Table IV. Hygroscopicity Tests

Fluid	Reflux bp, °F Dry	Reflux bp, °F Humidified	Water absorbed, %
SAE compatibility fluid	358	283	3.05
Average of seven commercial fluids	501	308	2.56
Run 2, Table I	566	529	<0.5
Run 16, Table III	564	468	<0.6

viscosities at −40°F and poorer (higher) ASTM slopes. However, the effect on rubber is less. Despite higher molecular weights, the ethoxyacetates (Table II) have slightly better low-temperature viscosities than the corresponding methoxyacetates (Runs 11 vs. 1 or 14 vs. 10), but their effect on rubber is larger.

Monoesters (Table III). Increasing the number of ether oxygens (Runs 16, 18, and 20) or shortening the terminal alkyl group (Runs 16 and 17) gives better (lower) rubber swell. At approximately the same molecular weight, increasing the ether oxygens at the expense of the terminal alkyl group produces poorer (higher) low-temperature viscosities (Runs 15 and 16 or 17 and 18). Where applicable, our results are in general agreement with those obtained by Brause et al. for similar compounds (*1*).

Hygroscopicities (Table IV). Two representative esters were humidified and compared with the SAE compatibility test fluid (*4*) and with the average of seven conventional brake fluids. The methoxyacetates absorbed much less water and maintained a much higher boiling point than the other fluids. Although the present compounds had many properties required for brake fluids, much additional work would be required to qualify them fully for use as brake fluids.

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Improved Synthesis of 5,6,7,8,-Tetrahydro-5,8-dimethyl-1-naphthols

Aluminum Phenolate–Catalyzed Cyclialkylation of Phenol with 1,5-Hexadiene

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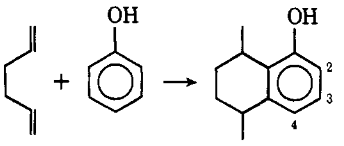
The aluminum phenolate–catalyzed cyclialkylation of phenols with 1,5-hexadiene represents an improved synthesis of derivatives of 5,6,7,8-tetrahydro-5,8-dimethyl-1-naphthol (I) compared with results using other catalysts. The reaction is subject to electronic and steric effects; electron-rich phenols give higher yields of derivatives of I while increasing bulk in the *para*-position or substitution in the *meta*-position of the starting phenol diminishes the yield of the desired cycliadduct.

Recently it was disclosed that 5,6,7,8-tetrahydro-5,8-dimethyl-1-naphthol (I) can be prepared in ca. 40% yield from the reaction of phenol and 1,5-hexadiene (4:1 mole ratio) in carbon disulfide at 30°C in the presence of boron trifluoride etherate (*1*). Substantial amounts of the corresponding 2-naphthol, ethers, and higher alkylated products were also obtained.



I

We wished to develop a convenient synthesis of derivatives of I which would increase the yield of the 2,3-cycliadducts while decreasing the phenol: 1,5-hexadiene ratio. This has been achieved by employing aluminum phenolates (from aluminum and the corresponding phenols) as catalysts.

From previous work (*2*), it is known that aluminum phenolate–catalyzed alkylation of phenol by olefins increases the probability of initial *ortho*-alkylation relative to ether formation and increases the probability of formation of *ortho*-alkylation products from subsequent alkylations by the alkyl phenyl ethers formed during the course of the reaction. It is not obvious whether alkyl phenyl ethers rearrange internally to 2-alkylphenols or whether they alkylate another phenol in the *ortho* position (*2*). In the cases investigated, the synthetic consequences would be identical.

When we used a phenol:1,5-hexadiene ratio of 1.9–4.6:1, a 55% yield of the desired unsubstituted cycliadduct was obtained. There was no significant yield variation over this concentration range. The reaction was studied with other phenols using a phenol:1,5-hexadiene ratio of 2.3-3.2:1. A comparison of the results reported in Table I indicates that the yields are greater for electron-rich phenols and poorer when substituents are present in the 3-position or large substituents are present in the 4-position of the starting phenol.

The reaction failed to produce a cycliadduct when the starting phenol contained a 4-nitro, 4-hydroxy, 4-amino, 4-acetamido, or a 4-thiomethyl group. In many of these cases, the phenol either sublimed or decomposed under the conditions of phenolate formation.

EXPERIMENTAL

Proton nmr spectra were recorded on a Varian A56/60 spectrometer and chemical shifts are reported in parts per million (ppm) downfield from TMS. Infrared spectra were

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Table I. Yields and Physical Properties of Derivatives of I[a]

	Product substitution				
	2	3	4	Yield, %	Bp, °C/mm
I	H	H	H	55	98–100/1.0
II	Me	H	H	65	92/0.5
III	H	Me	H	33	110–112/0.4
IV	H	H	Me	48	99–100/0.3
V	H	H	Et	33	112–113/0.8
VI	H	H	*n*-Pr	27	130–132/0.8
VII	*i*-Pr	H	H	64	112–113/0.3
VIII	Cl	H	H	25	95–96/0.3
IX	H	H	Cl	22	110–111/0.25
X	H	H	F	30	104–105/0.7
XI	H	H	OMe	39	136–137/0.5
XII	Me	H	Cl	22	103–105/0.3

[a] Elemental analyses (C, H, Cl, F) consistent with the proposed structures have been obtained (Analytical Department, Corporate Chemical Research Laboratory, Allied Chemical Corp.) and submitted for review.

