Anal. Calcd. for $C_{18}H_{13}NO_5S_2$: C, 55.80; H, 3.38; N, 3.62. Found: C, 56.11; H, 3.46; N, 3.88.

4-Benzenesulfonamido-2,6-dibenzenesulfonylphenol (XV).—A solution of 0.15 g. of sodium benzenesulfinate in 2 ml. of water was added to a warm solution of 0.20 g. of 2-benzenesulfonyl-1,4-quinone-4-benzenesulfonimide in 10 ml. of glacial acetic acid. The solution was diluted with 10 ml. of water and cooled. The white product was removed by filtration. The yield was 0.26 g. (96.3%). After recrystallization from acetic acid the product melted at 200°.

Anal. Calcd. for $C_{24}H_{19}NO_7S_3$: C, 54.43; H, 3.62; N, 2.65. Found: C, 54.62; H, 3.68; N, 2.64.

The 4-Benzenesulfonamido-2-benzenesulfonyl-1-naphthol (IIIe).—To a solution of 1.00 g. of 1,4-naphthoquinonemonobenzenesulfonimide in 30 ml. of boiling glacial acetic acid was added 1.00 g. of sodium benzenesulfinate. The color of the solution was quickly discharged. On cooling 1.32 g. (90%) of white, crystalline product separated. Recrystallization from acetic acid gave white needles, m.p. 204.5°.

Anal. Calcd. for $C_{22}H_{17}NO_5S_2$: C, 60.12; H, 3.90; N, 3.19. Found: C, 59.80; H, 4.01; N, 3.04.

2-Azido-4-benzenesulfonamidophenol (IIh).—A solution of 1.00 g. of sodium azide in 4 ml. of water was added to a warm solution of 1.50 g. of *p*-quinonemonobenzenesulfonimide in 30 ml. of acetic acid. After 5 minutes the solution was colorless and it was poured into 80 ml. of water contained in a flask wrapped with aluminum foil to prevent light from striking the product. When the mixture was cooled white needles separated weighing 1.67 g. (94.9%). The product decomposed on standing at room temperature and the decomposition was accelerated by light or heat. The product was recrystallized by dissolving in ethanol at room temperature, adding water to the cloud point and cooling. White needles were obtained, m.p. 121–122.5° dec. Because of the instability of the product it was not analyzed.

2-Acetamido-4-benzenesulfonamidophenol (IIj).—A solution of 6.0 g. of sodium hydrosulfite in 30 ml. of water was added to a solution of 1.00 g. of 2-azido-4-benzenesulfonamidophenol in 30 ml. of 5% aqueous sodium hydroxide. The resulting yellow solution was heated to boiling for 10 minutes, diluted with water and made slightly acidic with dilute hydrochloric acid. A white solid separated and was removed by filtration. The yield was 0.76 g. (83.5%), m.p. 165–168°. Attempts to purify this amine resulted in colored solutions from which colored solids were obtained. The crude material was therefore acetylated directly.

To a solution of 1.00 g. of crude 2-amino-4-benzenesulfonamidophenol in 100 ml. of 5% aqueous hydrochloric acid was added slowly a 5% aqueous solution of sodium hydroxide until the mixture became slightly turbid. The turbidity was removed by the addition of a few milliliters of hydrochloric acid. A few chips of ice were added, followed by 10 ml. of acetic anhydride. The mixture was shaken vigorously and a solution of 10 g. of sodium acetate in 100 ml. of water was introduced. On cooling white crystals separated. The yield was 1.03 g. (78.1%). Recrystallization from acetone–chloroform gave small, white crystals, m.p. 242–242.5° dec.

Anal. Calcd. for $C_{14}H_{14}N_2O_4S$: C, 54.89; H, 4.61; N, 9.15. Found: C, 54.73; H, 4.22; N, 8.86.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

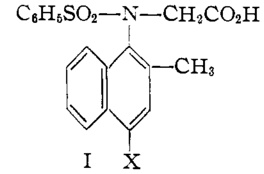
Restricted Rotation in Aryl Amines. XVIII. Effect of Remote Substituents on the Stability of Optically Active N-Benzenesulfonyl-N-carboxymethyl-3-benzylmesidine

BY ROGER ADAMS AND K. R. BROWER

RECEIVED AUGUST 1, 1955

In a series of optically active compounds having *m*-substituted benzyl groups in the 3-position of N-benzenesulfonyl-N-carboxymethylmesidine it was found that variation of the substituent caused no significant variation in the rate of racemization.

