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Conversions of Carbonyl Compounds *via* Their Polymeric Sulfonylhydrazones into Alkenes, Alkanes, and Nitriles

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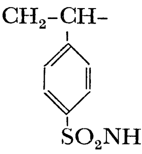
Resins consisting of cross-linked poly(styrene-divinylbenzene) matrices functionalized with hydrazinosulfonyl groups react with aldehydes and ketones to form the sulfonylhydrazone derivatives. The extent of the reaction is sensitive to the type of resin and the bulk of the carbonyl compound. When heated strongly under alkaline conditions, the sulfonylhydrazones release the corresponding alkenes; upon the $NaBH_4$ or $LiAlH_4$ treatment, they also release the corresponding alkanes; and, upon refluxing in methanol with potassium cyanide, they release nitriles containing one additional carbon atom.

The preparation of poly(*p*-vinylphenylsulfonylhydrazine) (**1**) and its use as a diazene source have been previously reported.[1,2)]

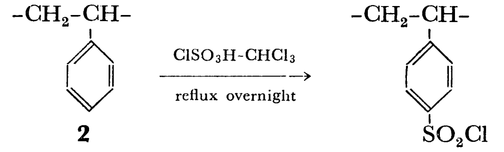


1

Our present interest was in exploring the potential of **1** as a possible polymer reagent for converting aldehydes and ketones into alkenes, alkanes, and nitriles *via* their hydrazones with **1**.

Results and Discussion

The polymers employed as starting reagents for this investigation were commercially available, macroreticular and gel-type styrene (St)-divinylbenzene (DVB) copolymers (**2**) (Table 1).



(1)

$$\mathbf{3} \xrightarrow{N_2H_4\text{-THF}} \mathbf{1} \qquad (2)$$

Each material (**2**) is readily converted, by refluxing it overnight in a solution of chlorosulfuric acid in chloroform, to the intermediate copoly(St- and DVBsulfonyl chloride) (**3**; 93—100% yield) (Eq. 1), and thence by the action of hydrazine–THF solutions to **1** (77—91% yield) (Eq. 2).

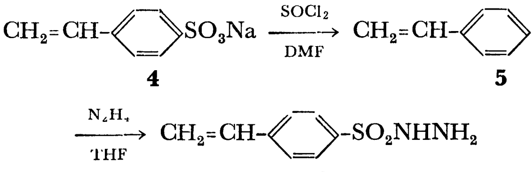
Table 1. Preparation of copoly(*p*-vinyl- and divinylphenylsulfonylhydrazone) (**1**)

No.	Polymer **2**	Polymer **3** Sulfonyl-chloride (mol%)[d)]	Polymer **1** Sulfonyl-hydrazine (mol%)[e)]
1	Macroreticular St-DVB copolymer[a)]	100	91
2	Macroreticular St-DVB copolymer[b)]	97	87
3	Gel-type St-DVB copolymer[c)]	93	77

a) Aldrich: 19,215-5. b) Containing 6% DVB (Mitsubishi Kasei). c) Containing 8% DVB (Mitsubishi Kasei). d) By weight increase. e) By CHN-analyses.

As can be seen in Table 1, macroreticular resins **2** (Nos. 1 and 2) provided higher conversions to **3** and thence to **1** than did gel-type resin **2** (No. 3).

Alternatively, the polymer **1** was prepared by the polymerization of the *p*-vinylphenylsulfonylhydrazine (**6**) synthesized starting with sodium *p*-styrenesulfonate (**4**) *via* sulfonyl chloride (**5**) (Eq. 3).



