TABLE III

N,N-ALKYLENEBIS[(2-SUBSTITUTED)GLYCINES]

				Analyses					
			Hydrol-ysis	Carbon		Hydrogen		Nitrogen	
Compd.[d]	M.P.	Yield, %	Method	Calcd.	Found	Calcd.	Found	Calcd.	Found
1	>280[a]	Quant.	II	65.8	65.1	6.2	6.2	8.5	8.6
2	234–235 (dec.)[b]	75	I	60.0	59.8	5.6	5.8	7.8	7.9
4	234–238 (dec.)	53	I	60.9	60.6	6.5	6.2	7.5	7.6
7	240–245 (dec.)	29	II	60.0	58.2	5.6	5.9	7.8	7.5
9	246 (dec.)	25	I	61.8	59.7	6.23	6.0	7.2	7.0
10	202–207 (dec.)	10	II	54.4	52.9	4.6	4.6	7.1	6.4
18[c]	—	17[c]	I	47.0	46.8	5.3	5.8	8.2	9.4

[a] Ref. 4 reports m.p. >250°. [b] Ref. 3 gives no m.p. [c] As the trihydrochloride, Cl, Calcd. 20.7, Found 20.7. [d] See footnote d, Table II.

was used as recrystallizing solvent. Pertinent data are reported in Table I.

Reaction with liquid hydrogen cyanide: Preparation of N,N′-alkylenebis(2-substituted)glycinonitriles. The general procedure consisted in adding to the Schiff base at 5–10° with efficient stirring, a 4 to 5 molar excess of liquid hydrogen cyanide or an amount sufficient to give a good slurry.[7] When reaction took place, solution of the Schiff base occurred within a few min., followed in some instances, by precipitation of the adduct. In such cases separation was affected by filtration followed by air drying or by adding a ten-fold volume of water and stirring thoroughly, followed by filtration and further washing with water. When precipitation did not occur, the excess liquid hydrogen cyanide was removed by aspiration or by evaporation at room temperature since the application of heat usually caused decomposition of the adducts. The adducts were generally analytically pure requiring no further purification. Pertinent data are listed in Table II. For convenience, reaction was conducted in a flask fitted with a sintered glass disc and stop-cock arrangement to minimize handling of the liquid hydrogen cyanide.

Hydrolysis of adducts. Preparation of N,N′-alkylenebis(2-substituted)glycines. Method I. The first general procedure involved adding 4–5 ml. of cold concentrated hydrochloric acid per gram of nitrile and, once the initial exothermic reaction had subsided, heating the mixture on a steam bath for a few min. The acids often separated as their hydrochlorides from which the free acids were obtained by neutralization. When separation did not occur, the free acids were isolated by neutralization with 30% sodium hydroxide to pH 4–5 followed by filtration and thorough washing with water, in which most were insoluble. Recrystallizations were effected from methanol.

Method II. The second general procedure was that of Schlesinger.[4] This consisted in adding 10 ml. of a concentrated hydrochloric acid-concentrated sulfuric acid mixture (1–5 by volume) per gram of nitrile at a temperature below 35°. After three days at room temperature, an equal volume of water was added, the mixture heated to reflux for one hour, and the acid isolated as above. Data on the various acids are summarized in Table III.

Acknowledgment. We are grateful to A. A. Carlson for preparing many of the Schiff bases.

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(7) Inasmuch as the reaction may be vigorously exothermic after passing through an induction period, it is strongly recommended that all the usual precautions for working with liquid hydrogen cyanide be observed and that the reaction be limited to a 0.1 mol. scale.

[CONTRIBUTION FROM THE POLYMER RESEARCH LABORATORY, THE DOW CHEMICAL CO.]

Organic Chemistry of α-Methylstyrene. I. Reactions Leading to N-(α,α-Dimethyl-substituted-benzyl)acrylamides

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The reactions of α-methylstyrene, p-chloro-α-methylstyrene, p-bromo-α-methylstyrene, and m-trifluoromethyl-α,α-dimethylbenzyl alcohol with acrylonitrile have been investigated and three of the corresponding N-substituted acrylamides prepared. α-Methylstyrene or p-substituted-α-methylstyrenes (p-substituent *ortho-para* directing) under the above reaction conditions preferentially dimerize rather than react with acrylonitrile. The carbonium ion from m-trifluoromethyl-α,α-dimethylbenzyl alcohol or the dehydration product appears to be less reactive with another m-trifluoromethyl-α-methylstyrene than with the nitrogen of acrylonitrile; the product obtained in good yield is N-(m-trifluoromethyl-α-α-dimethylbenzyl)-acrylamide.

The reaction of 2-phenyl-2-propanol with acid leads to the formation of 2-phenylpropene (α-methylstyrene) as the major product. If 2-phenylpropene is let stand in an acid medium under various conditions of solvent, acid strength, and temperature, three dimeric products result: 2,4-diphenyl-4-methylpentene-1 (II), 2,4-diphenyl-4-methylpentene-2 (III), and 1,1,3-trimethyl-3-phenylindane (IV). These products may be considered to arise from the reaction of a cumyl carbonium ion with 2-

phenylpropene to give initially the dimeric ion (I), which may lose a proton at either of two positions to give either the pentene-1 (II) or pentene-2 (III), a mixture of II and III, or I may intra-alkylate to give the indane (IV) (Fig. I).

