and kept cold until all of the methyl iodide had disappeared (approximately 1.5 hours) and the clear solution was then evaporated to dryness in vacuo at room temperature, followed by drying in a high vacuum for six hours at room temperature. The white, crystalline solid, 3.68 grams, melted at 232–235° C. with decomposition and represented a 95.5% yield. The elemental analysis is listed in Table I.

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Preparation and Characterization of Several Unsaturated Amines and Quaternary Ammonium Salts

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Twelve previously unreported unsaturated secondary or tertiary amines and nine previously unreported unsaturated quaternary ammonium salts have been prepared and characterized. An unsaturated quaternary ammonium salt containing an asymmetric nitrogen atom and one containing an asymmetric carbon atom were resolved to obtain the dextrorotatory isomer in each case.

DURING the course of an unsuccessful attempt to prepare optically active quaternary ammonium ion exchange resins, a number of previously unreported amines and quaternary ammonium salts were prepared. The physical properties and pertinent data on these new compounds along with the experimental details for resolution and isolation of one optically active antipode from each of two classes of asymmetric quaternary ammonium salts are reported. One class studied contained an asymmetric quaternary nitrogen atom while the other class contained an asymmetric carbon atom.

The amines were prepared in most cases by reaction of the appropriate alkenyl halide with the appropriate amine in presence of a proton acceptor (*2*). The physical properties, yields, and analytical data are reported in Table I.

The quaternary ammonium salts were prepared by reaction of the appropriate alkyl halide or alkenyl halide with the appropriate tertiary amine in a polar solvent such as acetone, according to well established procedures (*1*). The physical properties, yields, and analytical data in these quaternary ammonium salts are reported in Table II.

The *dl*-allylmethallylmethylphenylammonium bromide was resolved to obtain the dextrorotatory isomer in an optically pure state by use of *d*-camphor-10-sulfonic acid. The procedure used was a modified form of that reported by Pope and Peachey (*6*). The *d*-*d*-allylmethallylmethylphenylammonium camphor-10-sulfonate, after purification and determination of its optical properties was converted to *d*-allylmethallylmethylphenylammonium iodide by treating with an aqueous solution of potassium iodide from which the quaternary ammonium iodide precipitated. After purification and drying, its optical properties were determined. The molecular rotation of the iodide was found to be +26.6°. This value is in good agreement with the value of +27.36°, obtained from the maximum rotation obtained for the *d*-camphor-10-sulfonate after correction for the contribution of the camphor moeity (*4, 5*) (77.95° – 50.59° = 27.36°). *d*-Triallyl-2-octylammonium *p*-bromobenzenesulfonate was obtained by heating triallyamine with *d*-2-octyl *p*-bromobenzenesulfonate, and purification of the product. The physical properties, yields, and analytical data for these compounds are recorded in Table III.

As an intermediate for the preparation of *d*-triallyl-2-octylammonium *p*-bromobenzenesulfonate, *d*-2-octanol was prepared by the method of Cary, Vitcha, and Shriner (*3*). The product had a specific rotation of +6.50°, and was estimated to be 65% optically pure. This alcohol was converted to the *p*-bromobenzenesulfonate ester by reaction with the sulfonyl chloride. The purified ester had a specific rotation of +4.26° indicating it to be 60.2% optically pure. The analytical data and other physical properties for this compound are reported in the experimental section.

The resolution of *dl*-triallyl-*sec*-butylammonium bromide was also attempted by use of silver salts of *d*-camphor-10-sulfonic acid, *d*-3-bromocamphorsulfonic acid, and *d*-tartaric acid without success. The products were invariably viscous oils which could not be induced to crystallize. An attempt to resolve *dl*-diallyl-*sec*-butylamine was also unsuccessful.

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EXPERIMENTAL

Preparation of Amines. Since the procedures used for preparation of the amines used as intermediates in this work were similar, a typical preparation of a secondary amine and a tertiary amine will be reported.

