Capillary Column Gas Chromatography of Sulfur Heterocycles in Heavy Oils and Tars Using a Biphenylpolysiloxane Stationary Phase

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A newly synthesized biphenylpolysiloxane was found to be a highly selective stationary phase for the separation of sulfur heterocyclic isomers by capillary column gas chromatography. In conjunction with flame photometric detection, the sulfur heterocycles in various heavy oils and tars were determined. Phenaleno[6,7-*bc*]thiophene and 2-methylphenanthro[4,5-*bcd*]thiophene were identified for the first time in these materials.

Sulfur, in various forms, is present to some extent in all fossil fuels, petroleum residues, and coal-derived products. The detailed characterization of the polycyclic aromatic sulfur heterocycles (PASH) in these materials is important for several reasons. Many of the PASH are toxic (*1*) and/or mutagenic (*2–5*) in various biological test systems. Since noxious gases are produced during combustion of sulfur-containing fuels, it is desirable to remove the sulfur during the refining of the fuel. Furthermore, sulfur is notorius for poisoning of certain catalysts used in the upgrading process. An understanding of the forms of sulfur present is essential for the designing of the most efficient methods for removing sulfur from the final end products.

The PASH have not been characterized as extensively as the polycyclic aromatic hydrocarbons (PAH) and polycyclic aromatic nitrogen heterocycles (PANH) in heavy oils. The PASH have generally been determined using gas chromatography with sulfur-selective detection (*6–11*) or with mass spectrometry (*12–15*). However, positive identification of individual compounds is often difficult because of the large number of interfering compounds and PASH isomers that are present. Prefractionation steps are usually necessary before final analysis, even when using high-resolution gas chromatography. This laboratory has employed a modified procedure of Drushel and Sommers (*16*) to isolate the PASH fraction from coal liquids and shale oils (*17*). Relatively clean fractions were obtained, and many new PASH were identified for the first time. However, it was found that the recoveries of selected PASH varied from 0 to 70%, depending on the structures of the compounds (*18*).

Recently, Joyce and Uden (*19*) described a liquid chromatographic method for the isolation of thiophenic compounds from shale oil. Separate one-ring and two-ring aromatic fractions were first obtained by silica adsorption chromatography, and the thiophenes were then separated from these fractions by argentation chromatography on a silver nitrate coated silica column. Although complete separation was achieved for one-ring thiophenes, the benzothiophenes were enriched by approximately 96% in comparison to the naphthalenes. While no results were reported for higher molecular weight fractions, it is expected that this method would prove less satisfactory for compounds containing more than two rings.

Because of the complexities and shortcomings of the methods used for isolating PASH-rich fractions, recent efforts have again focused on high-resolution gas chromatography with sulfur-selective detection. High efficiency capillary columns coated with selective stationary phases have been found to be essential for resolving the numerous isomers present in various samples studied. In addition to the methylphenylpolysiloxane stationary phases (SE-52 and SE-54) normally used for the separation of polycyclic aromatic compounds, improved resolution of certain PASH isomer groups has been observed using capillary columns coated with a mixture of Superox 20M and SE-52 (found useful only for low-molecular-weight PASH in which the polar sulfur heteroatom exerts a significant effect on retention) (*20*), a mixture of *N,N'*-bis(*p*-butoxybenzylidene)-α,α'-bi-*p*-toluidine (BBBT) and SE-52 (*20*), and a mesogenic polysiloxane phase (*21*). No single column has yet been found that is capable of resolving all PASH isomers, but most compounds have been resolved by using two different selective columns.

In this study, a newly synthesized (*22*) biphenyl polysiloxane stationary phase was applied to the separation of PASH isomers in heavy oils and tars. The biphenyl groups in this stationary phase polymer could be polarized by the slightly polar PASH solutes, resulting in a unique selectivity.

EXPERIMENTAL SECTION

Four different heavy oils or tars were analyzed: (a) a coal tar sample, (b) a PAH/PASH fraction of a solvent refined coal (SRC II) heavy distillate, (c) a PAH/PASH fraction of a Wyoming Recluse crude oil, and (d) a PAH/PASH fraction of an Occidental shale oil. The PAH/PASH fractions were isolated as previously described (*23*).