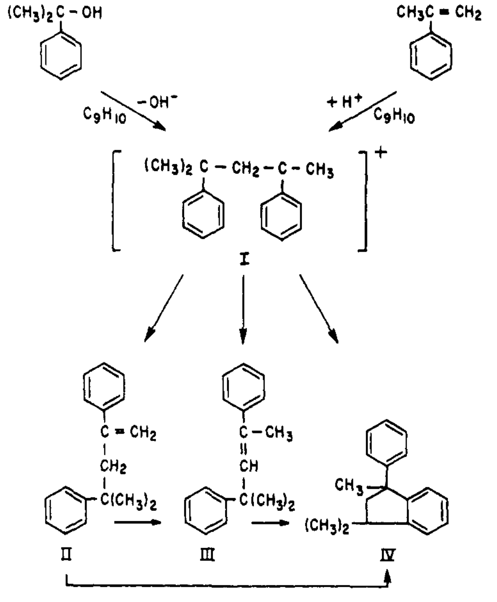
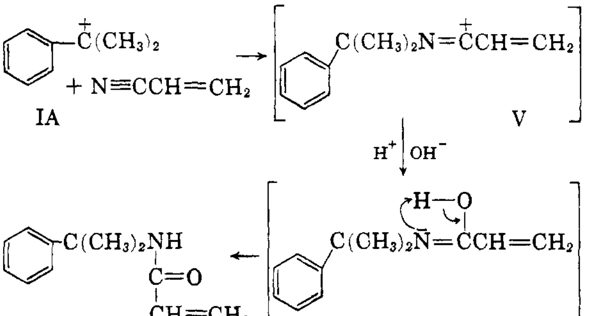


Figure 1

Bergmann and Weizmann[1] have reported the preparation of several ring substituted α-methylstyrenes, and Petropoulos[2,3] has reported an interesting series of experiments where the indane dimers of ring-substituted α-methylstyrenes are described. In a recent paper Overberger[4] reports that α-ethylstyrene reacts with stannic chloride at 0° for 1 hr. to give a mixture of dimers and trimers. The initial dimer was shown to be 3,5-diphenyl-5-methyl-2-heptene. If the reaction were prolonged, the indane-type dimer, 1,3-diethyl-1-methyl-3-phenylhydrindane was isolated. As there has been reasonable evidence for the existence of a protonated double bond in styrene or α-methylstyrene in the presence of a strong acid, it appeared reasonable to assume that a carbonium ion intermediate such as $C_6H_5(CH_3)_2C^+$(IA)[5] would react with nucleophilic reagents to give intermediates which might then be hydrolyzed to give useful and interesting products. There has been one reference to the preparation of an *N*-substituted acrylamide using the Ritter type reaction with styrene[9] and acrylonitrile.

Discussion. It was postulated that the reaction of α-methylstyrene with acrylonitrile under acidic conditions should proceed by way of a cumyl carbonium ion (IA), which could, in turn, attack the nitrogen of the acrylonitrile to give an intermediate (V), which would extract hydroxyl from the water present to give VI; this would tautomerize to give the desired product, *N*-cumylacrylamide (VII). When the original Ritter solvent and catalyst conditions—sulfuric acid in glacial acetic acid—were employed, little or no acrylamide was obtained. When tetrahydrofuran replaced the acetic acid and acrylonitrile was used in as much as a 10 mol. excess, as high as a 30% yield of *N*-cumylacrylamide was achieved. In the experiments using sulfuric and glacial acetic acids as reaction medium, little or no α-methylstyrene was recovered; most of the α-methylstyrene was converted to a mixture of the two liquid dimers and the solid indane dimer. When sulfuric acid–tetrahyrofuran was used as reaction medium, some α-methylstyrene was recovered but most of it was converted to a mixture of the liquid dimers (II and III); when the reaction was run for a relatively short time, only the pentene-1 dimer was found.[10]



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(1) E. Bergmann and A. Weizmann, *Trans. Faraday Soc.*, **32**, 1327 (1936).

(2) J. C. Petropoulos, U. S. Patent, **2,754,285** (July 10, 1956).

(3) J. C. Petropoulos and J. J. Fisher, *J. Am. Chem. Soc.*, **80**, 1938 (1958).

(4) C. G. Overberger, E. M. Pearce, and D. Tanner, *J. Am. Chem. Soc.*, **80**, 1761 (1958).

(5) In work reported after initiation of this program, Deno[6,7] utilized the Ritter reaction[8] of isobutylene and *t*-butyl alcohol with acrylonitrile (reaction leads to *N*-*t*-butylacrylamide) to study the kinetics of this acid-catalyzed reaction in various solvents. He concluded that the reaction proceeds by a mechanism which precludes, under the conditions used, the formation of an ion which we have chosen to consider as a free (or loosely solvated) carbonium ion.

(6) N. C. Deno, T. Edwards, and C. Perizzolo, *J. Am. Chem. Soc.*, **79**, 2108 (1957).

(7) N. C. Deno and C. Perizzolo, *J. Am. Chem. Soc.*, **79**, 1345 (1957).

(8) J. J. Ritter and co-workers, *J. Am. Chem. Soc.*, **70**, 4045–4048 (1948); **71**, 4128–4130 (1949); **73**, 4076 (1951); **74**, 763 (1952).

(9) A. L. Miller, U. S. Patent **2,790,789** (April 30, 1957).

(10) It was reasoned that if sulfuric and acetic acids not only gave the liquid dimers but a quantity of indane, and if in reducing the acid strength of the medium by using sulfuric acid–tetrahydrofuran no indane formed, then it should be possible to design a reaction where conditions would favor the competitive reaction of the cumyl carbonium with acrylonitrile (amide formation) rather than with itself (dimer formation). Originally it was thought that if the reactive species were the cumyl carbonium ion, then by starting with α,α-dimethylbenzyl alcohol, as soon as the alcohol was converted to the cumyl carbonium ion this would react with acrylonitrile because no α-methylstyrene would be present.

