopolystyrene in toluene at −10 °C. After 10 h at 70 °C the excess *n*-BuLi was washed away, and 2.5 molar equiv of $ClPPh_2$ was added.

Our research on polymer-supported reagents is aimed at demonstration of methods that could be scaled up to the manufacture of fine chemicals and pharmaceuticals. The 0.5% and 2% cross-linked polystyrenes used in most previous polymer-supported reagents are too gelatinous in solvent-swollen form for large-scale filtration, so our attention has been directed to more highly cross-linked, more rigid polystyrene supports. These materials, however, might give poor yields because of poor transport of reagents into and out of the more highly cross-linked polymer matrices, particularly if the reactant and product molecules are as large as many organic natural products. This paper reports the use of Wittig reagents supported on polystyrenes with up to 20% cross-linking and with reactants as large as a 3-keto steroid and a C_{19} aliphatic ketone.

Results

Conversions of 2%, 8%, and macroporous 20% divinylbenzene cross-linked polystyrenes (see Experimental Section) to polymer-bound triarylphosphonium salts were carried out by the methods in Scheme I. All three polymers gave bromopolystyrene (**2**)[11] in 100% yield.

Conversions of the bromopolystyrene to diphenylphosphinopolystyrene (**3**) proceeded with increasing difficulty in the order 2% < 8% < 20% macroporous cross-linked polymer by treatment with either lithium diphenylphosphide[13] or *n*-butyllithium and chlorodiphenylphosphine (see Table I). Conversions exceeded 90% with the 2% cross-linked polystyrene in 48 h at 20 °C, but an added 6 h at 65 °C was needed to reach an 83% conversion with lithium diphenylphosphide and the 8% cross-linked polystyrene. Even the extra 6 h at 65 °C provided only 35% phosphination of the 20% cross-linked macroporous polystyrene. A 38% conversion of the 20% cross-linked bromopolystyrene to phosphine was obtained by using *n*-butyllithium and chlorodiphenylphosphine. By the lithium diphenylphosphide method residual bromine in the 20% cross-linked polymer accounted for the low conversion. (See the Experimental Section for a sample calculation of the percent conversion.) By the *n*-butyllithium method there was almost no residual bromine.

Treatments of all of the polymer-bound phosphines with benzyl bromide and with methyl iodide gave benzyldiphenylpolystyrylphosphonium bromide (**4a**) and methyldiphenylpolystyrylphosphonium iodide (**4b**) in 86–96% yields, as determined by ion-exchange analyses (see Experimental Section) of the bromide and iodide contents of the polymer beads.

The benzylidenephosphoranes were generated by addition of an equimolar amount of sodium methoxide in methanol or sodium ethoxide in ethanol to the THF-swollen polymer-bound benzylphosphonium salt. The 2% and macroporous 20% cross-linked samples attained the characteristic orange-red phosphorane color in 3–4 h of stirring at room temperature. The 8% cross-linked sample required 12–16 h to attain full color.

Wittig reactions of the benzylidenephosphoranes with aldehydes were complete after 16 h at room temperature and 2–4 h at 60 °C with the 2% and macroporous 20% cross-linked polymers, and after 24 h at room temperature and 4 h at 60 °C with the 8% cross-linked polymer. Results are given in Table II. In some experiments with 2% cross-linked polystyrene 91–95% of the calculated quantity of bromide ion was released in the Wittig reaction, as determined by washing the NaBr from the polymer and titrating the solution for bromide ion. The yields of olefins and amounts of recovered aldehyde in Table II indicate that the rates of phosphorane formation and/or olefination decrease in the order 2% cross-linked > macroporous 20% cross-linked > 8% cross-linked polymer. The *Z*/*E* product ratios decrease in the order 2% > 8% > macroporous 20% cross-linked polymer.

The methylidenephosphoranes were generated by addition of 3 molar equiv of the sodium salt of dimethyl sulfoxide to the polymer-bound methylphosphonium salt swolen in a 1:1 (v/v) mixture of THF and Me_2SO and stirring for 6 h. The phosphorane polymer beads were green-black. The excess base was drained, and the polymer was washed with THF before addition of the carbonyl compound. A 5–25% excess of phosphonium salt was used with cyclohexanone, cinnamaldehyde, and benzophenone. A 40–50% excess of phosphonium salt was used, and the mixture was held 24 h at 60 °C with the larger ketones, 10-nonadecanone and cholest-4-en-3-one. Most of the recovered phosphine oxide polymers were analyzed for residual iodide ion. Results are given in Table III. Only the 8% cross-linked polymers contained I^-, indicating incomplete generation of the phosphorane. Yields of olefins in all cases depended on the polymer: 2% > macroporous 20% > 8% cross-linked.

Samples of the 2% cross-linked polystyryldiphenylphosphine oxide byproduct were reduced with trichlorosilane to the phosphine[6,13] in ≥90% yield, as determined by quantitative ^{31}P NMR analysis. The recycled polymers gave benzylphosphonium salts and (*E*)- and (*Z*)-stilbenes by Wittig reactions with benzaldehyde with no reduction in yield over three cycles. The 20% cross-linked macroporous polymer also was recycled and gave a 75% yield of stilbenes (see Table IV).