(3)

An attempt to synthesize **6** by the alkaline dehydrobromination of the *p*-(2-bromoethyl)phenylsulfonylhydrazine synthesized starting with (2-bromoethyl)benzene as in polymer (Eqs. 1 and 2) failed, presumably because of the high alkali-susceptibility of the prod-

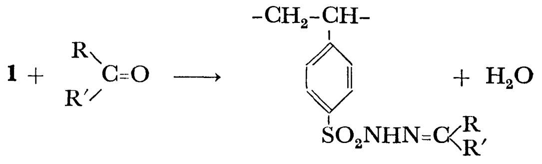
Table 2. Reaction of aldehydes and ketones with copoly(*p*-vinyl- and divinylphenylsulfonylhydrazine) (**1**)

No.	Polymer **1**[a)]	Aldehyde or ketone	Polymer **7** Sulfonylhydrazone (mol%)[b)]
1	1	Cyclohexanone	94
2	2	Cyclohexanone	86
3	3	Cyclohexanone	Trace[c)]
4	2	4-Methylcyclohexanone	64[d)]
5	1	Dibenzyl ketone	90
6	2	Dibenzyl ketone	41
7	2	Cyclododecanone	38[d)]
8	2	Camphor	No reaction[d)]
9	2	Camphor	15[e)]
10	2	Acetophenone	72
11	2	Benzophenone	58
12	2	Heptanal	79
13	3	Heptanal	Trace[c)]
14	2	Cyclohexanecarbaldehyde	72
15	2	Benzaldehyde	71

a) No. in Table 1. b) By weight increase. c) 3 h-reflux; carbonyl compound/polymer **1**=2/1 mol/mol. d) 5 h-reflux in methanol. e) 5 h-reflux in methanol containing 0.5% hydrochloric acid.

uct, **6**.

The reaction of the polymer **1** with aldehydes and ketones in refluxing ethanol to produce the corresponding hydrazones **7** (Eq. 4) provided varied results (Table 2).



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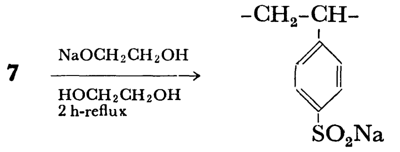
(4)

These results suggest that some of the hydrazinosulfonyl groups are in an environment too crowded to accommodate the hydrocarbon residues of bulky carbonyl compounds, even in the macroreticular form. Thus, cyclododecanone and camphor, typical bulky ketones, provided reactions of a low extent (Nos. 7, 8, and 9). The polymer **1**-3 with a gel structure also provided poor results (Nos. 3 and 13), presumably because of a lack of a swelling property for ethanol.

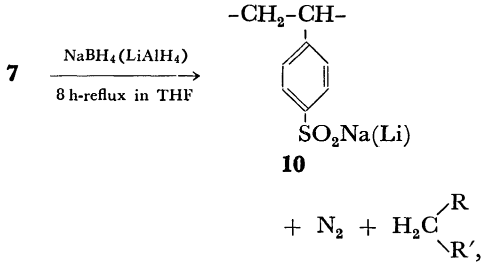
The polymeric arylsulfonylhydrazones (**8**) thus prepared were decomposed in the following two ways (Eqs. 5 and 6).



10

$+ N_2 + R'CH{=}CHR''$ (5)

8



10

$+ N_2 + H_2C(R)R'$ (6)

9

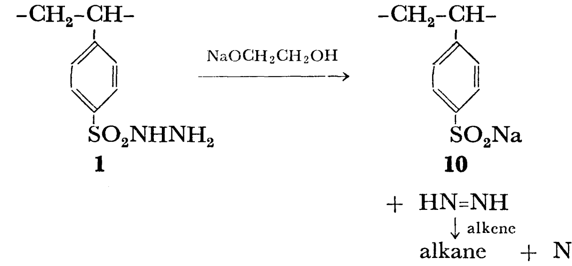
where R″ denotes the substituent attached to the α-carbon atom of the original carbonyl compound.

Table 3. Decomposition of copoly(p-vinyl- and divinylphenylsulfonylhydrazone) (**7**)

Sulfonylhydrazone[a] (**7**)	Alkene (**8**) by Eq. 5 (mol%)	Alkane (**9**) by Eq. 6 (mol%)/**7**
1	Cyclohexene, 9%	—
4	—	Methylcyclohexane, 13%, (19%)[b]
5	1,3-Diphenyl-1-propene, 77%	—
6	—	1,3-Diphenylpropane, 31%, (26%)[b]
7	Cyclododecene, 40%	—
9	—	Bornane, 6%, (0.8%)[b]
11	—	Diphenylmethane, 18%, (16%)[b]
15	—	Toluene, 11%, (9%)[b]
16[c]	—	Propylbenzene, 27%, (27%)[b]

a) No. in Table 2. b) With gel-type resin. c) With benzylacetone for the polymer **1**-2.