Most of the PASH standard reference compounds were synthesized as described elsewhere (*24*). Capillary columns were prepared by coating fused silica capillary tubing (0.31 mm i.d.; Hewlett-Packard, Avondale, PA) with SE-54 and a 25% biphenyl, 75% methyl polysiloxane (17.2 m and 20.8 m, respectively, and 0.25 μm film thickness) which was synthesized in this laboratory (*22*). The biphenyl stationary phase was cross linked with azo-*tert*-butane (*25*). Both columns were conditioned overnight at 280 °C under nitrogen gas flow.

An HP 5880 gas chromatograph equipped with a flame photometric detector (FPD) and operated in the splitless injection mode was used. The hydrogen carrier gas was adjusted to a linear velocity between 40 and 100 cm s^{-1}, and the detector sensitivity was set to give full-scale response for 30 ng of benzo[*b*]naphtho[1,2-*d*]thiophene. Compounds were identified by comparison of retention data of the standards and samples on the

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Table I. Peak Assignments and Selected Concentrations for Identified Sulfur Heterocycles

peak no.	compound	concentration,[a] ppm coal tar	SRC-II	Wyoming crude oil	Occidental shale oil
2	benzo[*b*]thiophene				740
3	C_1-benzo[*b*]thiophene				1600
4	C_2-benzo[*b*]thiophene				5900
5	C_3-benzo[*b*]thiophene				4200
6	dibenzothiophene and/or naphtho[1,2-*b*]thiophene	4700	8500	2.2	210
7	naphtho[2,1-*b*]thiophene	230			
8	naphtho[2,3-*b*]thiophene	190			
9	4-methyldibenzothiophene	30	1900	9.1	
10	2-methyldibenzothiophene	13	1700	0.4	
11	3-methyldibenzothiophene	21	780	0.6	
12	1-methyldibenzothiophene				
13	C_2-dibenzothiophene		570	8.1	
14	phenanthro[4,5-*bcd*]thiophene	780	310		
15	phenaleno[6,7-*bc*]thiophene	100			
16	2-methylphenanthro[4,5-*bcd*]thiophene	34			
17	benzo[*b*]naphtho[1,2-*d*]thiophene and/or benzo[*b*]naphtho[1,2-*b*]thiophene	1700	460		
18	phenanthro[9,10-*b*]thiophene				
19	phenanthro[4,3-*b*]thiophene and/or anthra[1,2-*b*]thiophene and/or benzo[*b*]naphtho[2,3-*d*]thiophene	400			
20	phenanthro[1,2-*b*]thiophene and/or phenanthro[3,4-*b*]thiophene	130			
21	anthra[2,1-*b*]thiophene				
22	phenanthro[2,1-*b*]thiophene				
23	phenanthro[2,3-*b*]thiophene and/or phenanthro[3,2-*b*]thiophene				

[a] Concentration given in ppm of organic extract.

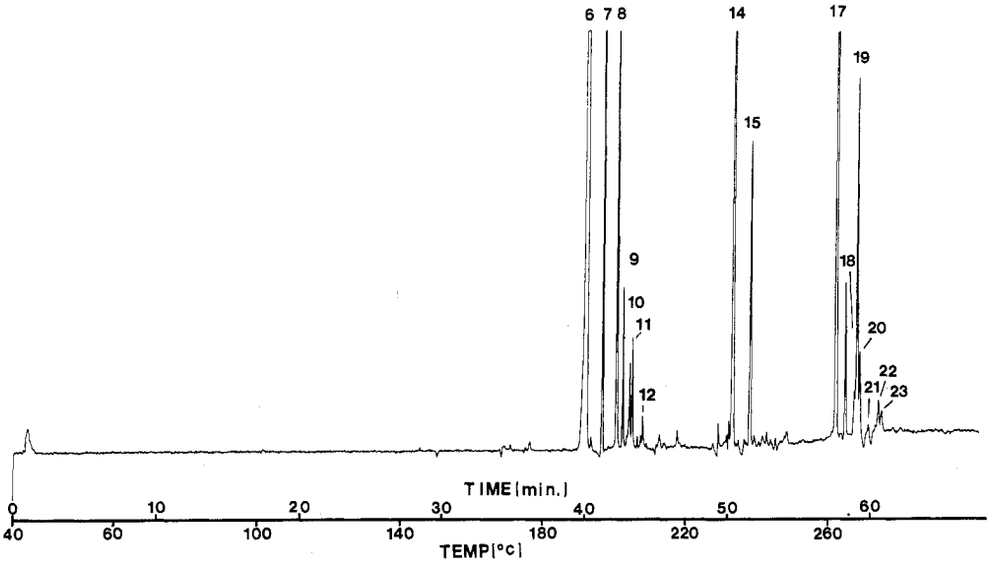

Figure 1. Chromatogram of coal tar on 25% biphenylpolysiloxane column: temperature program from 40 °C to 265 °C at 4 °C min^{-1} after an initial 2-min isothermal period; hydrogen carrier gas at 50 cm s^{-1}. Peak numbers refer to compounds listed in Table I.