Table II. Principal Infrared Bands of Derivatives of I (Cm^{-1})[b]

Compound	Aromatic	(Substitution pattern)	Ar—O	O—H
I	740, 790	(1,2,3)	1270	3400
II	809	(1,2,3,4)	1190–1235	3540
III	838	(1,2,3,5)	1250	3460
IV	805	(1,2,3,4)	1255	3400
V	812	(1,2,3,4)	1265	3450
VI	810	(1,2,3,4)	1265	3450
VII	813	(1,2,3,4)	1190–1225	3570
VIII	805	(1,2,3,4)	1250	3530
IX	812	(1,2,3,4)	1190	3465
X	806	(1,2,3,4)	1230	3420
XI	800	(1,2,3,4)	1250	3400
XII	862	(1,2,3,4,5)	1220	3550

[b] Samples neat.

Table III. Proton Nmr Spectra of Derivatives of I

(Ppm downfield from TMS in CCl_4)

Compound	ArH	OH	Other[a]
I	6.2–7.0 (m, 3)[b]	5.16 (s, 1)	. .
II	6.40–6.86 (ABq, 2, J = 7.5 Hz)	4.62 (s, 1)	2.12 (s, 3, $ArCH_3$)
III	6.16, 6.45 (Unresolved, 1 each)	5.44 (s, 1)	2.13 (s, 3, $ArCH_3$)
IV	6.1–6.8 (ABq, 2, J = 8 Hz)	5.05 (s, 1)	2.18 (s, 3, $ArCH_3$)
V	6.62–6.85 (ABq, 2, J = 8 Hz)	5.12 (s, 1)	0.98–1.42 (m, 9, includes $CH_2C\underline{H}_3$) 2.30–2.83 (Pair of q, 2, J = 7.3 Hz diastereomeric $ArCH_2$)
VI	6.20–6.80 (ABq, 2, J = 8 Hz)	5.33 (s, 1)	0.82–1.28 (m, 9, includes $CH_2C\underline{H}_3$) 1.28–2.18 (m, 6, includes $C\underline{H}_2CH_3$) 2.23–2.72 (m, 2, $ArCH_2$)
VII	6.46–6.98 (ABq, 2, J = 8 Hz)	4.56 (s, 1)	1.03–1.30 [Pair of d, 12, J = 7 Hz includes $CH(C\underline{H}_3)_2$] 2.65–3.30 [m, 3, includes $C\underline{H}(CH_3)_2$]
VIII	6.58–6.94 (ABq, 2, J = 8 Hz)	5.50 (s, 1)	. .
IX	6.27–7.04 (ABq, 2, J = 8.2 Hz)	5.22 (s, 1)	. .
X	6.27–6.92 (m, 2)	5.31 (s, 1)	. .
XI	6.37 (Coincident s, 2)	5.52 (s, 1)	3.66 (s, 3, OCH_3)
XII	6.78 (s, 1)	4.95 (s, 1)	2.07 (s, 3, $ArCH_3$)

[a] In addition, all spectra contain $CHC\underline{H}_3$ as a pair of doublets, 6, J = 7 Hz at 0.8–1.3 ppm, CH_2 as m, 4 at 1.3–2.3 ppm, and ArCH as m, 2 at 2.5–3.4 ppm.

[b] Identified as I previously by comparison of the aromatic absorption to that of 5,6,7,8-tetrahydro-1-naphthol (Sadtler nmr spectrum 2694M). See ref. *1*.

recorded on a Perkin-Elmer 21 spectrophotometer. All phenols were obtained from Eastman or Aldrich Chemical Co.

General Method of Cyclialkylation. In a typical experiment, the appropriate phenol and the aluminum powder (5 mol % based on the starting phenol) were heated at 150-200°C until hydrogen evolution ceased. CAUTION: This evolution is quite exothermic; use a 2-liter 3-necked flask fitted with two condensers to sufficiently control the reaction on a 2-mole scale. A safety shield is recommended; also a hood because of the evolution of hydrogen.

The 1,5-hexadiene (25-40 mol % based on the starting phenol) is added at such a rate as to maintain the reaction temperature as high as possible at atmospheric pressure (160-230°C depending on the starting phenol) and still have a reasonable rate of addition. If the reaction temperature drops below 160°C, there is negligible reaction. The temperature is maintained for 1 hr after the addition is completed. The mixture is cooled and poured onto a slurry of ice-hydrochloric acid and extracted with ether. The ether phase is dried (Na_2SO_4), and the product is separated by distillation.

The main impurities are 1:1 ethers which boil at a lower temperature than the cycliadduct, the 5,6,7,8-tetrahydro-5,8-dimethyl-2-naphthol derivative which distills at a higher temperature, and higher molecular weight products which do not distill under the conditions employed.

When phenol or electron-rich phenols were employed, isolation was effected by distillation. When phenols with chloro or fluoro groups were used, substantial amounts of 1:1 ethers were produced; in these cases, it was necessary to chromatograph the desired distillation fraction on a silica gel column with the less polar ether being eluted with 1:1 hexane:chloroform and purified by redistillation. The progress of the column chromatography could be followed effectively by gas-liquid partition chromatography (glpc) or thin-layer chromatography. Examination of the glpc results indicates no significant loss of product in this additional step.

The results of these experiments are described in Table I; spectral analyses are presented in Tables II and III. Microanalyses have been submitted for review.

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