It is known that tosylhydrazones react with a solution of sodium in ethylene glycol to give diazo compounds, which subsequently decompose with the elimination of nitrogen to form alkenes.[3] This reaction was applied to the polymer **7** with the intention of converting carbonyl compounds to the corresponding alkenes (Eq. 5). Thus, a polymeric sulfonylhydrazone was dispersed in ethylene glycol containing a large excess of sodium, and the mixture was stirred under reflux for 2 h. The alkene (**8**) thus generated was extracted with either carbon tetrachloride or ether. The results are given in Table 3. The apparent low value obtained for the hydrazone with cyclohexanone (**7**-1) seems to be caused partly by the loss of the low-boiling product, cyclohexene, by evaporation during the reaction and the subsequent isolation process, since cyclohexanone tosylhydrazone gave cyclohexene almost quantitatively under similar reaction conditions.[3] Another cause of decrease in the yield of alkene is the formation of alkane, presumably due to the production of diazene from the remaining hydrazinosulfonyl group (**1**) in **7** and the subsequent hydrogenation of the alkene,[1] as is indicated in Eq. 7:



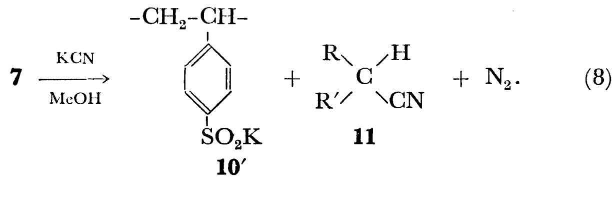
(7)

The production of alkanes could be recognized by means of the mass and ^{1}H-NMR spectra in all instances. Since the IR spectra of the resins which had been subjected to the procedure of Eq. 5 indicated no absorptions at 1320 and 1160 cm^{-1} attributable to hydrazones or hydrazines, but indicated every evidence of sodium poly(styrenesulfinate) (**10**), including a strong absorption at 960 cm^{-1},[4] the decomposition of **7** appears to take place completely under the present experimental conditions. The results of elemental analyses indicating the absence of nitrogen also support this conclusion.

Another way of decomposition, that indicated in Eq. 6, is also known for tosylhydrazones,[5] which are reduced with sodium borohydride or lithium aluminium hydride to liberate alkanes under relatively mild conditions, thereby constituting a general way of converting carbonyl compounds to alkanes. Thus, a polymeric sulfonylhydrazone **7** was dispersed in THF, and the mixture was refluxed for 8 h in the presence of a large excess of $NaBH_4$ ($LiAlH_4$ for **7**-11 and **7**-15).

The experimental conditions adopted here were the standard ones for low-molecular weight analogs.[5] Table 3 also indicates the results thus obtained. The relatively low yields of alkanes and the generally small differences between macroreticular and gel-type resins may indicate that the rate of reaction is governed by the permeation and diffusion of reductant $NaBH_4$ or $LiAlH_4$ into resin beads. Judging together with the fact that the IR spectra for macroreticular resins after the decomposition still indicate the absorptions attributable to the remaining hydrazones, it is likely that the reaction takes place mainly at the inner surfaces of resin beads, thereby indicating a poor permeability of the reductant under the present experimental conditions, although satisfactory yields were obtained for low-molecular weight analogs under these conditions.

The third trial carried out on the polymeric sulfonylhydrazine reagents (**1**) was the conversion of aldehydes and ketones *via* their hydrazones (**7**) into nitriles containing one additional carbon atom, as is indicated below:



(8)

The reaction is also known for arylsulfonylhydrazones,[6] and mild reaction conditions have been established. Thus, polymeric sulfonylhydrazone **7** was dispersed in methanol, and the mixture was refluxed with stirring in the presence of a large excess of potassium cyanide to liberate nitrile (**11**). A refluxing lasting approximately 72 h, twice as long as that for low-molecular weight analogs in homogeneous methanolic solutions,[6] was necessary to effect the complete decomposition of macroreticular **7**, as judged from the IR spectra. Table 4 summarizes the obtained results.