two different selectivity capillary columns and confirmed by gas chromatography/mass spectrometry (GC/MS). GC/MS was accomplished with an HP 5982A GC/MS system operated with 70-eV electron beam energy.

Since the FPD in this study was not equipped with a linearizer, semiquantitation of PASH in the samples analyzed was accomplished by comparing peak areas of the resolved components with the peak areas of a standard injection of benzo[*b*]thiophene, dibenzothiophene, and benzo[*b*]naphtho[1,2-*d*]thiophene under the same chromatographic conditions.

RESULTS AND DISCUSSION

Recent studies (*26*) have demonstrated that the 25% biphenylpolysiloxane stationary phase is superior to other stationary phases for the separation of polar polycyclic aromatic compound isomers such as the alkylated carbazoles and dibenzothiophenes. The polarizable biphenyl group in the stationary phase is more sensitive to structural differences in these isomers than are other functional groups. In this study, the chromatographic retention of a number of isomeric PASH were compared by using SE-54 and the biphenylpolysiloxane as stationary phases. Neither the SE-54 or the biphenyl column was able to resolve dibenzothiophene and naphtho[2,1-*b*]thiophene, which were easily resolved on a mixed phase consisting of 50% Superox 20M in SE-52 (*20*). Furthermore, there appears to be little difference in the resolution of four-ring PASH isomers on either phase. Presumably, as the molecular weights of the PASH increase, the interaction of the slightly polar sulfur functionality with the biphenyl phase

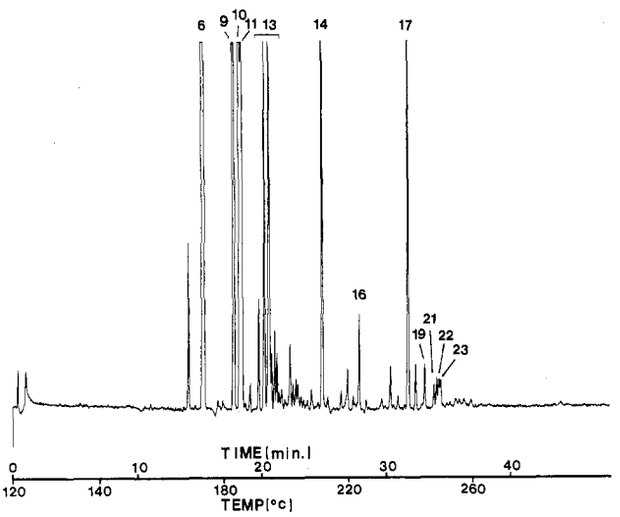

Figure 2. Chromatogram of SRC II PAH/PASH fraction on 25% biphenylpolysiloxane column: temperature program from 120 °C to 265 °C at 4 °C min^{-1} after an initial 2-min isothermal period; hydrogen carrier gas at 100 cm s^{-1}. Peak numbers refer to compounds listed in Table I.

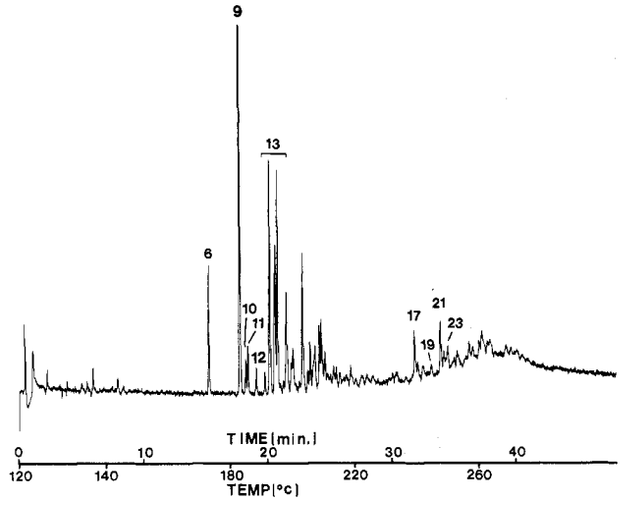

Figure 3. Chromatogram of Wyoming Recluse crude oil PAH/PASH fraction on 25% biphenylpolysiloxane column. Conditions are given in Figure 2. Peak numbers refer to compounds listed in Table I.