TABLE I

EFFECT OF FORMIC ACID AS CATALYST ON THE FORMATION OF REACTION PRODUCTS OF α-METHYLSTYRENE (118 G., 1 MOL.) AND ACRYLONITRILE

Run No.	Formic Acid %	Formic Acid Ml.	Acrylonitrile Moles	Conditions[d] Time, hr.	Conditions[d] T., °C.	N-Cumylacrylamide Isolated Yield G.	N-Cumylacrylamide Isolated Yield %	M.p.,[e] °C.	Pentene-1 Dimer[f] G.	Pentene-1 Dimer[f] %	Recovered α-Methylstyrene[f] G.	Recovered α-Methylstyrene[f] %
1	85	1000	2	18	25	1.6	0.85	112–112	93	84	6.1	5.5
2	85	1000	2	2.5	55	1.5	0.85	103–104	99	90	5.5	5.0
3	98	500	3	4.5	50	0.16	0.30	95–97	66	65	1.5	1.5
4	98	250	4	4.0	50	3.4	1.8	86–89	87	85	2.6	2.5
5	98	250	4	20	70	3.3	1.7	97–99	45	45	2.1	2.0
6	98	250	6	16	70	4.8	2.54	107–112	74	70	4.8	4.5
7	98	250	6	2(16)	85(25)	4.4	2.33	110–113	81	80	5.1	5.0
8	98	250	6	20	25	0.5	0.26	88–92	48	65	11.0	14.0
9	90	250	6	2(16)	85(25)	5.8	3.07	113–114	73	70	7.0	7.5
10	90	250	10	1.5	83	7.2	3.8	108–113	46	65	17.1	24.0
11	90	250	10	1.5	83	8.1	4.29	112–113	47	75	11.6	18.0
12[a]	98	46	2	4.0	70	No product			—	—	—	—
13[a]	80	54	2	4.0	70	No product			—	—	—	—
14[a]	85	108	2	4.0	70	No product			—	—	—	—
15[a]	90	250	6	4.0	70	2.4	1.27	113–114	—	—	—	—
22[b]	90	250	10	1.5	83	5.7	3.0	113–114	—	—	—	—
23[c]	90	250	10	1.2(60)	82(25)	7.4	3.9	113–114	—	—	—	—

[a] Experiments 12–15 contained 200 ml. of tetrahydrofuran. [b] In experiment 22 the acrylonitrile and water were placed in flask and the α-methylstyrene–formic acid mixture added dropwise during 30 min. [c] In experiment 23 the acrylonitrile and α-methylstyrene were mixed in the flask and the formic acid added dropwise during 30 min. [d] Figures in brackets indicate times and temperatures after initial reaction before experiment was worked up. [e] Melting points below the 113–114 figure are crude products which, on recrystallization, gave material having the proper melting points. [f] Infrared analysis by Dr W. Potts.

TABLE II

REACTION OF 2-PHENYL-2-PROPANOL WITH ACRYLONITRILE IN A TETRAHYDROFURAN SOLUTION OF SULFURIC ACID. RATE STUDY

Run No.	Time, Hr.	Wt., G.	Yield, %	M.P. °C.	Monomer, %	α-Methylstyrene Reaction Products, % in Sample[a] 4-Methyl-2,4-diphenyl-pentene-1	α-Methylstyrene Reaction Products, % in Sample[a] 4-Methyl-2,4-diphenyl pentene-1
1	1	0.5	1.0	111	3.5	1.5	0.0
2	2	0.7	1.4	111	5.0	1.5	0.0
3	3	0.9	1.8	110	5.0	2.0	0.0
4	4	0.8	1.6	110	5.0	2.0	0.0
5	20	1.5	3.0	103	2.0	3.0	0.0
6	23	1.3	2.6	104	2.5	3.0	Trace
7	28	1.5	3.0	104	1.5	3.5	Trace
8	93	Oily residue; no			1.0	1.5	2.5
9	99	isolable solid			Trace	1.0	3.5
10	117	product			—	Trace	4.0
11	The residue from the reaction mixture was worked up in the standard fashion to give 176 g. of oily product; distillation of this gave pure pentene-2 dimer of α-methylstyrene, b.p. 144°/2.4 mm.						

[a] By infrared analysis, Dr. W. Potts.

Two parallel and nearly identical experiments were run, one using α,α-dimethylbenzyl alcohol (Table II) and the other using α-methylstyrene (Table III). At set times (see Experimental) samples were withdrawn from each reaction. Each sample was treated to isolate N-cumylacrylamide with the liquid residue being analyzed (infrared) for the various possible by-products α-methylstyrene, liquid dimers (II and III), and indane dimer (IV). Starting with either α-methylstyrene or α,α-dimethylbenzyl alcohol in sulfuric acid–tetrahydrofuran with an equivalent of acrylonitrile, both reactions gave measurable amounts of α-methylstyrene after 1 hr. A maximum yield of N-cumylacrylamide was in the neighborhood of 2 to 3% in either experiment. Both experiments gave an interesting set of results so far as dimerization of α-methylstyrene is concerned. The initial dimer formed under these conditions is the 4-methyl-2,4-diphenylpentene-1 (III) until after 20 hr. As the time of reaction increased, the pentene-1 disappeared and the percentage of the pentene-2 isomer increased. The residue from each reaction mixture gave *pure* pentene-2 isomers with no pentene-1 or indane isomer.

On the basis of a report that α-methylstyrene could be dimerized[11] to the liquid or solid dimers in

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(11) J. Hukki, *Acta Chem. Scand.*, 3, 279–296 (1949).