Discussion

Successful polymer-supported syntheses require penetration of the reagents from solution into all of the functional sites in the polymer gel. The method by which the potentially reactive sites are introduced, the swelling of the polymer matrix, the size of the penetrating reagent,

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Table II. Olefins from Polymer-Supported Benzylphosphonium Salts[a]

copolymer, % cross-linking	mequiv of P$^+$	aldehyde	mequiv of aldehyde	product	% yield[b]	isomer ratio[i]	% recovered aldehyde	Br$^-$ released,[c] mequiv
2	2.42	PhCHO	2.5	PhCH=CHPh	93	57/43	<0.5[d]	0.00
8	2.60		2.23		73	48/52	16	*e*
20[f]	2.38		1.86		80	28/72	18	*e*
2	2.45	PhCH=CHCHO	3.27	PhCH=CHCH=CHPh	89	40/60	2.5[d]	2.32
8	2.00		1.85		77[g]	35/65	<0.5[d]	*e*
20[f]	2.06		2.09		72[h]	17/83	10.5	*e*
2	2.53	PhCH=C(CH$_3$)CHO	2.53	PhCH=C(CH$_3$)CH=CHPh	89	30/70	6	2.31
2	3.20	*n*-C$_{11}$H$_{23}$CHO	3.07	*n*-C$_{11}$H$_{23}$CH=CHPh	*e*	43/57	2.5	*e*

[a] The phosphorane was generated with an equimolar amount of sodium methoxide or sodium ethoxide at −10 °C, the mixture was warmed to room temperature, aldehyde was added, and the mixture was stirred 16 h at 20 °C and 2 h at 60 °C. [b] By GLC analysis unless noted otherwise. [c] By Volhard titration of the NaBr washed from recovered polymer or by Br$^-$ determination in recovered polymer. [d] Based on the calculated amount that could react with phosphorane. [e] Not determined. [f] Macroporous. [g] Recrystallized yield. [h] Yield based on ^{1}H NMR integration. [i] *Z/E* or *Z,E/E,E*.

Table III. Olefins from Polymer-Supported Methylphosphonium Salts[a]

copolymer, % cross-linking	mequiv of P$^+$	carbonyl compd	mequiv of carbonyl compd	product	% yield[b]	% recovd carbonyl compd[c]	I$^-$ left in polymer,[d] mequiv
2	2.55	(CH$_2$)$_5$CO	2.42	(CH$_2$)$_5$C=CH$_2$	99	0.0	0.00
2	2.75	PhCH=CHCHO	2.63	PhCH=CHCH=CH$_2$	95	0.0	0.00
8	3.22		2.73		52 (72)[e]	7	1.25
20[f]	3.15		2.65		83	0.0	*g*
2	2.75	Ph$_2$CO	2.52	Ph$_2$C=CH$_2$	94	0.0	*g*
8	3.48		2.78		61 (92)[e]	34	1.63
20[f]	2.45		2.30		74	10	0.00
2	3.79	(*n*-C$_9$H$_{19}$)$_2$CO	2.52	(*n*-C$_9$H$_{19}$)$_2$C=CH$_2$	96[h]	0.4	0.00
20[f]	2.47		1.74		62[h]	34[i]	0.00
2	3.74	cholest-4-en-3-one	2.48	3-methylenecholest-4-ene	91[h]	0.0	0.00
20[f]	2.40		1.62		87[h]	9.5	*g*

[a] The phosphorane was generated by adding 3 equiv of the sodium salt of Me$_2$SO to a mixture of the polymer in Me$_2$SO at −10 °C and warming to room temperature. The carbonyl compound was added, and the mixture was stirred 16 h at 20 °C and 4 h at 60 °C. [b] By GLC analysis. [c] Area percent of reactant and products in GLC analysis. [d] By ion-exchange analysis. [e] Yield in parentheses is based on phosphonium salt consumed. [f] Macroporous. [g] Not determined. [h] After addition of ketone the mixture was stirred and heated for 24 h at 60 °C and stirred 24 h at 20 °C. [i] Phosphorane was partially decomposed by accidental exposure to air before addition of 10-nonadecanone.

Table IV. Recycling of Polymers for Wittig Syntheses of Stilbene

cross-linking, %	cycle	Ar$_3$P=O polymer used, g	Ar$_3$P polymer recovd, g	Ar$_3$P polymer used, g	Ar$_3$P$^+$CH$_2$Ph polymer recovd, g	mequiv of P$^+$/g	P$^+$ polymer used, g	Ar$_3$P=O polymer recovd, g	% yield of stilbenes
2	1					1.24	1.97	1.69	93[a]
	2	11.1[b]	10.7	8.1	10.8	1.24	1.94	1.55	97[c]
	3	2.39[d]	2.30	2.30	2.91	1.30	2.28	1.76	97[c]
20	1					0.69	3.45	*e*	80
	2	5.99[b]	5.80	5.24	5.99	0.64	1.83	1.62	75

[a] Phosphorane was generated before benzaldehyde was added. [b] Combined phosphine oxide polymer from four different experiments. [c] Sodium ethoxide to generate phosphorane and benzaldehyde were added at the same time. [d] Part of the polymer recovered from cycle 2 shown and polymer from a duplicate of cycle 2 were used. [e] Not determined.

and the affinity of the reagent for the polymer all influence the accessibility of potentially reactive sites.[1k] Initial bromination of the cross-linked polystyrenes and alkylation of the polymer-bound phosphines with benzyl bromide and methyl iodide in benzene and in *N,N*-dimethylformamide proceeded in high yield with all three copolymers: 2%, 8%, and macroporous 20% cross-linked.