contributes less to the retention of the solute, and they elute principally according to vapor pressure. All four of the methyldibenzothiophenes were resolved on the biphenyl phase and identified in this coal-derived product.

In comparison to previous work (*18*) in which oxidation/reduction steps were used to isolate a "clean" PASH fraction from this same coal liquid, a number of compounds in which the thiophene ring is annellated only on one side were detected. These compounds include naphtho[2,1-*b*]thiophene, naphtho[2,3-*b*]thiophene and phenanthro[2,3-*b*]thiophene. In previous work, these compounds were removed during the fractionation steps. Table I lists the PASH identified in this study. In most cases, the compound identifications were confirmed by comparison of retention data on two different polarity stationary phases (SE-54 and the biphenylpolysiloxane) and mass spectral data with the same information from standard compounds.

Figures 1–4 show chromatograms of the sulfur heterocycles in a coal tar, an SRC II heavy distillate, a crude oil, and a shale oil, respectively. Differences exist in the PASH content of each of these samples. The coal tar contains principally unsubstituted PASH, while the coal liquid, shale oil, and petroleum crude contain increasing relative concentrations of

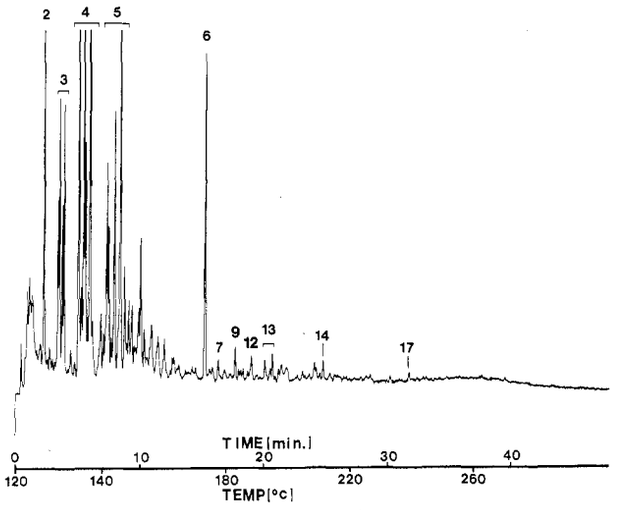

Figure 4. Chromatogram of Occidental shale oil PAH/PASH fraction on 25% biphenylpolysiloxane column. Conditions are given in Figure 2. Peak numbers refer to compounds listed in Table I.

alkyl-substituted PASH, respectively. The shale oil contains a relatively large concentration of low molecular weight PASH (alkylated benzo[*b*]thiophenes), while the coal tar contains the highest relative concentration of higher molecular weight compounds.

Two new compounds have been identified in this study: phenaleno[6,7-*bc*]thiophene and 2-methylphenanthro[4,5-*bcd*]thiophene.

Registry No. Benzo[*b*]thiophene, 95-15-8; naphtho[2,1-*b*]-thiophene, 233-02-3; naphtho[2,3-*b*]thiophene, 268-77-9; 4-methyldibenzothiophene, 7372-88-5; 2-methyldibenzothiophene, 20928-02-3; 3-methyldibenzothiophene, 16587-52-3; 1-methyldibenzothiophene, 31317-07-4; phenanthro[4,5-*bcd*]thiophene, 30796-92-0; phenaleno[6,7-*bc*]thiophene, 79965-99-4; 2-methylphenanthro[4,5-*bcd*]thiophene, 88114-00-5; phenanthro[9,10-*b*]-thiophene, 236-01-1; anthra[2,1-*b*]thiophene, 227-56-5; phenanthro[2,1-*b*]thiophene, 219-25-0; anthra[2,3-*b*]thiophene, 22108-55-0.