BUTYLMETHALLYLAMINE. A mixture of 32.8 grams (0.45 mole) of *n*-butylamine, 24.4 grams of sodium carbonate, and 40 ml. of water was placed in a 500-ml., three-necked flask. To this mixture was added dropwise, over a period of four hours, 40.8 grams (0.45 mole) of methallyl chloride. The reaction mixture was maintained at 100° throughout the addition and was stirred for 36 additional hours. The reaction mixture was cooled, filtered, and the amine layer separated. The amine layer was dried over sodium hydroxide pellets, and fractionated through an efficient column. A total of 41.7 grams (72.9%) of product was collected; b.p., 150–152° C./760 mm. As a byproduct from this reaction, 7.6 grams (19.0%) of butyldimethallylamine was obtained; b.p., 197–198° C./760 mm. The analytical data and physical properties for the amines are recorded in Table I.

ALLYLBUTYLMETHALLYLAMINE. In a 500-ml., three-necked flask, fitted with reflux condenser, stirrer, and addition funnel were placed 38.1 grams (0.3 mole) of butylmethallylamine, 17.0 grams of sodium carbonate, and 20.0 ml. of water. To this mixture was added dropwise over a four-hour period, 36.3 grams (0.3 mole) of allyl bromide while the contents of the flask were being stirred and heated at 100°. After being heated and stirred for 30 hours, the mixture was cooled, filtered, and the amine layer separated. After drying over sodium hydroxide pellets and fractionating through an efficient column, 43.4 grams (88.4%) of product was obtained; b.p., 181–183° C./760 mm.

Preparation of Quaternary Ammonium Bromides. The procedures used for preparation of the quaternary ammonium bromides were quite similar. Consequently, only one typical preparation will be included.

dl-ALLYLBUTYLMETHALLYLMETHYLAMMONIUM BROMIDE. Into a three-necked, 500-ml. flask, fitted with a gas inlet tube, a stirrer, and a dry ice condenser, were placed 42 grams (0.25 mole) of allylbutylmethallylamine and 50 ml. of acetone. Methyl bromide was then bubbled through the solution until it was saturated. The solution was gently refluxed for six hours, and allowed to stand for three days during which time crystallization occurred. The flask was cooled in an ice-salt bath, and a large crop of crystalline product separated. The contents were filtered and washed several times with dry ethyl ether. A further crop of crystals was obtained by adding dry ether to the filtrate. Total yield: 38 grams (58%). The product was extremely hygroscopic and was stored in a vacuum desiccator over anhydrous calcium chloride at 1 mm. pressure. A portion of the salt was recrystallized by dissolving in hot acetone and addition of a small amount of dry ether to initiate the crystallization. The melting point became constant at 142° C. after three recrystallizations.

Resolution of Optically Active Quaternary Ammonium Salts. Attempts were made to resolve several crystalline unsaturated quaternary ammonium salts during the course of this work. Successful attempts were limited to one compound containing an asymmetric nitrogen center, allylmethallylmethylphenylammonium iodide, and one compound containing an asymmetric carbon center, triallyl-2-octylammonium *p*-bromobenzenesulfonate. Optical rotation measurements throughout this work were made on a Rudolph Model 80 High-Precision Polarimeter having as its smallest scale division 0.002°. Samples were allowed to come to equilibrium with the temperature in the air-conditioned room in which the instrument was housed, and the temperatures recorded are those of the room at the time the readings were made. A sodium vapor lamp served as a light source. Observed angles of rotation were

Table I. Physical Properties and Analytical Data for Unsaturated Secondary and Tertiary Amines

