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Arylsulfimide Polymers. IV. Prototype Transamidations-A Comparison of the Reactions of Benzamides, Benzimides, Sulfonamides, Sulfonimides, and Saccharins

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Arylsulfimide Polymers. IV. Prototype Transamidations—A Comparison of the Reactions of Benzamides, Benzimides, Sulfonamides, Sulfonimides, and Saccharins

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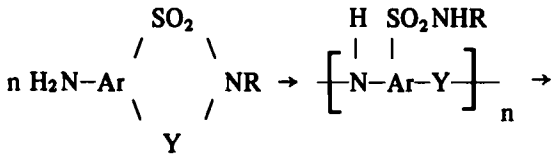
SUMMARY

Transamidation reactions of nonpolymerizing systems involving benzamides, phthalimides, arylsulfonamides, benzenedisulfonamides and -disulfonimides, and saccharins are described. The study includes reactions of both N-substituted and unsubstituted amides and imides with anilines and aniline hydrochlorides. An evaluation of the results of these reactions, aimed at establishing the optimum conditions for transamidations in polymerizing systems, is also presented.

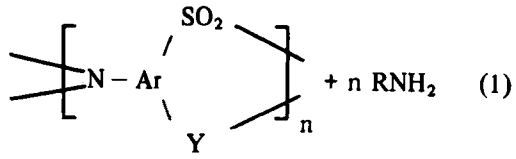
INTRODUCTION

Previous papers in this series [1] have reported the syntheses of monomers to be used in the preparation of sulfimide polymers with the general structures shown below [compounds (II) and (IV)].

Among the synthetic procedures considered for the preparation of these polymers were transamidation reactions such as those shown in Eqs. (1) and (2). Transamidation polymerizations of this kind have not been described



(I)



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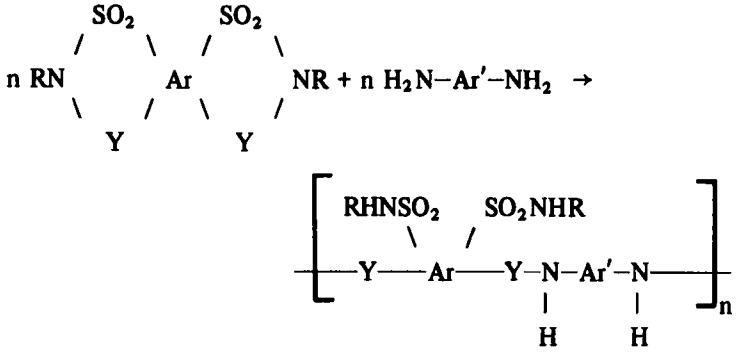

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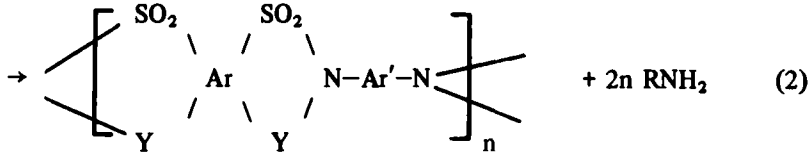
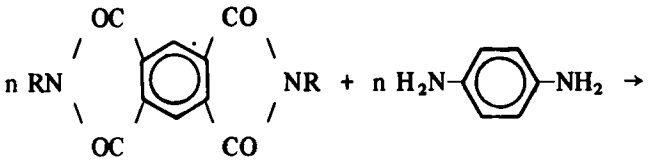
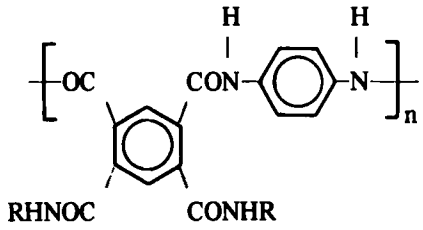


(IV)

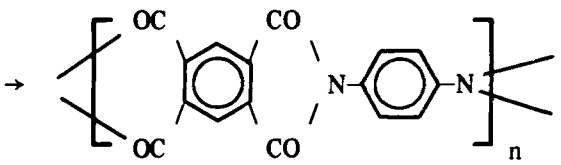
Ar = aromatic ring; R = H or alkyl group; Y = CO or SO_2.

in the literature, and before applying these exchange reactions to the preparation of polymers, it was considered necessary to establish that the reactions would be substantially free of side reactions that could lead to undesirable by-products and that the yields would at least be high, if not quantitative. Data obtained on appropriate nonpolymerizing systems would serve as a basis for evaluating the suitability of transamidation reactions in polymerizing systems. Information of this kind would also prove useful in the synthesis of polycarbimides from such simple monomers as pyromellitic diimide and p-phenylenediamine [Eq. (3)].





(V)



(3)

(VI)

Our interest in the polysulfimides [(II) and (IV)] was based on the belief that these polymers would exhibit thermal stabilities comparable to or better than those shown by polycarbimides [2-4]. Those structural features which confer thermal stability are usually found in insoluble, infusible, intractable, brick-dust polymers. A desirable feature of any reaction sequence leading to such polymers is an intermediate stage in which a tractable or

soluble prepolymer of hemipolymer is formed. Such hemipolymers could be easily fabricated prior to their conversion to the thermally stable polymer. From Eqs. (1)-(3), it can be seen that the intermediate diamides [(I), (III), and (V)] play this important role since the polydiamides would be more soluble and tractable than the polyimide products.