Previous papers in this series have reported that variation of the 4-substituent in optically active N-benzenesulfonyl-N-carboxymethyl-1-amino-2-methylnaphthalenes (I) produces variations in the rate of racemization, amounting in the most extreme case to a factor of twenty.[1,2] The half-lives of the nitro compound ($X = NO_2$), the amino compound ($X = NH_2$) and the unsubstituted compound were 0.42, 9.7 and 4.9 hr., respectively.

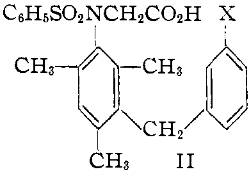


I

The effect has been explained on the basis of variations in the resonance stabilization of the coplanar transition state by the *para* substituent,[1,2] but there is no assurance that other factors such as inductive and field effects are not involved.

The purpose of the present investigation has been to determine the susceptibility of the racemization reaction to substituents too well isolated from the reaction center to contribute any but field effects. For this purpose compounds having *m*-substituted benzyl groups attached to the 3-position of N-benzenesulfonyl-N-carboxymethylmesidine (II) have been prepared and studied.

From the table below it is seen that variation of the substituent causes remarkably little variation in the half-lives of the compounds of the present series.



II

X	Half-life, hr.
H	11.5 ± 0.2
CH_3	11.3 ± .4
Br	12.8 ± .3
CN	12.1 ± .2
CH_3O	12.3 ± .2

The synthesis of the benzyl, *m*-methylbenzyl, *m*-bromobenzyl and *m*-nitrobenzyl derivatives was effected by benzylation of mesitylene with the appropriate benzyl chloride, followed by nitration, reduction and introduction of the benzenesulfonyl and carboxymethyl groups on the amino nitrogen in that order. The nitration of the *m*-nitrobenzylmesitylene provided the dinitro compound with one nitro group in the mesitylene ring and the other on the benzyl group. Selective catalytic reduction

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(1) R. Adams and R. H. Mattson, THIS JOURNAL, **76**, 4925 (1954).

(2) R. Adams and K. V. Y. Sundstrom, *ibid.*, **76**, 5474 (1954).

TABLE I

BENZYLMESITYLENES

m-Subst. of benzyl group	B.p., 1.0 mm., °C.	M.p., °C.	Yield, %	Formula	Carbon, %		Hydrogen, %	
					Calcd.	Found	Calcd.	Found
H	120–130	....	65	....	...	...	..	..
CH_3	130–136	Oil	65	$C_{17}H_{20}$	91.03	90.75	8.97	8.74
Br	145–153	Oil	73	$C_{16}H_{17}Br$	66.46	66.37	5.93	5.85
CN	162–172	87.0–88[a]	67	$C_{17}H_{17}N$	86.78	86.78	7.27	7.48
NO_2	165–175	82.5–83.5[a]	75	$C_{16}H_{17}NO_2$	75.27	75.00	6.71	6.57

[a] Recrystallized from methanol.

TABLE II

BENZYLNITROMESITYLENES

m-Subst. in benzyl group	B.p., 1.0 mm., °C.	M.p., °C.	Formula	Carbon, %		Hydrogen, %	
				Calcd.	Found	Calcd.	Found
H	160–170	Oil	$C_{16}H_{17}NO_2$	75.26	74.72	6.71	6.73
CH_3	160–170	89–90[a]	$C_{17}H_{19}NO_2$	75.80	75.92	7.13	7.02
Br[b]	175–192	67–68[a]	$C_{16}H_{16}BrNO_2$	57.51	58.43	4.84	4.68
CN	.....	119–120[a]	$C_{17}H_{16}N_2O_2$	72.85	72.81	5.74	5.68
NO_2	.....	115–116[a]	$C_{16}H_{16}N_2O_4$	63.99	64.22	5.37	5.37

[a] Recrystallized from methanol. [b] Calcd.: N, 4.19; Br, 23.81. Found: N, 4.02; Br, 23.40.

transformed the nitro on the benzyl group to an amino. This amino compound was diazotized and the amino group replaced by hydroxyl which was methylated to the *m*-methoxybenzyl derivative. The nitro group in the mesitylene nucleus was then reduced with hydrazine and Raney nickel.