In spite of the complete decomposition of **7**, the yields of nitrile isolated are generally lower than those for the corresponding tosylhydrazones, even with macroreticular resins. Particularly in the case of **7**-11, a nucleophilic attack of the solvent methanol of the sp^2-carbon atom of the hydrazone resulted in the production of methyl diphenylmethyl ether, with the absence of the expected product. In other sulfonylhydrazones with macroreticular resins, however, the expected nitriles were isolated to appreciable extents, leaving potassium poly(styrenesulfinate) (**10′**). The macroreticular potassium poly(styrenesulfinate) thus produced was oxidized with aqueous bromine to afford poly(styrenesulfonic acid), which was then treated with chlorosulfuric acid to afford poly(styrenesulfonyl chloride) (**3**) almost quantitatively. This resin, **3**, could be reused as effectively as the fresh resins from **2**.

Table 4. Conversion of aldehydes and ketones into nitriles

Sulfonylhydrazone[a) (**7**)	Nitrile (**11**) by Eq. 8 (mol%)/**7**
2	Cyclohexanecarbonitrile, 20%
3	Cyclohexanecarbonitrile, 0%
10	2-Phenylpropionitrile, 7%
11	Diphenylacetonitrile, 0%
12	Octanenitrile, 22%
13	Octanenitrile, 3%
14	Cyclohexylacetonitrile, 20%
15	Phenylacetonitrile, 12%

a) No. in Table 2.

The production of poly(styrenesulfinates) (**10** and **10′**) is common to all the reactions (Eqs. 5, 6, and 8) investigated here. Good reusability and the easy separation of **10** or **10′** from the low-molecular weight decomposition products constitute the advantages of this type of polymer reagent, although the rates and extents of the reactions of Eqs. 5, 6, and 8 are generally inferior to those of the corresponding low-molecular weight analogs.

Experimental

The infrared (IR), ^1H-NMR, and mass spectra were recorded on a Hitachi 215 spectrophotometer, a JNM-PMX 60 spectrometer, and a Hitachi RMU-6M spectrometer respectively. The elemental analyses were done with a Perkin-Elmer 240 instrument.

*Copoly(styrene- and divinylbenzenesulfonyl chloride) (**3**).* A copoly(styrene-divinylbenzene) (**2**; 2.6 g, 25 mmol) was stirred in chloroform (100 ml) and then chlorosulfuric acid (20 ml, 250 mmol) was added dropwise. The mixture was subsequently stirred overnight under reflux, with the exclusion of moisture. The mixture was then filtered, and the resin was stirred for 30 min successively in chloroform (100 ml) and acetonitrile (100 ml), followed by thorough washing with water and vacuum drying to a constant weight. The results thus obtained are given in Table 1. The IR spectra of the products (**3**) indicated absorptions at 1170 and 1370 cm^{-1} characteristic of the sulfonyl chloride.

*Copoly(*p*-vinyl- and divinylphenylsulfonylhydrazine) (**1**).* The polymer **3** (4.05 g, 20 mmol) was stirred in THF (150 ml) externally cooled in an ice bath, after which hydrazine hydrate (5.7 ml, 80 mmol) was added dropwise. The reaction mixture was then stirred for further 30 min. The resin was filtered off, stirred in iced 1 mol dm^{-3} hydrochloric acid (150 ml) for 30 min, filtered, washed with water, further stirred in iced 1 mol dm^{-3} sodium hydrogencarbonate (150 ml), filtered, washed again with water, stirred in cold water for 30 min, filtered, and finally dried. The results thus obtained are also given in Table 1. The IR spectra of the products (**1**) indicated absorptions at 1150 and 1310 cm^{-1} characteristic of the sulfonylhydrazine, with the absence of that at 1370 cm^{-1} (sulfonyl chloride).

