VERIFICATION OF INFRARED VIBRATIONAL FREQUENCIES ASSOCIATED WITH AZIRIDINE RING

The characteristic infrared frequencies of N-substituted aziridines were summarized by Spell (10) as follows: ring C—H stretching; 3040–3090 cm^{-1} (asymmetrical stretching vibrations), 2979–3005 cm^{-1} (symmetrical stretching vibrations); symmetrical-ring breathing vibration; 1250–1360 cm^{-1}; ring CH_2 wagging; 1150–70 cm^{-1}; ring deformation and CH_2 rocking modes; 745–860 cm^{-1}. Because data from deuterated aziridines and vibrational analyses of N-substituted aziridines were previously not available, some of these assignments are strictly empirical.

Applying Hooke's law (9) and assuming that a C—H bond and a C—D bond have the same force constant, the ratio of the C—H to C—D frequency can be calculated to be 1.38. Thus N-phenylaziridine-2-d_2 can be used to verify the various carbon-hydrogen vibrations.

The following infrared data in cm^{-1} were obtained from N-phenylaziridine-2-d_2:

Methylene group	CH$_2$ stretching		CH$_2$ wag	CH$_2$ rock
	Asym	Sym		
CH$_2$	3060	2890	1170	898
CD$_2$	2310	2170	834	660
rCH/rCD	1.33	1.38	1.40	1.36

The rCH/rCD ratios are all in very good agreement with those calculated by Hooke's law. Therefore, the empirically assigned CH_2 stretching, CH_2 wagging, and CH_2 rocking vibrational frequencies of the aziridine ring have now been verified by isotopic data. The fact that the ring breathing vibrations were correlated with Hammett sigma values also verifies their assignments.

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Preparation and Physical Properties of Some Methoxy- and Ethoxyacetates

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Esters of methoxy- and ethoxyacetic acid with glycols or glycol ethers were prepared and evaluated. The physical properties determined were viscosities (212°, 122°, 100°, and —40°F), ASTM viscosity slopes, pour points, effect on rubber, and hygroscopicity. The effect of molecular structure on physical properties is discussed.

Conventional brake fluids are largely formulated from alkylene glycols and their ethers. Being hygroscopic, they soon deteriorate because of moisture absorption (3). Even small amounts of moisture can lower the boiling point of a brake fluid to an extent where under severe usage, vapor lock with loss of braking action may result. Moisture also increases the low-temperature viscosities and causes sluggish brake response at low temperatures.

Two approaches to overcome the problem of hygroscopicity have recently been used. The first uses fluids which are less hygroscopic than glycols and glycol ethers (2). In the second approach the moisture is chemically removed by reaction with the base fluid (5). A new approach based on esters of methoxy- and ethoxyacetic acids is presented here.

EXPERIMENTAL

Where available, reagent-grade chemicals were used for the ester syntheses. All other chemicals were high-quality commercial products. Starting materials were used as received Stoichiometric amounts of alkoxyacetic acid and glycol or glycol ether were refluxed in toluene using sulfuric acid as catalyst. After water no longer azeotroped in the Dean-Stark trap, calcium oxide or hydroxide sufficient to neutralize the sulfuric acid was added to the cooled product. After filtration, the product was stripped and distilled in vacuo through a vacuum-jacketed Vigreux column, 5.5 in. long. Elemental analyses (C, H) in agreement with the theory were obtained and submitted for review.

Physical properties were determined by ASTM methods except as follows: In the pour point determination only one cooling bath, Dry Ice–acetone, was used. Reflux boiling point (Table IV) and effect on rubber were determined by SAE procedures (4). Briefly, the effect on rubber (rubber swell) was determined as the diameter increase of a standard SBR wheel cylinder cup (original diameter 1.1 in.) after heating to 120°C for 70 hr. For automotive brake fluids, the Society of Automotive Engineers specifies the following limits for the properties tested here: kinematic viscosities at 212°F, 1.5 cSt minimum; at 122°F, 3.5 cSt minimum; at —40°F, 1800 cSt maximum; and rubber swell, 0.006–0.055 in. The hygro-

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scopicity tests of Table IV were performed at 80% relative humidity for 3.5 hr at 75°F.

DISCUSSION

Diesters (Tables I and II). Increasing the chain length of the glycol portion of the molecule produces more favorable (lower) ASTM viscosity slopes but poorer (higher) rubber swell (Runs 1 through 4). Increased branching gives poorer ASTM slopes (Runs 3, 6, and 7). It also increases the effect on rubber and gives higher (poorer) viscosities at −40°F (e.g., Runs 4 vs. 8 or 2 vs. 5). Run 1 has an unusually high viscosity at −40°F. This may be caused by incipient loss of chain flexibility and free rotation because the relatively closely spaced ester groups in this molecule are beginning to interfere with each other. Replacing the central methylene group in Run 4 by an ether oxygen, Run 10, results in poorer (higher)

Table I. Esters of Methoxyacetic Acid and Glycols

$$\overset{\text{O}}{\underset{\text{||}}{(\text{CH}_3\text{OCH}_2\text{CO})_2\text{R}}} \quad \text{(I)}$$