Compound	B. P.	n^{25}_D	d^{25}_{25}	Yield, %	MR_D		Empirical Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
	t, ° C. Mm.				Calcd.	Obs.		Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
Butylmethallylamine	150-2/760	1.4301	0.7747	72.9	42.427	42.43	$C_8H_{17}N$	75.6	75.2	13.1	13.1	11.0	10.6
Allyl-2-chlorallylamine	71-2/67	1.4668	0.9763	60.0	37.591	37.47	$C_8H_{10}NCl$	54.8	54.5	7.68	7.60	10.6	10.4
Butyldimethallylamine	197-8/760	1.4456	0.7948	19.0	59.790	60.73	$C_{12}H_{25}N$	79.6	79.2	12.5	12.5	7.73	8.20
Butyldicrotylamine	128-30/56	1.4531	0.7980	60.5	60.782	61.28	$C_{12}H_{25}N$	79.6	79.9	12.7	12.7	7.73	7.60
Allylbutylmethallylamine	181-3/760	1.4422	0.7898	88.4	55.170	55.94	$C_{11}H_{21}N$	79.0	78.8	12.6	12.4	8.39	8.45
dl-Diallyl-*sec*-butylamine[a]	90-2/70	1.4390	0.8075	61.5	51.546	49.95	$C_{10}H_{19}N$	78.4	78.1	12.4	12.1	9.15	9.60
Butyl-2-chlorallylmethallylamine	86-7/9.5	1.4618	0.9070	69.8	61.031	61.06	$C_{10}H_{20}NCl$	65.7	66.1	9.95	9.72	6.97	6.79
N,N-Methallylmethylaniline	104-6/13	1.5579	0.9395	34.5	54.390	55.24	$C_{11}H_{15}N$	82.0	82.0	9.31	9.21	8.56	8.70
N,N-2-Chlorallylmethallylaniline[a]	136-7/9.0	1.5545	1.050	21.1	67.226	67.64	$C_{13}H_{16}NCl$	70.5	70.6	7.28	7.15	6.35	6.34
N,N-Crotylmethallylaniline[a]	107-10/2.8	1.5437	0.9327	73.0	67.777	68.00	$C_{14}H_{19}N$	83.5	83.9	9.49	9.27	6.98	6.80
dl-*N,N*-Diallyl-α-phenylethylamine	103-4/5.7	1.5150	0.9175	47.5	66.417	66.15	$C_{14}H_{19}N$	83.5	83.5	9.49	9.28	6.98	6.80
Allyl-2-chlorallylmethallylamine[a]	79-80/30	1.4689	0.9268	55.0	55.946	55.74	$C_{10}H_{16}NCl$	64.9	65.0	8.66	8.60	7.55	7.58

[a] The specific gravity and refractive index determinations were made at 27° rather than at 25°.

Table II. Unsaturated Quaternary Ammonium Halides

Ammonium Bromide	Formula	M.P.[a], ° C.	Analyses, %Br Calcd.	Analyses, %Br Found	Yield, %
dl-Allylbutylmethallylmethyl	$C_{12}H_{24}NBr$	142	30.48	30.43 30.47	58.0
dl-Allylmethallylmethylphenyl	$C_{12}H_{20}NBr$	119	28.32	28.63 28.52	65.4
Dimethallylmethylphenyl[b]	$C_{15}H_{22}NCl$	123	14.08	13.82 13.85	3.6
dl-Allyl-2-chlorallylmethallylphenyl	$C_{16}H_{21}NClBr$	[c]	23.33	22.07 22.64	78.9
dl-Triallyl-α-phenylethyl	$C_{17}H_{24}NBr$	[c]	24.81	24.58 24.71	75.2
dl-Diallylmethyl-α-phenylethyl	$C_{15}H_{22}NBr$	[c]	27.03	26.86 26.83	83.0
dl-Triallyl-2-octyl[d]	$C_{23}H_{36}NSO_3Br$	89–90	. . .	. . .	23.0
dl-Triallyl-*sec*-butyl	$C_{13}H_{24}NBr$	96–97	29.17	29.22 29.06	81.8
dl-Diallylmethyl-*sec*-butyl	$C_{11}H_{22}NBr$	108–110	32.26	32.01 32.17	68.1