The nitro group of 3-(*m*-cyanobenzyl)-nitromesitylene could not be reduced without concomitant reduction of the cyano group, and it was necessary to convert the latter to carboxamido previous to the reduction step. Benzenesulfonylation of the amino group and reconversion of the carboxamido group to cyano were caused simultaneously by the action of the benzenesulfonyl chloride in pyridine, a method which has also been described recently by Stephens, Bianco and Pilgrim.[3]

Roberts and Moreland[4] have studied the internal ion–dipole interactions of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acid derivatives and found rather large substituent effects; for example, the ratio of the rates of ester hydrolysis for the 4-OH and 4-H compounds was twenty-to-one. In these molecules the substituents have separations of 7–8 Å.

In the racemizations of the mesidines described in this communication dimethylformamide was used as solvent at a temperature of 118°. The compound may exist largely as the carboxylate ion. The scale model of the molecule shows that the spatial separation between the reaction center and the substituent may vary between the limits of direct contact and 10 Å. The compounds of Roberts and Moreland have such a structure that the groups affecting each other are at essentially a fixed distance. In the mesidines, on the other hand, it is possible that such substituent effects will be small since free rotation of the benzyl group will diminish the probability that the charge and dipole will be properly oriented for the operation of a large field effect and, in any event, the inductive effect must be negligible.

The authors are indebted to Mr. Joseph Nemeth and co-workers for the microanalyses.

Experimental

Preparation of *m*-Substituted Benzylmesitylenes.—The procedure of Louise[5] for the synthesis of benzylmesitylene from benzyl chloride and mesitylene was applied to the appropriate *m*-substituted benzyl chlorides.[6] The results are summarized in Table I.

Preparation of 2-(*m*-Substituted Benzyl)-nitromesitylenes.—A solution of 0.2 *M* of *m*-substituted benzylmesitylene in 60 ml. of acetic anhydride was chilled to −15° by addition of Dry Ice and maintained at that temperature while a solution of 8.5 ml. of fuming nitric acid (sp. gr. 1.5), 10 ml. of acetic acid and 10 ml. of acetic anhydride was added with stirring in the course of a few minutes. In the case of 3-*m*-cyanobenzylnitromesitylene and 3-*m*-nitrobenzylnitromesitylene the product crystallized from the reaction mixture after standing 10–15 minutes and was removed by suction filtration. The other compounds of the series were isolated by pouring the reaction mixture into water, treating with an excess of aqueous ammonia and extraction with ether. The ether layer was shaken with 5% aqueous sodium hydroxide to remove α-nitrated by-products, washed, dried and distilled in vacuum. Approximately 50% yield was obtained in every case.

Preparation of 3-(*m*-Substituted Benzyl)-mesidines.—The nitro compounds were reduced by the method of Balcom and Furst[7] using hydrazine as the reducing agent with Raney nickel catalyst. Other reducing agents such as hydrogen over platinum or stannous chloride were found to react sluggishly, presumably owing to steric hindrance by the two *o*-methyl groups. The amines were not isolated in a pure state before use in the following step.

Preparation of N-Benzenesulfonyl-4-(*m*-Substituted Benzyl)-mesidines.—The crude amine was mixed with 1.5 molar equivalents each of benzenesulfonyl chloride and 5% aqueous sodium bicarbonate and warmed to 100° on the hot-plate. After 20–30 minutes of heating and intermittent agitation the reaction mixture thickened and crystallized. The product was removed by filtration and recrystallized from ethanol.

Preparation of N-Benzenesulfonyl-N-carboxymethyl-3-(*m*-Substituted Benzyl)-mesidines.—To a solution of the N-benzenesulfonylbenzylmesidine and 1.1 molar equivalents of potassium ethoxide in 7 parts of absolute ethanol was added 1.1 molar equivalents of ethyl bromoacetate. Precipitation of potassium bromide began immediately and was

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(3) C. Stephens, E. Bianco and F. Pilgrim, THIS JOURNAL, **77**, 1701 (1955).

(4) J. D. Roberts and W. L. Moreland, Jr., *ibid.*, **75**, 2167 (1953).

(5) E. Louise, *Ann. chim.*, [6] **6**, 177 (1895).

(6) The vapor phase α-chlorination of a variety of toluene derivatives has been described by G. Asolkar and P. Guha, *J. Indian Chem. Soc.*, **23**, 47 (1946).

(7) D. Balcom and A. Furst, THIS JOURNAL, **75**, 4334 (1953).