Macroporous polymers differ from the conventional cross-linked polystyrenes by the presence of permanent pores in the polymer, even in the dry form.[1k,14] Each polymer bead is composed of a large number of microparticles fused together such that the bead contains about 50% pores by volume. The most probable pore size of the macroporous polymer used in this research is 900 Å (in the dry form as measured by mercury penetration porosimetry).[15] The microparticles are approximately the same size as the pores. Consequently, penetration of a reagent to a reactive site requires transport from bulk liquid to the particle surface, transport through the liquid-filled macropores of the polymer, and transport through a path of less than 900 Å of the 20% cross-linked polymer matrix. Diffusion through the macropores should proceed at the same rate as diffusion through a quiet liquid. Diffusion through the polymer matrix will be much slower. Transport of molecules to the reactive sites in a macro-

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porous polymer is much faster than in a nonmacroporous polymer of the same macroparticle size and degree of cross-linking because most of the transport occurs through liquid-filled pores rather than through the cross-linked matrix. Macroporous polymers can be used for ion-exchange resins,[16] for catalyst supports,[17] and for organic syntheses such as the Wittig reactions described here at a much higher degree of cross-linking than nonmacroporous polymers.

Some of the functional sites in the more highly cross-linked brominated polystyrenes failed to react with lithium diphenylphosphide (Table I). Extended reaction time at reflux improved the phosphination yield with the 8% cross-linked polymer. In the 20% cross-linked phosphinated polymer residual bromine accounted for all of the sites that were not transformed to phosphine. (See the Experimental Section for a sample calculation of the percent conversion.)

Treatment of the brominated polystyrenes first with *n*-butyllithium and then with chlorodiphenylphosphine in THF[11] gave 80% conversion to phosphine in the 2% cross-linked polymer but only 38% conversion in the 20% cross-linked polymer. Since there was no residual bromine in the phosphinated polymers, the *n*-butyllithium must have reached all of the active sites and reacted by bromine/lithium exchange. Apparently the chlorodiphenylphosphine failed to reach 20% of the lithiated sites in the 2% cross-linked polymer and 62% of the sites in the 20% cross-linked polymer. Overall loss of bromine without incorporation of phosphorus could have occurred by protonation of residual polystyryllithium during the water washing of the phosphine product. Alternatively, some replacement of hydrogen by bromine could occur by a side reaction accompanying $S_{RN}1$ substitution in which an aryl free radical abstracts a hydrogen atom from the THF solvent.[18]

The yields of Wittig reactions of polystyrene-bound benzyltriarylphosphonium salts ranged from 72% to 93%, higher than in previous reports[3,4,7] except for the phase-transfer catalysis experiments of Hodge.[8] Yields were highest with the 2% cross-linked support, which indicates that some of the phosphonium sites did not react with the base, sodium methoxide or sodium ethoxide, or with the aldehydes in the 8% and macroporous 20% cross-linked polymers.

The yields of Wittig reactions of polystyrene-bound methyltriarylphosphonium salts ranged from 52% to 99% by GLC analysis, higher than in an earlier report.[4] The recovered polymeric phosphine oxides with 8% cross-linking contained 39% and 47% of the original iodide ion (Table III), indicating that generation of the phosphorane was incomplete. The sodium salt of dimethyl sulfoxide in dimethyl sulfoxide failed to penetrate to some of the phosphonium sites. This accounts for the lowest yields with the 8% cross-linked polymer. Evidently the much shorter diffusion path required to reach the active sites in the macroporous polymer enabled higher conversion to phosphorane at 20% cross-linking than at 8% cross-linking without macroporosity. The 20% cross-linked polymer, however, gave lower yields of olefins than the 2% cross-linked polymer, even though it contained no residual iodide ion. This must be due to a failure of the aldehydes and ketones to penetrate to all of the phosphorane sites in the 20% cross-linked polymer. Longer reaction times might have afforded higher yields. Even the large ketones, 10-nonadecanone and cholest-4-en-3-one, penetrated the 20% cross-linked macroporous polymer to give good yields from reactions with the methylenetriarylphosphorane.

Why are our yields higher than the yields in most literature reports of reactions of polymer-supported Wittig regents? We believe two major factors are involved: the method of generation of the phosphorane and the method of original functionalization of the polystyrene. In some earlier investigations the polymer-bound phosphines were prepared by copolymerization of *p*-styryldiphenylphosphine, styrene, and divinylbenzene.[3,4] The copolymer reactivity ratios for styrene (m_1) and *p*-styryldiphenylphosphine (m_2) are $r_1 = 0.46$–0.53 and $r_2 = 1.11$–1.43.[19] Those for styrene and *m*-divinylbenzene (m_2) are $r_1 =$ 0.5–0.9 and $r_2 =$ 0.6–1.1, and those for styrene and *p*-divinylbenzene (m_2) are $r_1 =$ 0.2–0.7 and $r_2 =$ 1.0–1.2.[20] Both the *p*-styryldiphenylphosphine and the divinylbenzene are incorporated into the polymer faster than styrene itself during free radical polymerization. The phosphine groups are preferentially incorporated into the more highly cross-linked regions of nonuniformly cross-linked polymers. Some of these sites are difficult or impossible for an external reagent to reach even when the 2% cross-linked polymer is swollen. In contrast, when bromination of cross-linked polystyrene is the initial method of functionalization, any selectivity leads to bromine incorporation at the more accessible sites in the polymer matrix. In our investigation the reagent which had most difficulty penetrating the cross-linked polymers was lithium diphenylphosphide. In the subsequent phosphonium salt formation, phosphorane generation, and olefination, the alkyl halide, the base, and the carbonyl compound only needed to penetrate to reactive sites in the polymer that had already been reached by lithium diphenylphosphide. Consequently, the Wittig reactions gave higher yields than in previous investigations in which the original functionalization was performed by copolymerization with *p*-styryldiphenylphosphine.

