

Table 1. Polymerization of CHO by WCl₆- and MoCl₅-Based Catalysts^a

Exp. No.	Catalyst Systems ^b (mole ratio)	M/C ^c (mole ratio)	Temp (°C)	P. Y. ^d (%)	\bar{M}_n ^e	\bar{M}_w ^e
1	WCl ₆	500	-20	0	—	—
2	WCl ₆ -EtAlCl ₂ (1 : 2)	500	-20	98	5700	19500
3	WCl ₆ -EtAlCl ₂ (1 : 2)	250	-20	94	7200	25200
4	WCl ₆ -EtAlCl ₂ (1 : 2)	500	90	59	6800	21100
5	MoCl ₅ -EtAlCl ₂ (1 : 2)	500	-20	99	9800	19700
6	MoCl ₅ -EtAlCl ₂ (1 : 2)	250	-20	95	11300	27900
7	MoCl ₅ -(n-Bu) ₄ Sn (1 : 2)	500	-20	0	—	—

^aPolymerization was carried out in chlorobenzene for 24 hr. Initial monomer concentration was 2 M. ^bMixture of catalyst and cocatalyst was aged at 30°C for 15 min before use. ^cMole ratio of monomer to catalyst. ^dMethanol-insoluble polymer yield. ^eDetermined by GPC in tetrahydrofuran solution using calibration curve for polystyrene.

acetylene derivatives¹¹ were also found to be very effective catalyst system in this polymerization of CHO. The mole ratio of monomer to catalyst (M/C) was relatively higher in comparison with those of the polymerization of acetylene derivatives by the same catalysts. The adequate mole ratio of cocatalyst to catalyst and the polymerization temperature were 2 and -20°C, respectively. WCl₆-(n-Bu)₄Sn catalyst systems shows no catalytic activities in this polymerization.

IR spectrum of poly (CHO) prepared by WCl₆-EtAlCl₂ catalyst system shows the aliphatic C-H stretching frequency at 2858 and 2935 cm⁻¹ and it shows an absorption band at 1087 cm⁻¹ owing to C-O-C stretching frequency. The ¹H-NMR spectrum of poly (CHO) prepared by WCl₆-EtAlCl₂ catalyst system shows the peaks at 3.2 and 3.8 ppm due to the protons of carbon adjacent to the ether linkage. The peaks between 1.2 and 2.0 ppm is assigned to be the protons of methylene carbons. The number average molecular weight (\bar{M}_n)s of the resulting poly (CHO) were ranged from 5700 to 11300. The polydispersity (\bar{M}_w/\bar{M}_n)s were ranged from 2.01 to 3.50. Conclusively WCl₆-EtAlCl₂ and MoCl₅-EtAlCl₂ were found to be very effective catalyst systems for the polymerization of CHO.

A more detailed description of these polymerization, as well as characterization of the resulting poly (CHO), will be discussed elsewhere.

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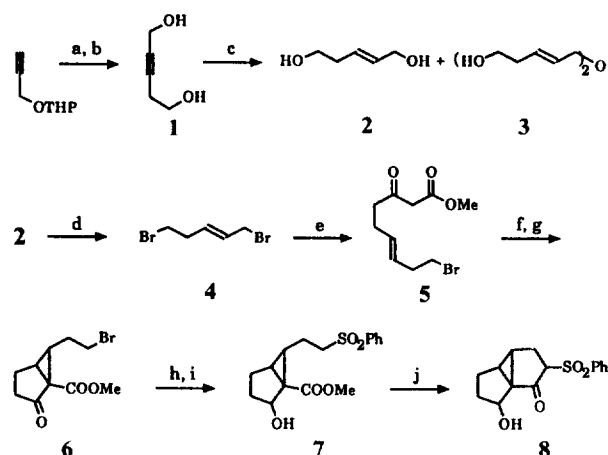
A Practical Synthetic Route to Tricyclo [4.3.0.0^{1,5}]nonane Derivatives

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The transitory formation of cyclopropanes has been often employed in terpene synthesis because their transformation enables otherwise synthetically difficult compounds to be accessible. Cyclopropanes are cleaved reductively or under acidic conditions to afford methyl or functionalized methylene groups.¹ Acid-mediated ring opening of α -hydroxycyclopropanes provides a route to chain lengthening.² The most versatile chemistry in such transformations of cyclopropyl derivatives certainly stems from cyclopropyl ketones derived from diazoketones and alkenes intramolecularly. Nucleophilic cleav-