The literature on transamidation of simple aromatic amides and imides is meager. The reactions of phthalimide with methylamine were studied [5] by Spring and Woods in 1945. In 1953, Klamann reported [6] on the reactions of benzamide and phthalimide with aniline hydrochloride but not on their reactions with aniline. Other investigators [7, 8] studied the reactions of saccharin with aniline and aniline hydrochloride, but the reactions of N-substituted saccharins with aromatic amines do not appear to have been published. The literature also fails, apparently, to describe transamidation reactions involving aryl sulfonamides and disulfonimides with amines.

Accordingly, to determine the conditions under which the reactions would proceed satisfactorily, the transamidations of selected amides and imides were investigated. Since the polymerization systems would involve the reaction of $ArNH_2$ with compounds containing such functions as $ArCONR-$, $ArCONROC-$, $ArSO_2NR-$, $ArSO_2NROC-$, and $ArSO_2NRO_2S-$, the prototype reactions were performed with the appropriate simple compounds shown in Table 1.

Aniline (XX) was chosen as the arylamine in most of these reactions except in a few cases in which the electronegatively substituted anilines, p-chloroaniline, mp, 72.5°C (XXI), and p-nitroaniline, mp, 147.8°C (XXII), were used.

EXPERIMENTAL

The syntheses of reagents [compounds (I)-(XIX)] followed published procedures given in the references cited in Table 1. Compounds (XXIII)-(XXXV) were also synthesized by published procedures, as detailed in the references in Table 2. These latter compounds were used as reference materials. Products from transamidation reactions were compared with these authentic samples to establish the identity of the reaction products.

Since the procedure used for the transamidations was substantially the same in all cases, it will be described generally. Usually, the reactants were mixed in a 100-ml, round-bottomed flask equipped with a gas inlet, condenser, thermometer, an electric heating mantle controlled by a variable

transformer, and a gas outlet attached to a trap cooled to -78°C. A slow stream of deoxygenated nitrogen was passed through the flask before heating was started; then the reaction was performed at appropriate temperatures for various periods of time. When aniline was used as one of the reactants, the temperature used was that of the reflux temperature (184°C) of aniline; higher temperatures were also evaluated with some of the substituted anilines and the aniline hydrochlorides. In a number of reactions involving the free amine, a small amount of catalyst, usually zinc chloride or aniline hydrochloride, was used. When the reaction was terminated, the mixture was allowed to cool to room temperature, and the products were isolated, purified by recrystallization to constant melting points, and identified by comparison of their infrared spectra and melting points with those of authentic samples.

The procedure described above provides for the reaction of the amide and amine in a melt under nonequilibrium conditions under which volatile products were allowed to escape. In a few cases, the reactions were performed in sealed vessels to maintain equilibrium conditions.

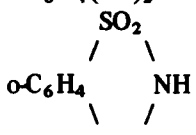
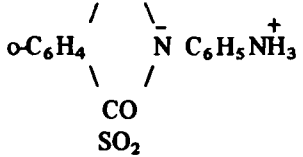
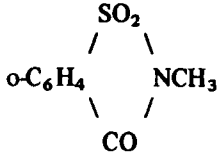
Tables 3-7 summarize the data on transamidation reactions with benzamides (Table 3), phthalimides (Table 4), aryl sulfonamides (Table 5), benzenedisulfonamides and -disulfonimides (Table 6), and saccharins (Table 7). It should be noted that the yields given in these tables are for purified products. In most instances, the reactions had proceeded further than these yields indicate (see, for example, Table 6, reaction 78).

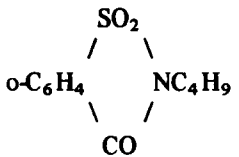
DISCUSSION

These prototype studies were intended to provide a basis for estimating the optimum conditions for transamidations in polymerizing systems. The studies were divided into three general categories: a consideration of the reactions of amides and imides of carboxylic acids, of sulfonic acids, and of the mixed acids or saccharins.

From the data in Table 3, it is immediately obvious that the reaction involving benzamides is catalyzed by aniline hydrochloride. Thus, aniline and benzamide produced 61% of benzanilide after 7 hr at 184°C, but when a small amount of aniline hydrochloride was added, the yield of benzanilide was 91% after 7 hr at 184°C. Similar results were observed with N-methylbenzamide and aniline. The reaction of N,N-dimethylbenzamide and aniline showed this catalysis most clearly. In the absence of aniline hydrochloride, the yield of benzanilide was only 10% after 4 hr at 184°C, but

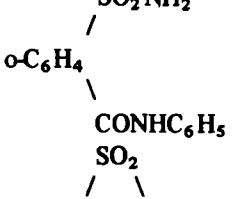
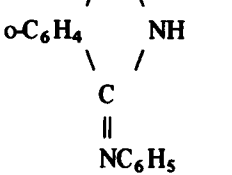
Table 1. Starting Materials Prepared for Transamidation Studies