TABLE III

N-BENZENESULFONYL-3-(*m*-SUBSTITUTED BENZYL)-MESIDINES

m-Subst. in benzyl group	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
H	148–149	$C_{22}H_{23}NO_2S$	72.28	71.69	6.30	5.95
CH_3	154.5–155.5	$C_{23}H_{25}NO_2S$	72.81	72.76	6.64	6.67
Br	132–133	$C_{22}H_{22}BrNO_2S$	59.46	59.26	5.00	4.89
CH_3O	142–143	$C_{23}H_{25}NO_3S$	69.82	70.10	6.37	6.38

essentially complete after 20 min. To the filtered solution was added 1.5 molar equivalents of sodium hydroxide in the form of a 20% aqueous solution, and the ethanol was distilled off with occasional admixture of water to the point of turbidity. The volume of the solution was maintained nearly constant in this manner until all the ethanol had been expelled and a clear aqueous solution remained. A slight turbidity which appeared on cooling was removed by extraction with ether and the product was precipitated by acidification with hydrochloric acid. The compounds were recrystallized first from ethanol–water mixture and then from benzene–petroleum ether mixture.

TABLE IV

N-BENZENESULFONYL-N-CARBOXYMETHYL-3-(*m*-SUBSTITUTED BENZYL)-MESIDINES

m-Subst. of benzyl group	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
H	203–204	$C_{24}H_{25}NO_4S$	68.07	68.38	5.95	6.13
CH_3	170–173	$C_{25}H_{27}NO_4S$	68.62	68.62	6.22	5.99
Br[a]	173–175	$C_{24}H_{24}BrNO_4S$	57.31	57.95	4.82	5.00
CN	83–84	$C_{25}H_{24}N_2O_4S$	66.94	66.77	5.39	5.46
CH_3O	142–143	$C_{25}H_{27}NO_5S$	66.20	66.25	6.00	6.08

[a] Calcd.: Br, 15.90. Found: Br, 15.54.

3-(*m*-Carboxybenzyl)-nitromesitylene.—A suspension of 2 g. of 3-(*m*-cyanobenzyl)-nitromesitylene in a solution of 2 g. of sodium hydroxide in 30 ml. of 1:1 ethanol–water was heated under reflux for 3 hours. The resulting clear solution was evaporated until all ethanol had been removed, decolorized with charcoal and acidified with hydrochloric acid. The crude acid amounted to 2.0 g. Recrystallization from methanol gave 1.8 g., m.p. 212–213°.

Anal. Calcd. for $C_{17}H_{17}NO_4$: C, 68.21; H, 5.74. Found: C, 68.53; H, 5.99.

3-(*m*-Carboxamidobenzyl)-mesidine.—A mixture of 52 g. of 3-(*m*-carboxybenzyl)-nitromesitylene and 40 g. of phosphorus pentachloride was gently warmed until a clear liquid resulted. The mixture was poured onto ice, and the crude, solid acid chloride was separated and added to 300 ml. of aqueous ammonia. After being stirred 10 minutes at room temperature the mixture was brought to a boil and filtered.

A suspension of 50 g. of the crude amide in 200 ml. of methanol together with 5 g. of Raney nickel catalyst was hydrogenated at atm. pressure. A nearly quantitative yield of 3-(*m*-carboxamidobenzyl)-mesidine was obtained. It was purified by recrystallization from ethanol, m.p. 197–198°.

Anal. Calcd. for $C_{17}H_{20}N_2O$: C, 76.09; H, 7.51. Found: C, 76.04; H, 7.44.

N-Benzenesulfonyl-3-(*m*-cyanobenzyl)-mesidine.—A mixture of 2.5 g. of 3-(*m*-carboxamidobenzyl)-mesidine, 3 ml. of benzenesulfonyl chloride and 5 ml. of pyridine was heated on the steam-bath for one hour. The reaction mixture was poured into water and after standing on the steam-bath for a few minutes the precipitated oil solidified. Recrystallization from ethanol gave 2.5 g. (69%) of product, m.p. 154–155°.

Anal. Calcd. for $C_{23}H_{22}N_2O_2S$: C, 70.74; H, 5.68. Found: C, 70.75; H, 5.87.

3-(*m*-Aminobenzyl)-nitromesitylene.—Since the sterically hindered nitro group of the mesitylene ring reacts very sluggishly, the selective hydrogenation of 3-(*m*-nitrobenzyl)-nitromesitylene was undertaken.