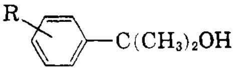
TABLE III

REACTION OF α-METHYLSTYRENE WITH ACRYLONITRILE IN A TETRAHYDROFURAN SOLUTION OF SULFURIC ACID. RATE STUDY

	Sample		*N*-Cumylacrylamide			α-Methylstyrene Reaction Products	
Run No.	Time, hr.	Wt., g.	Yield, %	M.p., °C.	Monomer, %	4-Methyl-2,4-diphenyl pentene-1, %	4-Methyl-2,4-diphenyl-pentene-2, %
1	1	0.2	0.4	103–107	3.5	1.0	0.0
2	2	0.2	0.4	111	4.5	1.5	0.0
3	3	0.3	0.6	111	3.0	2.0	0.0
4	4	0.5	1.0	111	2.5	3.0	0.0
5	20	0.9	1.8	108	1.0	3.0	1.0
6	23	1.1	2.2	108	1.0	2.0	5.0
7	28	1.0	2.0	103	1.0	2.0	4.5
8	93	Oily residue; no isolable product			0.0	Trace	6.0
9	99	Oily residue; no isolable product			0.0	0.0	6.0
10	117	Oily residue; no isolable product			0.0	0.0	6.0
11	The residue from the reaction mixture was worked up in the standard fashion to give 255.6 g. of oily product; distillation of this gave pure pentene-2 dimer of α-methylstyrene, b.p. 144°/2.4 mm.						

TABLE IV

RING-SUBSTITUTED-α,α-DIMETHYLBENZYL ALCOHOLS



	Yield					Reported Constants		
Substituent R	G.	%	B.p., °C.	Pres., mm.	n_D^{25}	B.p., °C.	Pres. mm.	n_D^{25}
H	100	60	45–47	0.8	1.5300	202[a]	760	$1.5314^{19°}$
p-Br	No pure product isolated; olefin formation on distillation[b]							
p-Cl	20	52	M.p. 31–32°		—	M.p. 43.2[a,b]		—
p-CH_3O	Only olefin isolated under any conditions used							
p-$(CH_3)_3C$	150	80	M.p. 78.5°		—	M.p. 79[c]		—
m-CF_3	120	59	73.5	2.5	1.4572	91.5[d]	10	1.4572

[a] *Cf.* E. Bergmann and A. Weizmann, *Trans. Faraday Soc.*, **32**, 1327 (1936). [b] H. C. Brown, Y. Okamoto, and G. Ham, *J. Am. Chem. Soc.*, **79**, 1906 (1957). [c] L. Walther, *J. Pharm. Chim.*, **27**, 476 (1938); *cf.*, *Chem. Abstr.*, **32**, 6237 (1938). [d] G. B. Bachman and L. L. Lewis, *J. Am. Chem. Soc.*, **69**, 2022 (1947).

formic acid, it was hoped that by using a modification of his procedure and by adding either an excess or equivalents of acrylonitrile, the formation of *N*-(α,α-dimethylbenzyl)acrylamide would be the preferred course of the reaction. When more concentrated formic acid was used with either α-methylstyrene or the tertiary carbinol, the yield of liquid dimers was higher and the concentration of polymers was lower. When equivalents of α-methylstyrene, acrylonitrile, and formic acid were mixed and heated, only a trace of the *N*-cumylacrylamide was obtained (Table I). In no experiment, even with a ten-fold excess of acrylonitrile, was there isolated a reasonable yield of the desired product, *N*-(α,α-dimethylbenzyl)acrylamide.

Further experiments made it possible to prepare the *N*-cumylacrylamide in as high as 30% yield using 10 mol. excesses of acrylonitrile and the sulfuric acid–tetrahydrofuran mixture as reaction medium. Other ring-substituted α-methylstyrenes, where the substituent was *p*-Cl, *p*-Br, *p*-CH_3O-, and *p*-*t*-butyl, were utilized in a standardized procedure in attempts to prepare the corresponding *N*-(*p*-substituted α,α-dimethylbenzyl)acrylamides. The α-methylstyrenes were prepared (see Table V) from the corresponding tertiary alcohols (see Table IV) either by dehydration as a separate reaction or spontaneously during attempted distillation of the intermediate tertiary alcohol. From the data presented, it would appear that an *ortho-para* directing substituent in the *para*-position did little to improve the competition of the cumyl carbonium ion with its corresponding α-methylstyrene *vs.* reaction with acrylonitrile. It would appear that, as nucleophilic reagents, the α-methylstyrenes are stronger than the nitrogen in acrylonitrile.[12]

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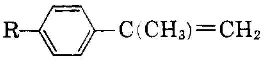
(12) In discussing the reaction of precursors of α-methylstyrene or ring-substituted α-methylstyrenes, it should be noted that Brown[13–17] has published an extensive series of papers where it can be seen that the reactive intermediates, the cumyl carbonium ions may be envisioned as being identical with those described here.

TABLE V

PARA-SUBSTITUTED-α-METHYLSTYRENES

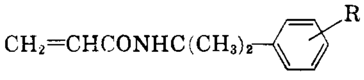

$R-C_6H_4-C(CH_3)=CH_2$

Substituent R	Method[a]	Yield G.	Yield %	B.P., °C./Mm.	n_D^{25}	Literature B.p., °C.	Literature n_D^{20}	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
H	DA	Plant matl.		50–51/12	1.5350	48.5/10	1.5358[b]	—	—	—	—
Cl	IDA	86	41	80–81/0.8	1.5808	228	1.5835[c,h]	54.57	59.94	4.58	4.63[f]
Br	DA, IDA	80	52	86/5	1.5558	88/15	1.5543[d,h]	70.82	68.80	5.94	5.61[g]
CH_3O	IDA	68	40	70–74/1 M.p. 32	—	99.5/101/4.5[e,h] M.p. 33	—	81.04	80.96	8.16	8.10

[a] DA, dehydration of the corresponding alcohol; IDA, instantaneous dehydration of the corresponding alcohol during purification of the alcohol. [b] R. R. Driesbach, *Physical Properties of Chemical Compounds, Adv. in Chem. Ser.* No. 15, 1955; page 160. [c] K. Ziegler and P. Zimmermann, *Ber*, **55B,** 3406 (1922). [d] D. T. Mowry, W. F. Huber, and E. L. Ringwald, *J. Am. Chem. Soc.*, **69,** 851 (1947). [e] Y. Okamoto and H. C. Brown, *J. Am. Chem. Soc.*, **79,** 1909 (1957). [f] Bromine. Calcd., 40.35; found; 40.29. [g] Chlorine. Calcd., 23.23; found, 23.84. [h] See also, D. Seymour and K. B. Wolfstirn, *J. Am. Chem. Soc.*, **70,** 1177 (1948).