The second factor which is crucial for high yields in polymer-supported Wittig reactions is use of a solvent/base system that promotes transport of the base to the phosphonium sites. Previous workers used sodium hydride or potassium *tert*-butoxide in THF[3] or *n*-butyllithium in dioxane[5,6] and obtained apparently incomplete phosphorane formation. The sodium alkoxide/alcohol/THF method works better for the benzylidenephosphoranes. We suspect that the use of a small amount of methanol in THF promotes swelling of the phosphonium ion sites within the polymer matrix, whereas use of only THF as the solvent fails to swell the potentially reactive sites enough for the base to penetrate to all of them. With the methylphosphonium salts the use of dimethyl sulfoxide as the solvent should enable swelling of all of the phosphonium sites. The combination of dichloromethane and water used in the phase-transfer-catalyzed method of phosphorane formation[8] from activated phosphonium salts also should promote swelling of the active sites better than a nonpolar organic solvent such as THF alone.

Previously Heitz and Michels[5] compared 0.5% and 2% cross-linked polystyrenes as supports for Wittig reagents and obtained higher yields with the 0.5% cross-linked polymer. Their typical procedure employed a 37% excess of phosphonium salt over carbonyl compound and used excess *n*-butyllithium in dioxane to form the phosphorane, followed by extensive washing to remove the excess base.

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Although their polymers were functionalized by bromination and sodium diphenylphosphide treatment of the cross-linked polystyrene, some sites failed to react with *n*-butyllithium. Our results demonstrate that use of more highly cross-linked polystyrenes is no barrier to high-yield olefinations with polymer-supported Wittig reagents. Moreover, on a large scale the more highly cross-linked, more rigid polymers are much easier to filter from reaction mixtures than the highly gelatinous solvent-swollen 0.5% and 2% cross-linked polystyrenes.

With the 20% cross-linked support the lithium diphenylphosphide reaction defined the number of sites in the polymer to be used in the subsequent Wittig reaction. Even though the phosphination proceeded in only 35% yield, the subsequent steps with less bulky reagents gave good yields. Thus if polymer-supported Wittig reactions are to be applied to precious or expensive alkyl halides or carbonyl compounds, it is possible to accept a low yield in the phosphination step and expect a good yield in the critical Wittig reaction.

A puzzling but synthetically useful result of this investigation is the marked increase in the fraction of the (*E*)-stilbene and (*E*,*E*)-1,4-diphenyl-1,3-butadiene with increased cross-linking of the polystyrene support. The results might be due to different solvation of the reactive sites in the different supports, but we have no really satisfactory explanation.

Conclusions

Polystyrenes cross-linked with as much as 20% divinylbenzene are suitable supports for Wittig reagents. Even large ketones such as 10-nonadecanone and cholest-4-en-3-one react with the polymer-bound methylenetriarylphosphorane in high yield. The success of the syntheses depends upon preparation of the reagent via bromination and phosphination of a cross-linked polystyrene, rather than by a copolymerization using *p*-styryldiphenylphosphine, and upon generation of the phosphorane with a base/solvent system that swells the phosphonium sites in the polymer network. The byproduct polymeric phosphine oxides are reduced to phosphines and reused for Wittig reactions with no reduction in yield.

Experimental Section

Reagents and Solvents. Tetrahydrofuran (THF) was dried over anhydrous $MgSO_4$ and distilled from the sodium ketyl of benzophenone under nitrogen. Chlorodiphenylphosphine was distilled under vacuum. Benzene and toluene were distilled from CaH_2. Dimethyl sulfoxide was vacuum distilled under nitrogen. All other chemicals were reagent grade and were used without further purification. Sodium methoxide and sodium ethoxide were prepared by dissolving a weighed amount of freshly cut sodium in a measured volume of the alcohol in a nitrogen atmosphere. Dimethylsulfinyl carbanion was generated in a nitrogen atmosphere by adding a weighed quantity of dry sodium hydride to dimethyl sulfoxide and heating the mixture to 50–65 °C until the sodium hydride dissolved.[21] The 2% and 8% cross-linked polystyrenes were prepared in this laboratory by suspension polymerization.[22] The 60/100-mesh fraction was used for all subsequent experiments. The macroporous 20% cross-linked polystyrene was provided by the Rohm and Haas Co. It was 25/60 mesh and had a BET nitrogen adsorption surface area of 70–80 m^2/g, ca. 50% volume porosity, and a most-probable pore diameter of 900 Å by Hg penetration porosimetry.

Analyses. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Gas chromatographic analyses were performed on a Hewlett-Packard Model 5840A instrument with a 6 ft × 0.125 in. o.d. nickel column of 20% SE-30 on 80/100-mesh Chromosorb Q and a thermal-conductivity detector. Preparative GLC was done on an Aerograph Model A90-P instrument operated isothermally with a 6 ft × 0.25 in. o.d. copper column of 15% SE-30 on Gas Chrom Q 80/100 mesh. ^1H NMR spectra were obtained on a Varian Model XL-100(15) instrument at 100 MHz. The IR spectra were recorded on a Perkin-Elmer Model 681 instrument. Elemental analyses were carried out by Midwest MicroLabs (Indianapolis, IN) or by Galbraith Laboratories (Knoxville, TN).

General Procedures with Polymeric Reagents. All polymer samples were washed and dried in a vacuum oven immediately before use. All reactions were conducted under nitrogen in three-necked round-bottomed flasks equipped with an overhead stirrer, serum stopper, nitrogen inlet, and reflux condenser (whenever needed). Polymer samples were allowed to swell in the solvent for 0.5 h without stirring before the start of a reaction. The Teflon blade of the stirrer was positioned high enough to avoid friction between the beads and the walls of the flask. These precautions with swelling and stirring enabled us to recover the reacted polymers with little or no breakage of beads. Cross-linked polystyrenes were washed with dichloromethane, acetone, and methanol and dried at 60 °C overnight. All polymer filtration and washing were performed in medium-porosity fritted funnels from Kimble Glass Co. Reaction temperatures of ca. −10 °C were achieved by use of an ice/salt balth.