A solution of 40 g. of 3-(*m*-nitrobenzyl)-nitromesitylene in 200 ml. of benzene was hydrogenated over platinum oxide catalyst at 3 atm. to the uptake of 3 mole equivalents of hydrogen. No further absorption occurred during the following 2 hours. Evaporation of the benzene gave 33 g. (93%) of yellow solid which was purified by recrystallization from methanol, m.p. 107–108°.

Anal. Calcd. for $C_{16}H_{18}N_2O_2$: C, 71.62; H, 6.01. Found: C, 71.18; H, 6.18.

3-(*m*-Methoxybenzyl)-nitromesitylene.—A solution of 50 g. of 3-(*m*-aminobenzyl)-nitromesitylene in 200 ml. of warm 25% sulfuric acid was cooled to 0° whereupon much of the amine salt crystallized out. A solution of 15 g. of sodium nitrite in 60 ml. of water was added rapidly and after stirring for a few minutes a clear solution resulted. This diazonium solution was poured into 200 ml. of 10% sulfuric acid maintained near the boiling point during the addition. The black viscous oil which separated was dissolved in a solution of 7 g. of sodium hydroxide in 200 ml. of water, and 13 ml. of dimethyl sulfate was added with stirring at 40°. The methylated product separated as a viscous black oil which was taken up in ether, washed with acid and alkali, dried, and distilled in vacuum. The distillate, weighing 24 g., b.p. 170–210° (3 mm.), crystallized on addition of methanol and was recrystallized from the same solvent. The yield was 19 g. (36%), m.p. 51–52°.

Anal. Calcd. for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71. Found: C, 71.96; H, 6.76.

Resolution of Various Acids.—The cinchonidine salts of the N-benzenesulfonyl-N-carboxymethyl-3-(*m*-substituted benzyl)-mesidines were prepared by dissolving acid and alkaloid in 5 parts of methanol. Crystallization of the first

TABLE V

ROTATIONS OF CINCHONIDINE SALTS OF THE MESIDINES

m-Substituent in benzyl group	M.p., °C.	$[\alpha]^t_D$ in DMF	Temp., °C.
H	120	−60.5 ± 1.0	20
CH_3	168–170	−72.5 ± 1.0	20
Br	179–180	−72.0 ± 1.0	20
CN	94	−71.8 ± 1.0	30
OCH_3	122	−62.5 ± 1.0	28

TABLE VI

ROTATIONS OF OPTICALLY ACTIVE MESIDINES

m-Substituent in benzyl group	M.p., °C.	$[\alpha]^t_D$ in DMF	Temp., °C.
H	179–180	−53.5 ± 1.0	26
CH_3	142–143	−48.5 ± 1.0	20
Br	131–133	−64.5 ± 1.0	20
CN	132–134	−59.5 ± 1.0	30
OCH_3	166–167	−59.5 ± 1.0	28

RACEMIZATION OF 1-N-BENZENESULFONYL-N-CARBOXYMETHYL-3-BENZYLMESIDINE

c = 40 g./l. (dimethylformamide), t = 118°

Sample	Δt, hr.	$-\alpha$	$\ln \alpha_0/\alpha$	k, hr.$^{-1}$
1	12.75	1.01	0.750	0.059
2	11.75	1.06	.695	.059
3	10.6	1.13	.635	.060
4	9.9	1.18	.590	.060
5	8.75	1.25	.534	.061
6	7.75	1.36	.450	.058
7	6.75	1.42	.404	.060
8	5.75	1.50	.350	.061
9	1.6	1.92	.104	(.065)
10	0	2.13	0	....

k_{av} = 0.060 ± 0.001 hr.$^{-1}$

$t_{1/2}$ = 11.5 ± 0.2 hr.

salt prepared (*m*-methylbenzyl derivative) required several days, although seeds of this salt induced crystallization of other salts in a much shorter time. In every case crystallization stopped after approximately 70% of the less soluble isomer had been removed. The first fractions were nearly optically pure, and recrystallization from ethanol did not change the specific rotation by an amount greater than the experimental error. The characteristics of the salts are described in Table V.