*p-Styrenesulfonyl Chloride (**5**).* A mixture of thionyl chloride (50 ml), 4-*t*-butylcatechol (0.3 g), and anhydrous *N,N*-dimethylfomamide (DMF; 60 ml) was stirred in an ice bath. Sodium *p*-styrenesulfonate (**4**; Tokyo Kasei; 20 g, 86 mmol) was added in small portions, and the mixture was stirred for 3 h to afford a homogeneous solution; it was then left to stand for 24 h in a refrigerator. The reaction mixture was then poured into ice water (300 ml) and extracted twice with benzene (each 200 ml). The extract was washed twice with water (each 200 ml), dried over anhydrous sodium sulfate, and concentrated on a rotary evaporator below 40 °C. Upon drying *in vacuo*, a pale yellow liquid was obtained in a 95% yield. Found: C, 47.01; H, 3.88%. Calcd for $C_8H_7O_2SCl$: C, 47.41, H, 3.48%. IR ($CHCl_3$) 1580 (aryl), 1360 (S=O), 980, 910 (vinyl) cm^{-1}. NMR ($CDCl_3$) δ=5.7 (d, 1H, $C\underline{H}_2$=CH–), 6.1 (d, 1H, $C\underline{H}_2$=CH–), 6.9 (q, 1H, CH_2=C$\underline{H}$–), 7.6—8.3 (q, 4H, ArH). Mass (*m/e*) 202 (M^+).

p-Vinylphenylsulfonylhydrazine (6). Hydrazine hydrate (3 ml, 50 mmol) was dropped with stirring into a solution of **5** (4 g, 20 mmol) in THF (20 ml), cooled in an ice bath. The turbid mixture was stirred for further 15 min and then poured into 200 ml of water with vigorous stirring. Stirring was continued for a while to separate a crude product, which was purified by dissolution in a small amount of THF and subsequent precipitation into hexane to afford fine colorless needles (mp 90—92 °C) in a 75% yield. Found: C, 48.46; H, 5.20; N, 14.11%. Calcd for $C_8H_{10}N_2SO_2$: C, 48.47; H, 5.08; N, 14.13%. IR (KBr) 3250 (NH_2, NH), 1600 (Ar), 1310, 1150 (SO_2), 1620, 1000, 930 (vinyl) cm^{-1}. NMR (DMSO-d_6+$CDCl_3$) δ=3.9 (b, 2H, NH_2), 5.6 (d, 1H, $C\underline{H}_2$=CH–), 6.1 (d, 1H, $C\underline{H}_2$=CH–), 7.0 (q, 1H, CH_2=C$\underline{H}$–), 7.9 (q, 4H, ArH), 7.5—9.0 (b, 1H, NH). Mass (*m/e*) 198 (M^+, 13), 42 (100).

*Polymer **1** Obtained by the Polymerization of **6**.* A solution of **4** (0.89 g) and α,α'-azobisisobutyronitrile (40 mg) in DMF (10 ml) was put into a glass ampoule, which was then evacuated, filled with nitrogen, and sealed in a conventional manner. Polymerization was carried out at 50 °C for 48 h. The contents of the ampoule were precipitated into methanol to isolate a white powder in an 80% conversion. The polymer was soluble in DMF and dimethyl sulfoxide and afforded a value of the intrinsic viscosity [η] of 0.22 dl/g in DMF at 30 °C. The IR (KBr) spectrum of the polymer was essentially identical with that of **1** with absorptions at 1310 and 1150 cm^{-1} characteristic of the sulfonylhydrazine.

*Formation of Copoly(p-vinyl- and divinylphenylsulfonylhydrazones) (**7**).* In a typical example corresponding with No. 2 in Table 2, a solution of cyclohexanone (2.72 ml, 26.3 mmol) in ethanol (70 ml) was added to a vacuum-dried polymer, **1**-2 (3.47 g, 17.5 mmol). The mixture was heated under reflux for 0.5 h, with the exclusion of the moisture. The resin was then filtered off, stirred in methanol (100 ml) for 30 min, filtered, washed thoroughly with methanol, and dried *in vacuo* to a constant weight.