Bromination of cross-linked polystyrenes was carried out in CCl_4 with thallic acetate sesquihydrate as a catalyst.[11] The product was washed with dichloromethane, acetone, and methanol and dried at 80 °C under vacuum. Analyses of bromine incorporated into the polymers agreed with the amounts of bromine used in the preparations. Most samples contained ca. 3.0 mequiv of Br/g.

Phosphination of Bromopolystyrene. (A) Lithium Diphenylphosphide Method.[13] A solution of 50 mL of THF and 16 mL (0.086 mol) of chlorodiphenylphosphine was added dropwise at −10 °C to 1.55 g (0.223 mol) of lithium metal ribbon which was cut into pieces about 3 × 4 mm in size. The mixture was stirred for 16 h at room temperature. The lithium diphenylphosphide solution was transferred by syringe to a pressure-equalizing addition funnel and added dropwise to a stirred mixture of 10.0 g of 2% cross-linked bromopolystyrene (3.10 mequiv of Br/g) in 50 mL of THF at −10 °C. Another 50 mL of THF was added, and the mixture was stirred for 48 h at 20 °C. A nitrogen-purged mixture of acetone/water (2:1 by volume, 50 mL) was added, and the mixture was stirred for 15 min. The solution was decanted, another 50 mL of acetone/water was added, and the mixture was transferred with acetone washing to a filter funnel under nitrogen.[23] The mixture was filtered under a slight pressure of nitrogen. The polymer was washed sequentially with 15 mL of acetone, 10 mL of THF, and 10 mL of diethyl ether seven times and dried at 100 °C under vacuum to give 13.1 g of phosphine polymer. Anal. Found: P, 6.47 (2.09 mequiv/g).

The same procedure with 25.10 g of the 8% cross-linked bromopolystyrene yielded 30.52 g of phosphine with 1.60 mequiv of P/g. In a second experiment 48.5 g of the 8% cross-linked bromopolystyrene and lithium diphenylphosphide in THF were refluxed for 6 h after being stirred at 20 °C for 48 h to yield 60.4 g of phosphine polymer. Anal. Found: P, 6.26 (2.02 mequiv/g).

By the same procedure 15.0 g of the 20% cross-linked macroporous bromopolystyrene gave 15.7 g of phosphine polymer (after some accidental loss during filtration) containing 3.0% P (0.97 mequiv/g). A second trial which employed 48 h of stirring at 20 °C and 6 h at reflux gave the same phosphine content.

(B) *n*-Butyllithium Method. The three-necked flask had a glass frit, a stopcock, and a 24/40 joint at the bottom. To 10.0 g (31.0 mequiv of Br) of 2% cross-linked bromopolystyrene in 50 mL of toluene at −10 °C was added dropwise 60 mL (96 mmol) of 1.6 M *n*-BuLi in hexane. The mixture was stirred for 1 h at room temperature and for 10 h at 70 °C. The mixture was cooled

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[21] Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1962**, *84*, 866–867.

[22] Balakrishnan, T.; Ford, W. T. *J. Appl. Polym. Sci.* **1982**, *27*, 133–138.

[23] Colwell, A. R.; Duckwall, L. R.; Brooks, R.; McManus, S. P. *J. Org. Chem.* **1981**, *46*, 3097–3102.

and filtered through the frit under slight nitrogen pressure. The polymer was washed five times with toluene. The flask was cooled to −10 °C, 80 mL of THF was added, and 30 mL (167 mmol) of chlorodiphenylphosphine was added dropwise. The mixture was stirred for 4 h, filtered, washed, and dried as in method A to give 12.4 g of phosphine polymer. Anal. Found: P, 5.77 (1.86 mequiv/g); Br, 0.00.

With 10.0 g of the 20% cross-linked macroporous bromopolystyrene the same procedure was used (except heating at 70 °C lasted 24 h) to give 10.9 g of phosphine polymer. Anal. Found: P, 3.5 (1.13 mequiv/g); Br, 0.03 mequiv/g.

Benzyltriarylphosphonium Salts. Benzyl bromide (5 mL, 42 mmol) was added dropwise with stirring to a suspension of 10.0 g of the 2% cross-linked phosphine polymer (21 mequiv) in 70 mL of *N,N*-dimethylformamide. The mixture was stirred for 48 h at 70 °C, cooled, filtered, washed sequentially with 10 mL of benzene, 10 mL of dichloromethane, and 10 mL of diethyl ether ten times over 8 h, and dried at 60 °C under vacuum to give 13.5 g of phosphonium salt. Anal. Found: Br^-, 1.36 mequiv/g (93% yield, by ion-exchange analysis).

By the same procedure 6.97 g of the 8% cross-linked and 10.8 g of the macroporous 20% cross-linked phosphine polymers gave 8.67 and 11.9 g of phosphonium salts containing 1.00 and 0.69 mequiv of Br/g, which correspond with yields of 86% and 96%.

Methyltriarylphosphonium Salts. The procedure used for preparation of benzyltriarylphosphonium salts was followed by using methyl iodide instead of benzyl bromide. Cross-linking, phosphine polymer weights, phosphonium ion polymer weights and the amount of I^-/gram of product were as follows: 2%, 8.4 g, 11.0 g, 1.38 mequiv; 8%, 20.9 g, 28.6 g, 1.38 mequiv; 20%, 16.0 g, 17.5 g, 0.66 mequiv. Yields based on I^- analyses were 85–98%.