LITERATURE CITED

(1) Eastmond, D. A.; Booth, G. M.; Lee, M. L. *Arch. Environ. Contam. Toxicol.* **1984**, *13*, 105–111.
(2) Tilak, B. D. *Tetrahedron* **1960**, 76–95.
(3) Karcher, W.; Nelen, A.; Depaus, R.; van Eijk, J.; Glaude, P.; Jacob, J. In "Polynuclear Aromatic Hydrocarbons: Chemical Analysis and Biological Fate"; Cooke, M., Dennis, A., Eds.; Battelle Press: Columbus, OH, 1981; pp 317–327.
(4) Pelroy, R. A.; Stewart, D. L.; Tominaga, Y.; Iwao, M.; Castle, R. N.; Lee, M. L. *Mutat. Res.* **1983**, *117*, 31–40.
(5) McFall, T.; Booth, G. M.; Lee, M. L.; Tominaga, Y.; Pratap, R.; Tedjamulia, M.; Castle, R. N. *Mutat. Res.* **1984**, *135*, 97–103.
(6) Martin, R. L.; Grant, J. A. *Anal. Chem.* **1965**, *37*, 644–649.
(7) Martin, R. L.; Grant, J. A. *Anal. Chem.* **1965**, *37*, 649–657.
(8) Clugston, D. M.; George, A. E.; Montgomery, D. S.; Smiley, G. T.; Sawatzky, H. *Adv. Chem. Ser.* **1976**, *No. 151*, 11–19.
(9) Adlard, E. R.; Creaser, L. F.; Matthews, P. H. D. *Anal. Chem.* **1972**, *44*, 64–73.
(10) Wenzel, B.; Aiken, L. *J. Chromatogr. Sci.* **1979**, *17*, 503–509.
(11) Burchill, P.; Herod, A. A.; Pritchard, E. *J. Chromatogr.* **1982**, *242*, 51–64.
(12) Hastings, S. H.; Johnson, B. H.; Lumpkin, H. E. *Anal. Chem.* **1956**, *28*, 1243–1247.
(13) Gallegos, E. J.; Green, J. W.; Lindenan, L. P.; LeTourneau, R. L.; Teeter, R. M. *Anal. Chem.* **1967**, *39*, 1833–1838.
(14) Bodezek, D.; Krzyzonowsk, T.; Marzec, A. *Fuel* **1979**, *58*, 196–202.
(15) Paller, M.; Hlozek, V. *Monatsh. Chem.* **1975**, *106*, 1259–1284.
(16) Drushel, H. V.; Sommers, A. L. *Anal. Chem.* **1967**, *39*, 1819–1829.
(17) Willey, C.; Iwao, M.; Castle, R. N.; Lee, M. L. *Anal. Chem.* **1981**, *53*, 400–407.
(18) Kong, R. C.; Lee, M. L.; Iwao, M.; Tominaga, Y.; Pratap, R.; Thompson, R. D.; Castle, R. N. *Fuel*, **1984**, *63*, 707–713.
(19) Joyce, W. F.; Uden, P. C. *Anal. Chem.* **1983**, *55*, 540–549.
(20) Kong, R. C.; Lee, M. L.; Tominaga, Y.; Pratap, R.; Iwao, M.; Castle, R. N.; Wise, S. A. *J. Chromatogr. Sci.* **1982**, *20*, 502–510.
(21) Kong, R. C.; Lee, M. L.; Tominaga, Y.; Pratap, R.; Iwao, M.; Castle, R. N. *Anal. Chem.* **1982**, *54*, 1802–1806.
(22) Kuei, J. C.; Shelton, J. I.; Castle, L. W.; Kong, R. C.; Richter, B. E.; Bradshaw, J. S.; Lee, M. L. *HRC CC, J. High Resolut. Chromatogr.*

Chromatogr. Commun. **1984**, *7*, 13-18.
(23) Later, D. W.; Lee, M. L.; Bartle, K. D.; Kong, R. C.; Vassilaros, D. L. *Anal. Chem.* **1981**, *53*, 1612-1620.
(24) Castle, R. N.; Tedjamulia, M. L.; Tominaga, Y.; Pratap, R.; Sugiura, M.; Kudo, H.; Lee, M. L.; Iwao, M.; Thompson, R. D.; Martin, G. E.; Gampe, R. T., Jr.; Musmar, M. J.; Willcott, M. R., III; Smith, S. L.; Layton, W. J.; Hurd, R. E.; Johnson, L. F. *In* "Lectures in Heterocyclic Chemistry"; Castle, R. N., Ed.; Hetercorporation: Tampa, FL, 1984; Vol. 7, pp 1-52.
(25) Wright, B. W.; Peaden, P. A.; Lee, M. L.; Stark, T. *J. Chromatogr.* **1982**, *248*, 17-34.
(26) Lee, M. L.; Kuei, J. C.; Adams, N. W.; Tarbet, B. J.; Nishioka, M.; Jones, B. A.; Bradshaw, J. S. *J. Chromatogr.*, in press.