TABLE VI

N-(SUBSTITUTED-BENZYL)ACRYLAMIDES


$CH_2=CHCONHC(CH_3)_2-C_6H_4R$

Substituent R	Yield G.	Yield %	M.P., °C.	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
H	90	20	112–113	76.15	76.20	7.99	8.06	7.40	7.22
p-Cl	30	22	117–118	64.43	64.27	6.32	6.24	6.26[a]	6.11
m-CF_3	19	72	127–128	60.69	60.82	5.49	5.35	6.45[b]	5.45

[a] Chlorine. Calcd., 15.90; found, 15.47. [b] Fluorine. Calcd., 22.16; found, 22.66.

It was postulated that a strong *meta*- directing group in the *meta*- position to an α-methylstyrene should decrease the susceptibility of its parent alcohol to dehydration and should decrease the nucleophilicity of its derived α-methylstyrene. It was predicted that a trifluoromethyl group *meta* to the vinyl group in an α-methylstyrene should result in a carbonium ion reactive with acrylonitrile but less likely to react with its own α-methylstyrene. Trifluoromethylbenzene was brominated to give the *m*-bromobenzotrifluoride; this was converted by reaction of its Grignard reagent with acetone to *m*-trifluoromethyl-α,α-dimethylbenzyl alcohol. This was treated with acrylonitrile in acetic acid–sulfuric acid medium to give a 72% yield of the *N*-(*m*-trifluoromethyl-α,α-dimethylbenzyl)acrylamide (see Table VI).

The acrylamides successfully prepared were converted to their hexachlorocyclopentadiene Diels-Alder adducts as derivatives (see Table VII).

The acrylamides were emulsion polymerized and co-polymerized to give materials having softening points in homopolymers from 128–160°; copolymers of *N*-cumylacrylamide and styrene showed higher softening points (see TableVIII).

EXPERIMENTAL[18]

Preparation of N-(α,α-dimethylbenzyl)acrylamide (N-cumylacrylamide) from α-methylstyrene. Tetrahydrofuran as solvent. In a 3-l., three necked, round bottomed flask equipped with a stirrer, closed-circuit addition funnel, condenser with drying tube, and a thermometer was placed 1 l. of tetrahydrofuran. The flask was cooled in an ice bath and to it was added 196 g. (2 mol.) of concentrated sulfuric acid during 15 min. To the cooled mixture was added 116.6 g. (2.2 mol.) of acrylonitrile during 15 min. The temperature of the reaction mixture was raised to 25°, and 236 g. (2 mol.) of α-methylstyrene was added during 60 min. with stirring. The solution was homogeneous at this point and was allowed to stand for 48 hr. at 25°. The solution was then poured into a mixture of ice and water and neutralized with 50% sodium

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(13) H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, *J. Am. Chem. Soc.*, **79,** 1897 (1957).

(14) Y. Okamoto and H. C. Brown, *J. Am. Chem. Soc.*, **79,** 1903 (1957).

(15) H. C. Brown, Y. Okamoto, and G. Ham, *J. Am. Chem. Soc.*, **79,** 1906 (1957).

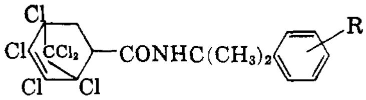
(16) Y. Okamoto and H. C. Brown, *J. Am. Chem. Soc.*, **79,** 1909 (1957).

(17) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79,** 1913 (1957).

(18) Melting points (capillary) are corrected. Elemental analyses by Dr. S. Shrader, The Dow Chemical Co., Midland, Mich.

TABLE VII

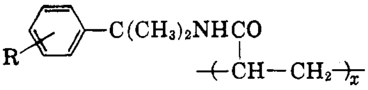
HEXACHLOROCYCLOPENTADIENE ADDUCTS OF THE *N*-(SUBSTITUTED-BENZYL)ACRYLAMIDES



Substituents			Yield		M.P.,	Percentage Composition							
						Carbon		Hydrogen		Nitrogen		Chlorine	
R_1	R_2	R_3	G.	%	°C.	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
CH_3	CH_3	H	20	85	144–145	44.19	43.88	3.27	3.15	3.03	3.10	46.04	45.85
CH_3	CH_3	*m*-CF_3	5	35	156–157	40.80	40.15	2.46	2.48	2.62	2.58	40.20	39.80
CH_3	CH_3	*p*-Cl	8	31	139–140	41.20	42.09	2.63	2.78	2.83	2.90	50.10	49.66

TABLE VIII

POLYMERS FROM *N*-(SUBSTITUTED-α,α-DIMETHYLBENZYL)ACRYLAMIDES



Substituent R	Polymerization		Co-monomer, %	Conversion, %	Specific Viscosity	Softening Point, C°
	Method	Catalyst				
H	Emul.	CHP	None	85–90	0.155	138–147
m-CF_3	Emul.	CHP + DETA	None	60–70	0.049	120–140
p-Cl	Emul.	CHP	None	80–85	0.157	138–156
H[a]	Emul.	CHP	Styrene 90[b]	75–80	2.155	180
H	Emul.	CHP	Styrene 70[b]	75–80	1.575	160–197
H	Emul.	CHP	Styrene 40[b]	75–80	0.451	150–170

[a] Other copolymers were made from the acrylamide with acrylonitrile, styrene, acrylamide, *N*-*t*-butylacrylamide, and methylmethacrylate; these were not characterized. [b] Nitrogen analysis of the isolated copolymers indicated that in each example only about one half of the acrylamide entered the copolymer.

hydroxide solution. Three 100-ml. portions of chloroform were used to extract the neutral mixture. The chloroform extracts were combined, washed with deionized water, dried over anhydrous magnesium sulfate, and filtered into a round bottomed flask. The chloroform was evaporated under vacuum and *n*-heptane was added to the residue; the crystalline product (33 g., 8.7%) was separated from the mother liquor by filtration and dried, m.p. 110–111.5°.