Ion-Exchange Analysis of Phosphonium Salts. The phosphonium salt was powdered in a "Wig-L-bug",[24] and a weighed 0.2–0.3-g amount was transferred to a dry 250-mL Erlenmeyer flask. DMF (5 mL) was added. After 0.25–0.5 h a solution of 3–5 drops of 8 M HNO_3 in 5 mL of 50% $NaNO_3$ was added. After 3 h the mixture was diluted with 100 mL of water for the bromides (200 mL of water for the iodides), 5 mL of 8 M HNO_3 was added, and the mixture was titrated by the Volhard method.

Wittig Reactions. (*Z*)- and (*E*)-Stilbenes. To 1.97 g (2.42 mequiv) of 2% cross-linked benzylphosphonium salt **4a** in 30 mL of THF at −10 °C was added 1.2 mL of 2.03 M sodium methoxide in methanol (2.44 mmol) dropwise with a syringe. The mixture was orange-red after 2 h of stirring at 20 °C. After another 1 h the mixture was cooled to −10 °C, and 0.25 g (2.5 mmol) of benzaldehyde was added dropwise. The mixture was stirred for 16 h at 20 °C, refluxed for 2 h, filtered, and washed sequentially with 5-mL portions of THF, dichloromethane, and diethyl ether ten times over 2 h. The combined filtrate was evaporated on a rotary evaporator. The residue was weighed and analyzed by GLC with diphenyl ether as an internal standard.

The sodium bromide byproduct of phosphorane generation was recovered by washing the filtered polymer with deionized water on a fritted funnel. The aqueous filtrate was analyzed for bromide ion by Mohr titration. After methyl phosphonium salt reactions the residual I^- in the phosphine oxide polymer was determined by ion-exchange analysis.

The same procedure was followed with the macroporous 20% cross-linked polystyrene. With the 8% cross-linked polystyrene, 16 h of stirring was allowed for phosphorane generation, and 24 h of stirring at room temperature and 4 h at reflux were allowed for olefin formation.

(*Z,E*)- and (*E,E*)-1,4-Diphenyl-1,3-butadiene. The procedure used for (*Z*)- and (*E*)-stilbene was followed with cinnamaldehyde in place of benzaldehyde. For GLC analysis octadecane was used as an internal standard. The *E,E* isomer crystallized from a solution of the product mixture in methanol: mp 151–152 °C (lit.[25] mp 152–153 °C). ^1H NMR ($CDCl_3$) δ 6.46–7.12 (AA′BB′, 4 H), 7.20–7.46 (m, 10 H).

2-Methyl-1,4-diphenyl-1,3-butadiene. The procedure used for (*Z*)- and (*E*)-stilbene was followed by using α-methylcinnamaldehyde in place of benzaldehyde. The *E,E* isomer was isolated as white crystals from methanol: mp 81–83 °C; ^1H NMR ($CDCl_3$) δ 2.1 (s, 3 H), 6.64 (s, 1 H), 6.66 (d, 1 H, J = 16 Hz), 6.94 (d, 1 H, J = 16 Hz), 7.2–7.5 (m, 10 H).

1-Phenyl-1-tridecene. The procedure used for (*Z*)- and (*E*)-stilbene was followed by using dodecanal in place of benzaldehyde. The relative amounts of *Z* and *E* isomers were determined by GLC of the crude product by assuming equal thermal conductivity response factors. The *Z* isomer was confirmed as the minor product from the vinyl hydrogen region of the NMR spectrum of the mixture: ^1H NMR ($CDCl_3$) δ 0.96 (m, 3 H), 1.3–1.5 (m, 18 H), 2.2–2.4 (m, 2 H), 5.62 (dt, 0.43 H, H-2 of *Z* isomer, J = 12, 7 Hz), 6.00–6.55 (m, 1.57 H, H-1 of *Z* isomer and H-1 and H-2 of *E* isomer), 7.0–7.5 (m, 5 H).

Methylenecyclohexane. To 2.04 g (2.55 mequiv) of 2% cross-linked methylphosphonium salt **4b** in 30 mL of a 1:1 (v/v) mixture of THF and Me_2SO at −10 °C was added 5.0 mL (6.75 mequiv) of the sodium salt of Me_2SO in Me_2SO. The mixture was stirred for 6 h. The polymer turned a green-black color. The polymer was filtered under nitrogen pressure, washed with THF, and cooled to −10 °C. Cyclohexanone (0.237 g, 2.42 mmol) was added dropwise. The mixture was stirred for 16 h at 20 °C and refluxed for 2 h. The polymer was filtered and washed with THF, dichloromethane, and diethyl ether as in the stilbene procedure. The filtrate was partially distilled, and the remaining liquid was analyzed by GLC with decane as an internal standard. A small sample was purified by preparative GLC at 80 °C and identified from its ^1H NMR and IR spectra.

The same procedure was followed with the 20% cross-linked macroporous polymer. With the 8% cross-linked polymer, 16 h of stirring at room temperature was allowed for phosphorane generation, and 24 h of stirring at room temperature and 4 h at reflux were allowed for olefin formation.

These procedures were followed also for syntheses of 1-phenyl-1,3-butadiene, 1,1-diphenylethylene, 2-nonyl-1-undecene, and 3-methylene-4-cholestene by using 2.5–3.5 mmol of base/mequiv of **4b**.