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Role of Thermal Dissociation in the Direct Gas–Liquid Chromatographic Determination of Amine Maleate Salts

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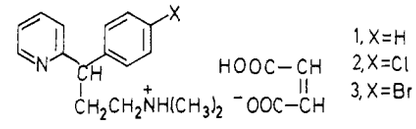
Thermoanalytical, GLC, and spectrometric data have provided evidence that the observation of analytically useful peaks from the direct gas chromatographic analysis of otherwise involatile maleic acid salts of a family of tertiary amines is the result of thermal dissociation of the salts to their respective free base and free acid moieties. The efficiency of the dissociation achieved upon injection of the salts into "unmodified" GLC systems is dependent upon the injection port temperature (IPT), as deduced from measurement of the molar responses of the peaks arising from both of the eluted components. Optimum response is obtained over only a narrow IPT range (near 200 °C in the case of the antihistamine salts tested). DTA and TGA experiments provided data which proved to be reliable predictors of the GLC behavior of the salts.

Despite their relative involatility, certain classes of amine salts (alkaloids and nitrogenous drugs) have been found to yield analytically useful peaks upon direct injection into gas–liquid chromatographic (GLC) systems (*1–9*) without prior conversion to their free bases or the use of alkali-modified forecolumns, analytical columns, or carrier gases. Based on the retention times of the peaks obtained by using such unmodified systems, it has been postulated that thermal dissociation of the salts in heated portions of the GLC system may be occurring to liberate the conjugate free bases, which then elute in the normal manner (*1*, *3–5*, *10*). If so, however, the fate of the acid part of the salts, even where the acid may be organic, has not been accounted for experimentally. Also, the quantitative reproducibility of the postulated thermal conversion has been questioned (*11*, *12*), although attempts to exploit the direct salt injection procedure for quantitative purposes have been reported (*8*, *13*).

In order to establish the general utility of determining amine salts via direct injection under nonextraordinary GLC conditions, the experimental limitations of the technique as well as further proof of the mechanism responsible for the observed GLC behavior were sought. For this purpose, the thermoanalytical and GLC characteristics of maleic acid salts of a series of commonly available antihistamines, viz., pheniramine (**1**), chlorpheniramine (**2**), and brompheniramine (**3**), have been examined. The maleic acid salt of *N,N*-dimethyl-*n*-propylamine (**4**) is also included in this study, since it serves as a simple experimental model for **1–3**, representing the "side chain" of the latter devoid of the substituents on the ω-carbon atom. The tertiary amine and organic acid which would be the products of the thermal dissociation of these compounds are readily detectable chromatographically. Detection and quantitation of the acid moiety as well as the basic portion of the salts under the GLC conditions employed would provide further confirmation of the thermal dissociation mechanism as the source of the GLC peaks obtained from these intrinsically involatile analytes. The thermoanalytical experiments were intended to provide a basis for explaining and predicting the observed GLC behavior.



1, X=H
2, X=Cl
3, X=Br

EXPERIMENTAL SECTION

Chemicals. The following chemicals were obtained from commercial sources and were used without further purification: pheniramine maleate (Hexagon Laboratories), chlorpheniramine maleate (H. Reisman Corp.), brompheniramine maleate (A. H. Robins), *N,N*-dimethyl-*n*-propylamine (Alfa Products), maleic acid (Alfa Products), maleic anhydride (J. T. Baker), propionic acid (Amend Drug Co.), octadecane (Chem Service), and hexadecane (Poly Science). Solvents employed were all reagent grade.

The maleic acid salt of *N,N*-dimethyl-*n*-propylamine (**4**) was synthesized by mixing a solution of 0.050 mol of the acid in 10 mL of acetone with 5 mL of a solution containing 0.055 mol of

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