When acetic acid was used instead of tetrahydrofuran as solvent, only dimeric products (from α-methylstyrene) were isolated.

Preparation of N-(α,α-dimethylbenzyl)acrylamide. Effect of formic acid as solvent and catalyst. In a 3-l., three-necked, round bottomed flask equipped with stirrer, reflux condenser, thermometer, and addition funnel was placed a mixture (see Table I) of acrylonitrile and formic acid with or without inert solvent. The contents of the flask were maintained at the indicated temperatures and 118 g. (1 mol.) of α-methylstyrene added. The mixture was stirred at the temperatures and for the times shown in Table I. The reaction mixture was poured into 1 l. of ice water and extracted with chloroform. The extracts were combined, dried over magnesium sulfate, filtered, and evaporated. The semisolid residue, in each case, was treated with 10 vol. of *n*-heptane and chilled. The separated solid was washed with heptane and dried to constant weight. The combined heptane washes and filtrate were evaporated and the residue was submitted to infrared analysis for determination of α-methylstyrene, liquid dimer, and indane content. The results of this series of experiments are in Table I.

Several very tentative conclusions may be reached on the basis of these experiments. A low concentration of formic acid in tetrahydrofuran (12, 14) gives a lower yield of *N*-substituted acrylamide at room temperature or at elevated temperatures. Under comparable conditions except for temperature (7, 8) the higher temperature favors amide formation. The order of mixing does not seem to make a great difference in the yield of amide (10, 22, 23). A ten-fold excess of acrylonitrile (10, 23) at higher reaction temperatures leads to higher yields of amide, but the conditions also give rise to polyacrylonitrile (infrared showed no amide in byproduct polymer). A somewhat better yield is obtained when the volatile reactants are removed under vacuum before addition to water; this may be due to loss in the aqueous layer of amide under usual isolation conditions.

Preparation of N-cumylacrylamide from 2-phenyl-2-propanol and α-methylstyrene. Rate studies. In two identical runs the following procedure was used, one using 2-phenyl-2-propanol and the other α-methylstyrene. In a 3-l., three necked, round bottomed flask equipped with a stirrer, closed circuit addition funnel, water-cooled reflux condenser protected with a drying tube, and a thermometer was placed 1 l. of tetrahydrofuran. The flask was cooled in an ice bath and to it was added 196 g. (2 mol.) of concentrated sulfuric acid during 10 min. To the cooled mixture was added 116.6 g. (2.2 mol.) of acrylonitrile during 15 min., the temperature raised to 45°, and the mixture was stirred for 30 min. While maintaining the temperature at 45°, 272.4 g. (2 mol.) of 2-phenyl-2-propanol (or 236 g., 2 mol. of α-methylstyrene) was added during 30 min. A temperature of 45° and agitation were maintained for the remainder of the reaction. At time intervals of 1, 2, 3, 4, 20, 23, 28, 93, 99, 117 hr. from addition of the 2-phenyl-2-propanol, 50 ml. portions were removed from the reaction flask by means of a pipette. Each 50-ml. sample was stirred into a mixture of ice and water which was then neutralized with 50% sodium hydroxide solution. Three 75-ml. portions of chloroform were used to extract the neutral mixtures. The chloroform extracts were combined, dried over anhydrous magnesium sulfate, and filtered into a round bottomed flask, and the chloroform was evaporated under vacuum. The residue was treated with 75 ml. of *n*-heptane and the crystalline product separated by filtration. The crystalline product was dried in a desiccator and the melting point was taken. The heptane filtrate was transferred to a 100-ml. volumetric flask and additional *n*-heptane was added to bring the volume to 100 ml. A 10-ml. sample was taken from each volumetric flask and was sent for analysis. The results are summarized in Table II for 2-phenyl-2-propanol and in Table III for α-methylstyrene.

Preparation of 2-(m-trifluoromethylphenyl)-2-propanol. In a 3-l., three necked, round bottomed flask equipped with a stirrer, closed circuit addition funnel, thermometer, and a water cooled reflux condenser protected with a drying tube was placed 34.8 g. (1.43 g.-atom) of magnesium turnings which were then covered with anhydrous diethyl ether. The flask was cooled in an ice bath and to it was added 321 g. (1.43 mol.) of 3-bromobenzotrifluoride with stirring during 90 min. The solution was refluxed gently for 2 hr., at which time no magnesium metal was visibly evident. The flask was cooled in an ice bath and 83 g. (1.43 mol.) of anhydrous acetone was added during 30 min. The solution was refluxed for 90 min. and stirring was continued at room temperature overnight. To the solution was added 180 ml. of saturated ammonium chloride solution during 15 min. The solution was stirred for 30 min. and the ether layer decanted. Four additional 200 ml. extracts which were made of the reaction residue were combined and washed with deionized water until the etheral solution was neutral. The neutral solution was dried over anhydrous magnesium sulfate, and filtered, and the solvent evaporated. Fractional distillation gave a main fraction of 208 g. (71.5%) of product, b.p. 80–82°/1.5 mm., n_D^{20} 1.4603 (see Table IV).

Other carbinols were prepared in an analogous fashion and the results are summarized in Table IV.