1-Phenyl-1,3-butadiene. The product was purified by preparative GLC at 180 °C and analyzed by GLC with tetradecane as the internal standard. It was stored with a small amount of 4-*tert*-butylcatechol as a polymerization inhibitor: ^1H NMR ($CDCl_3$) δ 5.04–5.30 (m, 2 H), 6.2–6.6 (m, 2 H), 6.68–6.84 (m, 1 H), 7.1–7.4 (m, 5 H).

1,1-Diphenylethylene. The product was analyzed by GLC with octadecane as an internal standard. A small sample was purified by preparative GLC at 240 °C and identified from its ^1H NMR and IR spectra.

2-Nonyl-1-undecene. For olefin formation 24 h at 60 °C and 24 h at 20 °C were allowed. The product was analyzed by GLC with hexadecane as the internal standard, and a small sample was purified by preparative GLC at 270 °C: ^1H NMR ($CDCl_3$) δ 0.8–1.0 (m, 6 H), 1.15–1.55 (m, 28 H), 1.8–2.1 (m, 4 H), 4.68 (br s, 2 H); IR (neat) 3070, 1645 cm^{-1}.

3-Methylene-4-cholestene. Olefin formation conditions were the same as for 2-nonyl-1-undecene. The product was recrystallized from methanol/acetone to give a 91% yield of white needles: mp 69–70.5 °C; ^1H NMR ($CDCl_3$) δ 0.7–2.5 (m, 43 H), 4.55–4.75 (m, 2 H), 5.8–5.9 (m, 1 H); IR (KBr) 3080, 1640, 1600 cm^{-1}.

^{31}P NMR Analysis of $CDCl_3$-Swollen Polymer. Pulsed Fourier transform spectra were obtained at 40.5 MHz by using a 90° pulse width, a 10000-Hz frequency range, 8192 data points, an 0.82-s acquisition time, a 6.0-s delay time between pulses, and 240–600 acquisitions per spectrum. No ^1H decoupling was employed to eliminate the nuclear Overhauser effect. Observed chemical shifts relative to external 85% H_3PO_4, peak widths at half-height, and T_1 values measured by the fast inversion recovery method were as follows: phosphine, δ −6.3, 100–130 Hz, 2.6 s; phosphine oxide, δ 28.8, 164–260 Hz, 2.0 s.

Reduction of Polystyryldiphenylphosphine Oxide to Polystyryldiphenylphosphine. To a stirred mixture of 11.1 g (22.6 mequiv) of 2% cross-linked polystyryldiphenylphosphine oxide in 50 mL of benzene was added dropwise 4.5 mL (35 mequiv) of *N,N*-dimethylaniline followed by 3.5 mL (35 mequiv) of trichlorosilane. The mixture was refluxed for 12–16 h, cooled, filtered, and washed sequentially with 15-mL portions of benzene, THF, and diethyl ether 12 times over 3 h. The phosphine was

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(24) Crescent Dental Mfg. Co., Lyons, IL.

(25) "Aldrich Chemical Co. Handbook of Organic Chemicals"; Aldrich Chemical Co.: Milwaukee, WI, 1981–1982.

dried at 80 °C under vacuum. The data are given in Table IV. ^{31}P NMR analysis showed 92% phosphine and 8% phosphine oxide sites. The second recycling of the same polymer resulted in 90% phosphine and 10% phosphine oxide sites.

Benzylpolystyryldiphenylphosphonium Salt from Recycled Polymer. The standard procedure gave a phosphonium salt content of 1.24 mequiv/g of polymer (89% yield) in the first recycle and 1.30 mequiv/g of polymer (92% yield) in the second recycle.

(*Z*)- and (*E*)-Stilbene from Recycled Polymer. The procedure described previously was followed except that the sodium ethoxide and the benzaldehyde were added dropwise simultaneously by syringe. Yields of isomeric mixtures were 96% for the first and 97% for the second recycle.

Calculation of the Percent Conversion. For the partial conversion of bromostyrene repeat units to styryldiphenylphosphine units by the lithium diphenylphosphide method with 20% cross-linked macroporous polystyrene, the percent conversion was calculated as follows. (1) With 20% divinylbenzene (DVB) cross-linking the copolymer also contains 16% ethylvinylbenzene (EVB) and 64% styrene (St) by weight, since the divinylbenzene monomer contained 55% DVB and 44% EVB by weight. The average molecular weight of one repeat unit is $[(0.20)(1 \text{ mmol}/130.2 \text{ mg of DVB}) + (0.16)(1 \text{ mmol}/132.2 \text{ mg of EVB}) + (0.64)(1 \text{ mmol}/104.1 \text{ mg of St})]^{-1} = 112.4$ mg of monomer/mmol of repeat units. (2) Assume all three kinds of repeat units are equally reactive with bromine. The brominated copolymer by elemental analysis contains 3.08 mequiv of brominated repeat units (BrSt)/g and $[1000 \text{ mg} - (3.08 \text{ mequiv})(191.4 \text{ mg of BrSt/mequiv})][112.4 \text{ mg/mequiv of nonbrominated repeat unit}]^{-1} = 3.65$ mequiv of nonbrominated repeat units/g. The brominated polystyrene has $[3.08/(3.08 + 3.65)] \times 100 = 46\%$ ring substitution. (3) After phosphination the polymer contains by elemental analysis 1.63 mequiv of BrSt/g and 0.97 phosphinated repeat units (Ph_2PSt)/g. Therefore $[1000 \text{ mg} - (1.63 \text{ mequiv})(191.4 \text{ mg of BrSt/mequiv}) - (0.97 \text{ mequiv of } Ph_2PSt)(296.7 \text{ mg of } Ph_2PSt\text{/mequiv})][112.4 \text{ mg/mequiv of unsubstituted repeat units}]^{-1} = 3.56$ mequiv of unsubstituted repeat units/g. The polymer contains $(1.63 + 0.97 + 3.56) = 6.16$ mequiv of repeat units/g, of which $(1.63/6.16)(100) = 26\%$ are BrSt, $(0.97/6.16)(100) = 16\%$ are Ph_2PSt, and 58% are unsubstituted. The 42% of substituted repeat units agrees within experimental error with the 46% of BrSt units in the starting brominated polystyrene. The percent conversion of BrSt to Ph_2PSt repeat units was $(16/46)(100) = 35\%$.