[a] All melting points are uncorrected. [b] Isolated as the ammonium chloride, and the analyses are given as % Cl. [c] M.p. was not determined because compound was not obtained in crystalline form. [d] Isolated as the ammonium *p*-bromobenzenesulfonate with the following analysis:

calcd. for $C_{23}H_{36}NSO_3Br$: C = 56.9%; H = 7.41%
obs. C = 56.3%; H = 7.01%

Table III. Analytical Data, Optically Active Unsaturated Quaternary Ammonium Salts

Compound	M.P., ° C.	C, G./100 Ml.	Solvent	$(\alpha)^{22}_{D}$	$(M)^{22}_{D}$	Yield %	Empirical Formula	Analyses, % Calcd. C	Analyses, % Calcd. H	Analyses, % Calcd. N	Analyses, % Found C	Analyses, % Found H	Analyses, % Found N
d-*d*-Allylmethallylmethylphenylammonium camphor-10-sulfonate	130-1	0.7420	water	+17.99	+77.95	2.7	$C_{24}H_{35}NO_4S$	66.7	8.15	3.23	66.5	8.09	2.89
d-Allylmethallylmethylphenylammonium iodide	114-5	0.5956	water	+8.06	+26.6	79.8	$C_{14}H_{20}ONI$	38.60[a]			38.21[a] 38.07		
d-Triallyl-2-octylammonium *p*-bromobenzenesulfonate	89-90	2.7000	ethanol	+1.30[b]	+4.54	73.9	$C_{23}H_{36}NSO_3Br$	56.9	7.41		56.4	6.99	

[a] The analyses are given as % I. [b] Constants are determined at 20°, and the product is believed to be 60.2% optically pure.

determined on duplicate samples, and at least five readings were taken approaching the endpoint from each side, the average value being used.

RESOLUTION OF *dl*-ALLYLMETHALLYLMETHYLPHENYLAMMONIUM BROMIDE. Silver oxide (76 grams), *d*-camphor-10-sulfonic acid (151 grams), and *dl*-allylmethallylmethylphenylammonium bromide (184 grams) were placed in an 800 ml. beaker containing approximately 500 ml. of acetone. The mixture was heated on a steam bath for two hours, cooled, and allowed to stand for two hours. The mixture was then heated to boiling, and the precipitated silver bromide was filtered from the hot solution. By cooling the filtrate to room temperature, and allowing the acetone to evaporate slowly, successive fractions of powdery crystals were obtained. These fractions were washed well with acetone, and the wash solution was combined with the filtrate to be further evaporated. The filtrate possessed a dark color at this point. The succeeding crops of crystals melted from 130 to 131° C., and a total of four crops was obtained before the filtrate became too gummy to work with. The specific rotation and the molecular rotation were determined in water solution at 22° C., for each of these four fractions, and the molecular rotation was based on the molecular weight of 433.3 expected for *d*-*d*-allylmethallylmethylphenylammonium camphor-10-sulfonate. The molecular rotation of *d*-silver camphor-10-sulfonate is reported as +49.4 at 16° by Pope and Gibson (*4*). The molecular rotation of three separate preparations of *d*-silver camphor-10-sulfonate was determined at 22°, and an average value of +50.59 was obtained. This value was chosen as the reference molecular rotation value of the *d*-camphor-10-sulfonate ion, and should be nearly constant for all salts of *d*-camphor-10-sulfonic acid. The value, $\Delta([M_D^{22}])$, was calculated, and is the difference between the molecular rotation obtained for the *d*-*d*-allylmethallylmethylphenylammonium camphor-10-sulfonate fractions, and the molecular rotation, +50.59, expected from the camphor-10-sulfonate ion. The value $\Delta([M]_D^{22})$ represents the contribution of the positive *d*-allylmethallylmethylphenylammonium ion to the molecular rotation, and should be essentially constant for all salts containing it, regardless of the negative ion present, if the salt is completely resolved. The values for the specific rotation, molecular rotation, and $\Delta([M]_D^{22})$ decreased for the four fractions of *d*-*d*-allylmethylphenylammonium camphor-10-sulfonate isolated by this procedure, indicating that less and less of the *d*-*d*-allylmethallylmethylphenylammonium camphor-10-sulfonate was being deposited.