Ring-substituted-α-methylstyrenes. Ring-substituted-α-methylstyrenes were prepared either inadvertently while attempting to distill the corresponding carbinols or by purposeful acetic anhydride dehydration of the carbinols. The results are summarized in Table V.

Preparation of N-(m-trifluoromethyl-α,α-dimethylbenzyl)-acrylamide. In a 3-l., three necked, round bottomed flask equipped with a stirrer, water-cooled reflux condenser protected with drying tube, addition funnel, and thermometer was placed 500 ml. of glacial acetic acid. To the flask, cooled in an ice bath were added 98 g. (1 mol.) of concentrated sulfuric acid and 58.3 g. (1.1 mol.) of acrylonitrile. The solution was warmed to 45° and 204 g. (1 mol.) of 2-(*m*-trifluoromethylphenyl)-2-propanol was added during 60 min. The temperature was raised to 70° for 5 hr. and the solution poured into an ice and water mixture. The mixture was neutralized with aqueous sodium hydroxide and the product precipitated. The solid was separated by filtration and recrystallized from a mixture of acetone, *n*-heptane, and benzene: to give a total of 51.9 g. (20%) of product, m.p. 122–123°.

Other successful acrylamide preparations are summarized in Table VI. As derivatives of the acrylamides, their hexachlorocyclopentadiene adducts were prepared in a standard fashion.[19]

Polymerization. Emulsion polymerization of N-cumylacrylamide (N-α,α-dimethylbenzyl)acrylamide. In a 350-ml. citrate-of-magnesia bottle were placed 150 ml. of a 5% Ivory soap solution, 30 g. (0.159 mol.) of *N*-cumylacrylamide, 214 mg. of a 70% cumene hydroperoxide solution (0.5% wt. equiv. based on monomer), and 103 mg. (1 mol. equivalent based on cumene hydroperoxide) of diethylenetriamine. The bottle was flushed with nitrogen and sealed. The bottle was rotated in a constant temperature bath at 80° for 19 hr. and then at 95° for 24 hr. The bottle was removed from the bath, cooled, and the contents were poured into 800 ml. of methanol. The precipitated polymer was separated, washed with methanol, and dissolved in benzene. The filtered benzene solution was lyophilized to give 22 g. (74%) of product. The polymer had the following properties: softening point, 134°, m.p. 136–140°; specific viscosity (1% in toluene) 0.061; and a heat distortion (compression molded bar) of 92°.

Anal. Calcd. for the pure polymer $(C_{12}H_{15}NO)_x$: N, 7.40. Found N, 6.86.

Emulsion copolymerization of N-cumylacrylamide (N-α,α-dimethylbenzyl)acrylamide. The preceding emulsion technique was employed in effecting the copolymerization of 1 g. portions of *N*-cumylacrylamide with acrylonitrile (1 meq.), styrene (1 and 3 meq.), acrylamide (1 meq.), *N-t*-butylacrylamide (1 meq.), and methyl methacrylate (1 meq.) in a rotating bath at 70° for 24 hr. Cumene hydroperoxide (1% based on total monomer concentration) was used as catalyst in 35 ml. of a 5% (Ivory) soap solution. The results from these preliminary experiments were: acrylonitrile—no polymer; styrene (1 equiv.)—moderate amount of rubbery precipitate; styrene (3 equiv.)—large amount of rubbery precipitate; acrylamide—no polymer; *N-t*-butylacrylamide—gummy brown precipitate which could be drawn to a figure, methyl methacrylate—gummy white polymer.

Emulsion polymerization of N-(m-trifluoromethyl-α,α-dimethylbenzyl)acrylamide. In a 350-ml. citrate-of-magnesia bottle were placed 150 ml. of a 5% Ivory soap solution, 10 g. (0.039 mol.) of the acrylamide, and 0.05 g. (0.5% by wt.) of 70% cumene hydroperoxide. The bottle was flushed with nitrogen and sealed. The bottle was rotated in a constant temperature bath at 70° for 38 hr.; 1 drop of cumene hydroperoxide was added and the bottle returned to the 70° bath for 24 hr.; 2 drops of diethylenetriamine was added and the bottle returned to the 70° bath for 6 hr. and then at 95° for 16 hr. The precipitated polymer was allowed to settle and most of the methanol decanted. The remaining solution was centrifuged and the polymer dissolved in benzene. The filtered benzene solution was lyophilized to give 8.5 g. (85%) of product. The polymer had the following properties: m.p. 121–140°; specific viscosity (1% in toluene) 0.049.

Anal. Calcd. for the pure polymer $(C_{13}H_{14}F_5NO)_x$: N, 8.65%. Found N, 8.13% (see Table VIII).

Emulsion copolymerization of N-(m-trifluoromethyl-α,α-dimethylbenzyl)acrylamide with styrene. The preceding emulsion polymerization technique was used to copolymerize the acrylamide with styrene. Three polymers were made, having monomer ratios of the acrylamide to styrene of 1:9, 3:7, and 6:4, which will be referred to as Nos. 1, 3, and 6, respectively. Each bottle contained 150 ml. of a 5% Ivory soap solution and the total amount of washed styrene used (20 g.) contained 1 g. cumene hydroperoxide. The bottles were placed in a constant temperature bath at 70° for 28 hr. Numbers 1 and 3 were removed from the bath, cooled and poured into 800 ml. of methanol; 1 drop of cumene hydroperoxide was added to No. 6 and the bottle returned to the 70° bath for 24 hr.; 2 drops of diethylene triamine was added and the bottle returned to the 70° bath for 6 hr. and then at 95° for 16 hr. The bottle was removed from the bath, cooled, and the contents were poured into 1 l. of methanol. The three precipitated polymers were filtered, redissolved in toluene, filtered, and precipitated again in 800 ml. of methanol. The resulting polymers were dried under vacuum. Polymer 1 was shiny, white, and hard; m.p., approximately 180°, specific viscosity (1% in toluene) 2.11.