Another calculation, which assumed that only styrene repeating units reacted with bromine, gave 27% BrSt, 16% Ph_2PSt, and 57% unsubstituted repeat units.

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Registry No. PhCH=CHCHO, 104-55-2; (*E*)-PhCH=C(CH_3)CHO, 15174-47-7; *n*-$C_{11}H_{23}$CHO, 112-54-9; (*E*)-PhCH=CHPh, 103-30-0; (*E*,*Z*)-PhCH=CHCH=CHPh, 5808-05-9; (*Z*,*E*)-PhCH=C(CH_3)CH=CHPh, 83897-70-5; (*E*)-*m*-$C_{11}H_{23}$CH=CHPh, 42036-74-8; $(CH_2)_5CO$, 108-94-1; Ph_2Co, 119-61-9; (*n*-$C_{10}H_{21})_2CO$, 19781-72-7; $(CH_2)_5C{=}CH_2$, 1192-37-6; PhC=CH_2, 530-48-3; (*n*-$C_{10}H_{21})_2C{=}CH_2$, 52636-68-7; (*E*,*E*)-PhCH=CHCH=CHPh, 538-81-8; (*E*)-PhCH=CHCHO, 14371-10-9; (*Z*)-PhCH=C(CH_3)CHO, 66051-14-7; (*Z*)-PhCH=CHPh, 645-49-8; (*E*,*E*)-PhCH=C(CH_3)CH=CHPh, 23637-43-6; (*Z*)-*n*-$C_{11}H_{23}$CH=CHPh, 83897-71-6; (*Z*)-PhCH=CHCHO, 57194-69-1; PhCH=CHCH=CH_2, 1515-78-2; benzaldehyde, 100-52-7; cholest-4-en-3-one, 601-57-0; 3-methylenecholest-4-ene, 4561-75-5; trichlorosilane, 19165-34-5; *N*,*N*-dimethylaniline, 121-69-7.

Oxidative Substitution of Nitroparaffin Salts[1]

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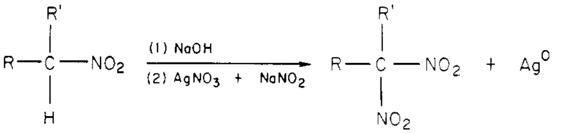
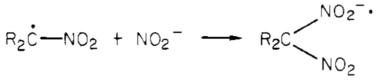
α,α-Dinitro compounds, α-nitro sulfones, and α-nitro nitriles are obtained in excellent yields when nitroparaffin salts are coupled to nitrite, benzenesulfinate, and cyanide ions by the agency of potassium ferricyanide.

Electron-transfer substitution at a saturated carbon atom is now well established.[2] Although most of the known examples are chain processes, it is of interest that the first example of an electron-transfer substitution process to be recognized (1964)[3] was the non-chain reaction of eq 1, which had been discovered in 1961.[4] The mechanism proposed in 1964 (eq 2–4) invoked collapse of a radical and an anion to give a radical anion, an idea that, while novel in 1964, is now routinely employed in any discussion of electron-transfer substitution.

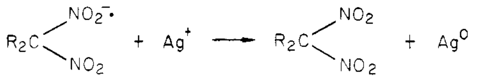


$$RR'CH{-}NO_2 \xrightarrow[(2)\ AgNO_3\ +\ NaNO_2]{(1)\ NaOH} RR'C(NO_2){-}NO_2 + Ag^0 \qquad (1)$$

$$R_2C^-{-}NO_2 + Ag^+ \longrightarrow R_2\dot{C}{-}NO_2 + Ag^0 \qquad (2)$$



$$R_2\dot{C}{-}NO_2 + NO_2^- \longrightarrow R_2C(NO_2^{-\bullet})(NO_2) \qquad (3)$$



$$R_2C(NO_2^{-\bullet})(NO_2) + Ag^+ \longrightarrow R_2C(NO_2)(NO_2) + Ag^0 \qquad (4)$$

In 1979 Matacz et al.[5] reported that aqueous potassium ferricyanide is a useful reagent for oxidatively substituting secondary nitroparaffin salts but that with the salts of

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[1] This is paper 26 in the series "Substitution Reactions which Proceed via Radical Anion Intermediates". For the preceding paper see: Kornblum, N.; Erickson, A. S. *J. Org. Chem.* **1981**, *46*, 1037.

[2] For reviews see: Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734. Kornblum, N. In "The Chemistry of Functional Groups, Supplement F: The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives"; Patai, S., Ed.; Wiley: New York, 1982; p 361.

[3] N Kornblum cited by Feuer, H. *Tetrahedron Suppl.* **1964**, *20*, 107.

[4] Kaplan, R. B.; Shechter, H. *J. Am. Chem. Soc.* **1961**, *83*, 3535. See footnote 6 of the paper by Kornblum, N.; Boyd, S. D.; Pinnick, H. W.; Smith, R. G. *Ibid.* **1971**, *93*, 4316 (1971).

[5] Matacz, Z.; Piotrowska, H.; Urbanski, T. *Pol. J. Chem.* **1979**, *53*, 187.