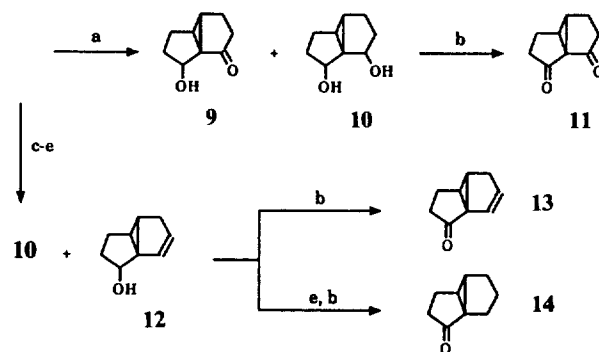


Reagents: (a) *n*-BuLi/HMPA/THF/0°C; BrCH₂CH₂OTHP/0°C, (b) CF₃COOH(cat.)/MeOH/RT, (c) LAH/THF/reflux, (d) NBS/Ph₃P/CH₂Cl₂/0°C, (e) Methyl acetoacetate/LDA/THF/0°C, (f) TsN₃/Et₃N/CH₂CN/RT, (g) Cu powder/CICH₂CH₂Cl/60°C, (h) NaBH₄/MeOH/RT, (i) PhSO₂Na/DMF/0°C → RT, (j) LDA/THF/0°C.

Scheme 1.

age of the cyclopropyl ketones results in not only intramolecular alkylation (or cyclization) but introduction of a functional group to γ -position of the carbonyl group.³ Although either of two bonds adjacent to the carbonyl group can be cleaved, regioselective opening of the cyclopropyl ketones seems to be achieved by stereoelectronic effect. The effect steers the cleavage of the bond perpendicular to the carbonyl group and controls the stereoselective introduction of nucleophile. For the systematic studies on the ring opening of cyclopropanes, of which the results may be applied to terpene synthesis, it is necessary to secure proper model compounds containing cyclopropyl moiety. In this context we herein wish to describe a practical synthetic route to tricyclo[4.3.0.0^{1,5}]nonane derivatives.⁴

Acetylide anion generated from tetrahydropyranyl (THP) ether of propargyl alcohol and *n*-butyllithium (*n*-BuLi) in THF was alkylated with THP ether of 2-bromoethanol in the presence of hexamethylphosphoramide (HMPA), and the resulting product was deprotected with a catalytic amount of trifluoroacetic acid in methanol to give diol **1** in 70% overall yield (Scheme 1). Conversion of triple bond of **1** into *trans*-olefinic double bond was accomplished with lithium aluminum hydride (LAH) in refluxing THF.⁵ When the reduction was carried out with an excess of LAH, substantial amount of ether **3** (up to 50% yield) was obtained. However, the portionwise addition of LAH (10 mol % per hour) overcame this difficulty to furnish the desired *trans*-olefinic diol **2** in 88% yield along with 12% of **3**. Treatment of **2** with *N*-bromosuccinimide (NBS) and triphenylphosphine⁶ produced dibromide **4** in 90% yield. Allylic position of **4** was regioselectively reacted with dianion⁷ generated from methyl acetoacetate and lithium diisopropylamide (LDA, 2 equivalents)⁸ in THF to afford methyl ester **5** in 81% yield.⁹ Methyl ester **5** was subjected to tosyl azide in triethylamine and acetonitrile,¹⁰ and the resulting diazo compound was cyclized in the presence of copper powder,¹¹ to provide bicyclic bromide **6** in 83% overall yield. Sodium borohydride reduction¹² of **6** followed by substitution with sodium benzenesulfinate in



Reagents: (a) 4~5% Na-Hg/MeOH/THF/-25°C, (b) Jones reagent/acetone/0°C, (c) NaBH₄/MeOH/RT, (d) Ac₂O/DMAP(cat.)/Et₃N/CH₂Cl₂/RT, (e) 5% Pd-C/H₂(1 atm)/K₂CO₃(cat.)/EtOAc/RT.

Scheme 2.

DMF gave a 7 : 1 mixture of phenylsulfone **7** and the corresponding benzenesulfinate ester in 99% combined overall yield due to the ambident character of the sulfinate anion.¹³ The addition of LDA (4 equivalents) to **7** in THF resulted in the formation of tricyclic sulfone **8** in 97% yield, of which the isomeric ratio was *ca.* 1 : 1 by NMR data.