Run no.	R	Yield, %	Bp, °C/mm	Refractive index, n^{25}_D	Kinematic viscosity, cSt, °F 212	122	100	−40	ASTM slope	Pour point, °F	Rubber swell, in.
1	—(CH₂)₂—	78	93/0.025	1.4373	1.58	4.18	5.94	2340	0.95	−75	0.019
2	—(CH₂)₃—	64	103–4/0.06	1.4381	1.68	3.99	5.56	767	0.85	Below −85	0.028
3	—(CH₂)₄—	68	127–8/0.05	1.4405	1.86	4.64	6.41	a	0.83	Solid	0.040
4	—(CH₂)₅—	76	137–9/0.08	1.4422	1.99	4.99	6.67	853	0.80	Below −85b	0.063
5	—CH(CH₃)CH₂—	86	95–7/0.03	1.4346	1.60	4.17	6.09	3279	0.95	−65	0.041
6	—CH(CH₃)CH₂CH₂—	73	98–108/0.06	1.4370	1.79	4.35	6.21	1890	0.86	−80	0.046
7	—CH(CH₃)(CH₃)CH—	75	99–108/0.06	1.4344	1.65	4.60	6.72	2010	0.97	−55	0.060
8	—CH₂C(CH₃)₂CH₂—	95	117–19/0.05	1.4381	1.79	4.99	7.08	3461	0.92	−70	0.072
9	—CH₂C(CH₃)₂CH₂OCC(CH₃)₂CH₂— (O ||)	76	158–61/0.07	1.4451	3.14	11.60	19.60	a	0.88	−45	0.050
10	—(CH₂)₂O(CH₂)₂—	81	136–40/0.04	1.4442	2.14	6.11	9.00	9540	0.88	−60	0.029

a Not determined. b Traces of crystallization at −85°F.

Table II. Esters of Ethoxyacetic Acid and Glycols

$$\overset{\text{O}}{\underset{\text{||}}{(\text{C}_2\text{H}_5\text{OCH}_2\text{CO})_2\text{R}}} \quad \text{(II)}$$

Run no.	R	Yield, %	Bp, °C/mm	Refractive index, n^{25}_D	Kinematic viscosity, cSt, °F 212	122	100	−40	ASTM slope	Pour point, °F	Rubber swell, in.
11	—(CH₂)₂—	85	111–3/0.03	1.4344	1.58	4.35	5.66	1,673	0.92	−75	0.055
12	—(CH₂)₄—	87	131–4/0.03	1.4386	1.90	4.70	6.57	a	0.83	−5b	0.093
13	—CH(CH₂OCH₃)CH₂—	76	136–8/0.04	1.4370	1.91	5.65	8.41	10,480	0.94	−60	0.062
14	—(CH₂)₂O(CH₂)₂—	93	146–7/0.06	1.4424	2.17	5.75	8.40	6,896	0.83	−65	0.043

a Not determined. b Crystallized.

Table III. Esters of Methoxyacetic Acid and Glycol Ethers

$$\overset{\text{O}}{\underset{\text{||}}{\text{CH}_3\text{OCH}_2\text{COR}}} \quad \text{(III)}$$

Run no.	R	Yield, %	Bp, °C/mm	Refractive index, n^{25}_D	Kinematic viscosity, cSt, °F 212	122	100	−40	ASTM slope	Pour point, °F	Rubber swell, in.
15	—(CH₂CH₂O)₂C₄H₉	53	96–103/0.15	1.4326	1.29	2.60	3.60	221	0.86	Below −90	0.159
16	—(CH₂CH₂O)₃CH₃	73	105–10/0.05	1.4389	1.43	3.34	4.89	473	0.82	−85	0.059
17	—(CH₂CH₂O)₃C₄H₉	74	129–31/0.2	1.4390	1.69	3.96	5.23	565	0.82	Below −85	0.154
18	—(CH₂CH₂O)₄CH₃	48a	137–43/0.05	1.4438	1.88	4.68	7.09	1206	0.87	−85	0.046
19	—(CH₂CH₂O)₄C₂H₅	43a	144–5/0.07	1.4432	1.90	4.75	6.57	1291	0.82	−80	0.063
20	—(CH₂CH₂O)₇.₂₂CH₃	63	175–253/ 0.25–0.19	1.4544	3.70	10.57	15.60	b	0.70	+5c	0.019
21	—[CH(CH₃)CH₂O]₂CH₃	49a	73–6/0.1	1.4357	1.08	2.30	2.90	177	0.93	Below −85	0.165
22	—CH(CH₃)CH₂OCH₂CH₂OC₄H₉	51	103–4/0.4	1.4304	1.30	2.80	3.60	211	0.86	Below −90	0.195

a Distilled twice. b Not determined. c Started to crystallize at +35°F.

Table IV. Hygroscopicity Tests

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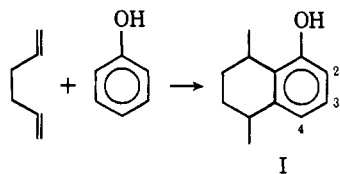
We wished to develop a convenient synthesis of derivatives of I which would increase the yield of the 2,3-cycliadducts while decreasing the phenol: 1,5-hexadiene ratio. This has been achieved by employing aluminum phenolates (from aluminum and the corresponding phenols) as catalysts.

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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