Anal. Calcd. for per cent nitrogen of the monomer ratio 1:9, 0.54%. Found: N, 0.27%.

Polymer 3 was hard, brittle, and white; softened at 160° became clear at 197°, specific viscosity (1% in toluene) 1.57.

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[19] *Cf.* C. W. Roberts, *Chem. and Ind.* (*London*), 110 (1958).

Anal. Calcd. for per cent nitrogen of the monomer ratio 3:7, 1.63%. Found: N, 1.11%.

Polymer 6 was a white powder; softened at 105°, had m.p. 120–125°, and a specific viscosity (1% in toluene) 0.45.

Anal. Calcd. for per cent nitrogen in the monomer ratio 6:4, 3.26%. Found: N, 1.56% (see Table VIII).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Orientation in the 10-Thiaxanthenone[1] Nucleus

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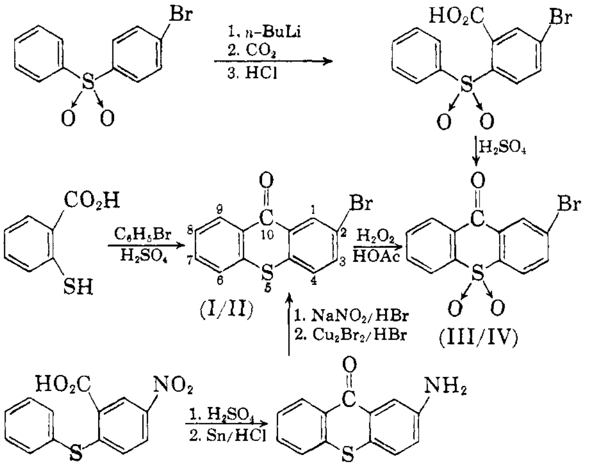
It has been found that cyclization by the procedure of Smiles of *o*-mercaptobenzoic acid with monosubstituted benzene derivatives in concentrated sulfuric acid leads to the formation of 10-thiaxanthenone compounds in which the substituent is in the 2-position. A mechanism incorporating a sulfenium ion accounts for these *o*-mercaptobenzoic acid cyclizations.

In the course of investigating the action of concentrated sulfuric acid on aromatic disulfides, Smiles[2,3] synthesized several substituted 10-thiaxanthenone derivatives. The position of the substituent has now been determined for some of these compounds.

Reaction of either 2,2′-dithiodibenzoic acid or *o*-mercaptobenzoic acid with bromobenzene in concentrated sulfuric acid gave a compound (I) with a melting point, 166–167°, which does not agree with that, 141°, reported for *x*-bromo-10-thiaxanthenone prepared initially by Smiles in an analogous manner.[3] The bromine atom was shown to be in the 2-position by the following sequence of reactions. A Sandmeyer reaction on 2-amino-10-thiaxanthenone[4] gave 2-bromo-10-thiaxanthenone (II) which showed no depression in melting point when admixed with the above *x*-bromo-10-thiaxanthenone (I). Additional evidence was furnished by infrared absorption measurements which indicated that the monosubstituent was related to 1,2,4-trisubstitution in a molecule. The position of the bromine atom was also established by another route. Metalation of 4-bromodiphenyl sulfone with *n*-butyllithium followed by carbonation gave 4-bromo-2-carboxydiphenyl sulfone.[5] Cyclization of this acid in concentrated sulfuric acid gave 2-bromo-10-thiaxanthenone-5,5-dioxide (III). This compound (III) was identical with the substance (IV) obtained by the oxidation of *x*-bromo-10-thiaxanthenone (I) with 30% hydrogen peroxide in glacial acetic acid.

Reaction of the strongly *ortho-para* directing anisole molecule with *o*-mercaptobenzoic acid gave an 80% yield of *x*-methoxy-10-thiaxanthenone.[2,6] The methoxy group was later shown to be in the 2-position by the cyclization of 2′-carboxy-4-methoxydiphenyl sulfide.[7] Cyclization of phenol with *o*-mercaptobenzoic acid gave *x*-hydroxy-10-thiaxanthenone.[8] The position of the hydroxy group in *x*-hydroxy-10-thiaxanthenone was determined by methylation and the resulting methoxy derivative was shown by Smiles and co-workers to be identical with the 2-methoxy-10-thiaxanthenone compound.[7,8]



2-Chloro-10-thiaxanthenone was prepared in a 53.4% yield by the reaction of chlorobenzene with *o*-mercaptobenzoic acid in concentrated sulfuric acid. Diazotization of 2-amino-10-thiaxanthenone followed by treatment with copper (I) chloride in hydrochloric acid yielded 2-chloro-10-thiaxanthenone and this compound was identical with that obtained from the cyclization reaction. Oxidation of 2-chloro-10-thiaxanthenone with 30% hydrogen peroxide in glacial acetic acid gave 2-chloro-10-thia-

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(1) The nomenclature and numbering are those recommended in the introduction to the 1952 Subject Index of "Chemical Abstracts."

(2) W. Prescott and S. Smiles, *J. Chem. Soc.*, 640 (1911).

(3) E. Marsden and S. Smiles, *J. Chem. Soc.*, 1353 (1911).

(4) F. Mayer, *Ber.*, **42**, 3046 (1909).

(5) W. Truce and M. Amos, *J. Am. Chem. Soc.*, **73**, 3013 (1951).

(6) S. Smiles and E. Davis, *J. Chem. Soc.*, 1290 (1910).

(7) K. Roberts and S. Smiles, *J. Chem. Soc.*, 863 (1929).

(8) W. Price and S. Smiles, *J. Chem. Soc.*, 3154 (1928).