The first fraction was recrystallized from acetone until the specific and molecular rotations became constant on three successive crystallizations. The value, $\Delta([M]_D^{22})$, was essentially constant indicating that the positive *d*-allylmethallylmethylphenylammonium ion should have a molecular rotation of approximately +27. Yield: 4.5 grams. The results of this resolution are recorded in Table III.

PREPARATION OF *d*-ALLYLMETHALLYLMETHYLPHENYLAMMONIUM IODIDE. Two grams of *d*-*d*-allylmethallylmethylphenylammonium camphor-10-sulfonate and 2.0 grams of potassium iodide were dissolved in 3 ml. of water. A white precipitate was formed, and was filtered immediately. It was dried overnight on a porous clay plate in a vacuum desiccator at 1 mm. pressure and had a sharp melting point at 114–115° C. Yield: 1.2 grams (79.8%). The physical properties and analytical data for this compound are recorded in Table III. The value of +26.6 for the molecular rotation of *d*-allylmethallylmethylphenylammonium iodide confirms the previous indication that the positive ammonium ion contributes the same amount to the molecular rotation regardless of the negative ion present.

RESOLUTION OF *dl*-TRIALLYL-2-OCTYLAMMONIUM *p*-BROMOBENZENESULFONATE. *d*-2-Octanol of approximately 65% optical purity was prepared by the method of Cary, Vitcha, and Shriner (*3*).

Preparation of *d*-2-octyl *p*-bromobenzenesulfonate. Into a 250-ml., three-necked flask were placed 73.3 grams of *p*-bromobenzenesulfonyl chloride and 30.2 grams of *d*-2-octanol. The mixture was cooled to 0° in an ice-salt bath, and 73.3 grams of pyridine was added over a period of two hours with stirring. Stirring was continued for an additional five hours at 0°. The reaction mixture was made acid to litmus by the addition of 5*N* hydrochloric acid, and the ester was extracted with ether. After washing with cold water, the extract was dried over anhydrous sodium sulfate, and the ether was removed with an aspirator. The ester solidified in an ice-room, m.p., 38° C. The specific rotation was +4.26 (c = 1.1757, ethanol) at 20°. Cary, Vitcha, and Shriner (*3*) report $[\alpha]_D^{25} = +7.06$ (c = 1.84) and a melting point of 31° C. The product was 60.2% optically pure, based on +7.06 as a reference specific rotation value assuming that no racemization occurred. The ester hydrolyzed very rapidly in air. Analysis: calculated for: $C_{14}H_{21}0_3SBr$: C = 48.1%; H = 6.02%. Found: C = 48.6%; H = 5.92%.

Preparation of *d*-triallyl-2-octylammonium *p*-bromobenzenesulfonate. Triallylamine (6.85 grams) and *d*-2-octyl *p*-bromobenzenesulfonate (17.5 grams) were mixed and heated under anhydrous conditions on a steam bath for 24 hours. Upon cooling, a thick oil remained. It was repeatedly washed with dry ether and was recrystallized by dissolving it in the minimum amount of hot absolute ethanol, adding dry ether until the first cloudiness appeared, and then allowing it to cool slowly, and filtering, m.p. 89–90° C., yield, 18 grams (73.9%). The specific rotation, $[\alpha]_D^{20}$, was +1.30 (c = 2.7000, ethanol). Theoretically, the product was 60.2% optically pure if no racemization occured, and $[\alpha]_D^{20}$ would be +2.15 for an optically pure sample under similar conditions. Attempts to convert the quaternary ammonium *p*-bromobenzenesulfonate into the quaternary ammonium iodide and bromide by mixing with aqueous solutions of potassium bromide and potassium iodide failed to give a crystalline product.

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