The same reaction conditions were applied to other carbonyl compounds, unless otherwise noted.

The IR spectra of all the polymers thus obtained indicated absorptions at 1620 (C=N), 1600 (Ar), 1320, and 1150 (SO_2) cm^{-1}.

*Decomposition of **7** by Alkali (Eq. 5).* Hydrazone **7** (1 g) was stirred in ethylene glycol (10 ml). Sodium (0.30 g) was added, and the mixture was heated under reflux for 2 h with stirring. The mixture was diluted with water (50 ml) and extracted with carbon tetrachloride or ether. The organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated on a rotary evaporator below 40 °C. The presence of alkene in the residue was confirmed by a study of the IR [1600—1640 cm^{-1} (C=C)] and mass spectra, and its content was determined from ^{1}H-NMR [δ=5—6 (CH=CH)].

The results thus obtained are given in Table 3. The IR spectra of the resins after alkaline decomposition indicated absorptions at 1600 (Ar), 1010, and 960 cm^{-1}, with the absence of those at 1320 and 1150 cm^{-1}. Elemental analyses indicated the absence of nitrogen.

*Decomposition of **7** with Reduction (Eq. 6).* Hydrazone **7** (10 mmol) was stirred in THF (70 ml), $NaBH_4$ (3.0 g, 80 mmol) was added, and the mixture was heated under reflux for 8 h with stirring. The mixture was then poured into iced dilute hydrochloric acid and extracted with ether. The organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated on a rotary evaporator. The presence of alkane in the residue was confirmed by a study of the IR and mass spectra, and its content was determined from ^{1}H-NMR. Table 3 also gives the results thus obtained, where $LiAlH_4$ was used in place of $NaBH_4$ for the hydrazone **7** from aromatic carbonyl compounds (**7**-11 and **7**-15).

*Decomposition of **7** with Production of Nitriles (Eq. 8).* Hydrazone **7** (5 mmol) was stirred in methanol (70 ml), potassium cyanide (0.98 g, 15 mmol) was added, and the mixture was heated, under gentle reflux, for 72 h. After water (70 ml) had then been added, the product was extracted with dichloromethane (140 ml) and the extract was washed with saturated aqueous sodium hydrogencarbonate (100 ml) and water (50 ml). The dried (Na_2SO_4) organic layer was concentrated on a rotary evaporator. The presence of nitrile in the residue was cofirmed by a study of the IR 2200—2250 cm^{-1} (CN) and mass spectra, and its content was determined from ^{1}H-NMR. The IR spectra of the resins after decomposition indicated absorptions at 1600, 1010, and 960 cm^{-1}, with the absence of those at 1150 and 1320 cm^{-1}.

Recycling of Used Resins. The macroreticular potassium poly(styrenesulfinate) (**10′**; 5 mmol) left after the decomposition of the polymers **7**-2 according to Eq. 8 was stirred in an aqueous solution of bromine (2.4 g in 100 ml) at room temperature for 1 h. The potassium poly(styrenesulfonate) thus produced was filtered, washed thoroughly with water, and dried. The polymer was then stirred in chlorosulfuric acid (20 g) at 80 °C for 8 h. The mixture was filtered with a glass filter, and the resin was washed successively with two 100 ml-portions of dichloromethane and THF, and dried to regenerate poly(styrenesulfonyl chloride) (**3**) almost quantitatively. The resin **3** thus obtained was then subjected to the same reaction procedures as those used for fresh resin **3** to afford hydrazine **1** and thence cyclohexanone hydrazone **7**. The yield of cyclohexanecarbonitrile generated by the decomposition following Eq. 8 was 22%, based on **7**.

The resin **10**, obtained after decomposition by Eq. 5, was subjected to the same regeneration procedures as above, and the resin **3** thus regenerated was converted again to hydrazone **7**-5, which was subsequently decomposed following Eq. 5 to afford 1,3-diphenyl-1-propene in a 75% yield.

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