Isolation and Racemization of Optically Active Acids.—The technique employed was essentially the same as that previously described.[2] The characteristics of the acids and a sample rate determination are described in Table VI. The errors in the rate constants and rotations are commensurate with the error in setting and reading the polarimeter (±0.01°).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Preparation of *o*-Vinylbenzyl *d*-*sec*-Butyl Sulfide.[1] An Attempted Asymmetric Polymer Synthesis

BY C. G. OVERBERGER AND LOUIS C. PALMER[2]

RECEIVED JULY 29, 1955

The preparation of *o*-vinylbenzyl *d*-*sec*-butyl sulfide is described. This optically active monomer was polymerized and copolymerized with a free radical catalyst in an attempt to effect an asymmetric polymer synthesis. After quantitatively removing the sulfur and the optically active group by hydrogenolysis with Raney nickel, the resulting polymer and copolymer were found to be optically inactive and an X-ray diagram of a stretched polymer film showed it to be non-oriented.

A number of amorphous polymers such as polystyrene and polymethyl methacrylates contain asymmetric carbon atoms in the backbone of the chain. It has been suggested that the presence of asymmetric carbon atoms randomly distributed in the polymer chain of both the *d*- and *l*-configurations makes each chain a racemic mixture or *meso* form which prevents proper orientation of chain segments for crystal formation. A polymer containing an excess of either the *d* or *l*-configuration would be of interest to test the validity of this postulate.

When a new asymmetric center is created in a molecule which already contains an optically active center adjacent to it, the resulting product may contain an excess of one diastereoisomer.[3] This well known concept of asymmetric synthesis has been employed previously in an attempt to prepare an asymmetric polymer; thus, Marvel, Frank and Prill[4] reported the polymerization of styrene and methyl methacrylate with two optically active peroxide initiators. A comparison of the physical properties of the above polymers with polymers prepared using the corresponding *dl*-initiators showed no essential differences. This result might be expected in view of a recent mathematical analysis of this type of situation by Frisch, Schuerch and Szwarc[5] who concluded that it was unlikely that an asymmetric polymer could be prepared by this method. Marvel and Overberger[6] polymerized an optically active monomer, *d*-*sec*-butyl *p*-vinylbenzoate, with a free radical initiator followed by hydrolysis of the active *sec*-butyl alcohol groups. The resulting polymer was optically inactive, again indicating no asymmetric induction in the growing polymer chain.

There is some reason to doubt that a polymer chain containing an excess of one configuration will exhibit optical activity since each carbon atom is asymmetric only by virtue of the fact that the chain is of different lengths on either side. The optical rotation of an asymmetric carbon atom appears to be strongly dependent on differences in the groups immediately attached to it but as the differences in two of the groups are removed further and further from the asymmetric center, the optical rotation decreases toward zero.[5,7] This particular difficulty may be avoided if the chain length is kept short or if the monomer is copolymerized.[5] Thus, in a copolymer, the groups immediately adjacent to some of the asymmetric centers would be different and these centers would be capable of rotating plane polarized light. The question of whether a completely alternating copolymer would be expected to be asymmetric does not concern us here.

The work reported here was concerned with the preparation of a monomer containing an optically active center sterically close to the double bond. It was desired to prepare a monomer which would polymerize by an ionic mechanism, as well as by a free radical mechanism for the ease of inducing asymmetry in an ionic transition state may be different from that for a free radical transition state. For a discussion of the generally accepted

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[1] This is the eleventh in a series of articles concerned with the synthesis of monomers and their polymerization; for the tenth paper in this series, see C. G. Overberger and I. C. Kogon, THIS JOURNAL, **76**, 1879 (1954).

[2] This paper comprises a portion of a thesis presented by Mr. Louis C. Palmer in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

[3] H. Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 2nd ed., p. 231.

[4] C. S. Marvel, R. L. Frank and E. Prill, THIS JOURNAL, **65**, 1647 (1943).

[5] H. L. Frisch, C. Schuerch and M. Szwarc, *J. Polymer Sci.*, **11**, 559 (1953).

[6] C. S. Marvel and C. G. Overberger, THIS JOURNAL, **68**, 2106 (1946).

[7] R. E. Marker, *ibid.*, **58**, 976 (1936). Since this work has been completed, crystalline polystyrene and polypropene have been reported (G. Natta, *et al.*, *ibid.*, **77**, 1708 (1955); G. Natta, *J. Polymer Sci.*, **16**, 143 (1955); C. W. Bunn and E. R. Howells, *ibid.*, **18**, 307 (1955)). These polymers, called isotactic, have been reported to contain crystalline areas having at least three monomer units with the same configuration. They are not optically active since they are long chains and contain planes of symmetry.