Since the desired tricyclic skeleton was installed in **8**, it was transformed into cyclopropyl ketone derivatives (Scheme 2). Sodium-amalgam reduction of **8** in the mixture of methanol and THF furnished a 1 : 1-2 mixture of keto alcohol **9** and diol **10**,¹² depending on the reaction time which was oxidized together with Jones reagent to produce dione **11** in 78% overall yield. Sequential treatment of **8** with sodium borohydride, acetic anhydride in the presence of 4-dimethylaminopyridine (DMAP) and 4-5% sodium-amalgam¹⁴ afforded **10**¹⁵ and olefinic alcohol **12** in 6% and 60% yield, respectively. While Jones oxidation of **12** provided olefinic ketone **13** in 82% yield, hydrogenation of **12** with 5% Pd on charcoal in the presence of potassium carbonate followed by Jones oxidation gave ketone **14** in 80% overall yield.¹⁶

Studies on the ring opening of tricyclo[4.3.0.0^{1,5}]nonane derivatives **11-14** are currently under investigation to build hydrindane systems.

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15. This compound was identical with **10** from sodium-amalgam reduction of **8**.
16. All new compounds showed satisfactory spectral data.

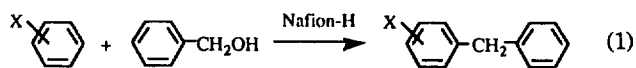
A Convenient Method for Benzylolation of Arenes over Perfluorinated Resinsulfonic Acid (Nafion-H)

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Alkylations of arenes with alcohols generally require molar amount of Lewis acid catalysts or concentrated sulfuric acid, which react with the alcohols to generate the corresponding carbocation intermediates.^{1,2} Although the reactions proceed under milder condition when benzyl alcohol is used, the catalysts are usually non-recoverable and should be removed in the work-up.³⁻⁵ We describe now the convenient and efficient method of Nafion-H (a solid perfluorinated resinsulfonic acid having sulfonic acid group in the amount of 0.01 to 5 mequiv/gram resin)^{6,7} catalyzed benzylolation of arenes with



benzyl alcohol. The reaction was carried out by refluxing a mixture of benzyl alcohol (1.0 g), substituted benzene (5.0 ml), and Nafion-H (0.2 g) for 8 hours. Water was removed with small amount of silica gel in a soxhlet thimble suspended just below refluxing condenser. The product were simply isolated by filtering the hot reaction mixture and distilling off the excess arene. The product yield and the *o/m/p* ratio

Table 1. Yields of Benzylolation of Arenes (XAr) with Benzyl Alcohol Using Nafion-H

X	Product ^a	Yield (%) ^b
H		73.6 (88.9) ^d
1,3,5-(CH ₃) ₃		73.3
CH ₃		68.1 (<i>o/m/p</i> = 41/9/15) ^f
CH ₃ O		85.1 (<i>o/m/p</i> = 43/11/46) ^f
NO ₂		76.1
N(CH ₃) ₃		trace

^aProducts were identified by physical constants and NMR spectra, ^bIsolated yields unless otherwise noted, ^cbp. 88-90°C/1.5 mmHg (lit.⁸ bp. 125.5°C/10 mmHg), ^dGC yield, ^ebp. 117-128°C/1.4 mmHg (lit.⁹ bp. 120-130°C/1.0 mmHg), ^fDetermined by GC (see text), ^gExcess amount (5.0 ml) of benzyl alcohol and smaller amount of nitrobenzene (1.0 g) were used.

were determined with gas chromatography on a 25 m capillary column of 5% phenylsilicon when necessary. The results are summarized in Table 1. The reactions are very clean and produce the desired benzylated products in high yields. Benzene and mesitylene afforded single products, whereas toluene and anisole produced mixtures of *o*-, *m*-, and *p*-disubstituted products as predicted by the directing effects of the substituents. For reaction of nitrobenzene, excess amount of benzyl alcohol had to be used because of the lower reactivity. These reactions apparently proceed by the reaction between substituted benzenes and benzyl cation generated on the catalyst surface. If the benzyl cation had long enough life time to migrate into the solution under the reaction condition, benzylolation of aniline derivatives may be realized without protecting the amino group. However, *N,N*-dimethylaniline did not react with benzyl alcohol under the same condition. It appears that both protonation and benzylolation occur on the catalyst surface and the former proceeds at much faster rate.

The present procedure provides an efficient method for benzylolation of benzene and substituted benzenes, except for aniline derivatives. In this procedure, only a catalytic amount of the acidic resin is needed, and the heterogeneous catalyst provides for a very simple work-up. Application of Nafion-H on other acid catalyzed reactions are in progress in our laboratory.

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