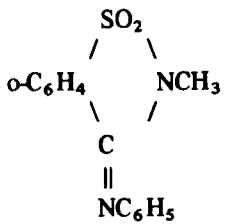
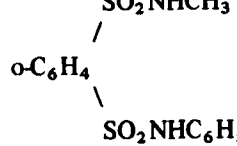
Compounds			Melting point, °C[a]	
No.	Name	Formula	Found	Literature
I	Benzamide	$C_6H_5CONH_2$	129	129 [6]
II	N-Methylbenzamide	$C_6H_5CONHCH_3$	79-80	80-82
III	N,N-Dimethylbenzamide	$C_6H_5CON(CH_3)2$	41-42	41-42 [10]
IV	Phthalimide	$o\text{-}C_6H_4(CO)_2NH$	232	232 [11]
V	N-Methylphthalimide	$o\text{-}C_6H_4(CO)_2NCH_3$	133-134	133 [5]
VI	Saccharin		228	228 [12]
VII	Anilinium saccharinate		90	90 [7]
VIII	N-Methylsaccharin		127-128	131-133 [13]

IX	N-n-Butylsaccharin		36–38	37–38 [14]
X	Benzenesulfonamide	$C_6H_5SO_2NH_2$	153–154	152–154 [15]
XI	p-Toluenesulfonamide	$p\text{-}CH_3C_6H_4SO_2NH_2$	137–138	137.5 [15]
XII	N-Methyl-p-toluene sulfonamide	$p\text{-}CH_3C_6H_4SO_2NHCH_3$	75–76	75 [15]
XIII	N,N-Dimethyl-p-toluenesulfonamide	$p\text{-}CH_3C_6H_4SO_2N(CH_3)_2$	79–80	80–81 [16]
XIV	Di-p-toluenesulfonamide	$(p\text{-}CH_3C_6H_4SO_2)_2NH$	170–172	171–172 [17]
XV	N-Methyl-di-p-toluenesulfonamide	$(p\text{-}CH_3C_6H_4SO_2)_2NCH_3$	124–125	124.5–125.5 [18]
XVI	o-Benzenedisulfonimide	$o\text{-}C_6H_4(SO_2)_2NH$	189–191	189 [19]
XVII	Anilinium o-benzene disulfonimidate	$o\text{-}C_6H_4(SO_2)_2N^-\ C_6H_5NH_3^+$	169–171	Not reported [20]
XVIII	N-Methyl-o-benzene disulfonimide	$o\text{-}C_6H_4(SO_2)_2NCH_3$	179–180	179 [21]
XIX	N,N′-Dimethyl-o-benzenedisulfonamide	$o\text{-}C_6H_4(SO_2NHCH_3)_2$	223–225	225 [21]

[a]All melting points were taken on a calibrated Fisher-Johns melting point apparatus.

Table 2. Compounds Prepared for Comparison with Products of Transamidation Reactions

Compounds			Melting point, °C[a]	
No.	Name	Formula	Found	Literature
XXIII	Benzanilide	$C_6H_5CONHC_6H_5$	161–163	163 [6]
XXIV	p′-Nitrobenzanilide	$p\text{-}O_2NC_6H_4NHCOC_6H_5$	196–198	197 [22]
XXV	p′-Chlorobenzanilide	$p\text{-}ClC_6H_4NHCOC_6H_5$	191–193	191–193 [23]
XXVI	N,N′-Dimethylphthalamide	$o\text{-}C_6H_4(CONHCH_3)_2$	184–186	184–186 [5]
XXVII	N,N′-Diphenylphthalamide	$o\text{-}C_6H_4(CONHC_6H_5)_2$	248–250	250–251 [24]
XXVIII	Phthalanil (N-phenyl phthalimide)	$o\text{-}C_6H_4(CO)_2NC_6H_5$	207–209	205–207 [11]
XXIX	o-Sulfamidobenzanilide		195	195 [7]
XXX	Phenylpseudosaccharin (3-phenylimino-1,2-benz isothiazole-1, 1-dioxide)		315	315 [8]

XXXI	N-Methylphenylpseudo saccharin (2-methyl-3-phenylimino-1,2-benziso thiazole-1,1-dioxide)		315	310 [25]
XXXII	N-Phenyl-p-toluene sulfonamide	$p\text{-}CH_3C_6H_4SO_2NHC_6H_5$	103	103 [26]
XXXIII	N-Phenyl-o-benzene disulfonimide	$o\text{-}C_6H_4(SO_2)_2NC_6H_5$	194–195	195 [27]
XXXIV	N,N′-Diphenyl-o-benzene disulfonamide	$o\text{-}C_6H_4(SO_2NHC_6H_5)_2$	242–244	241 [28]
XXXV	N-Methyl-N′-phenyl-o-benzenedisulfonamide		232	232 [28]

[a] All melting points were taken on a calibrated Fisher-Jones melting point apparatus.

Table 3. Transamidation Reactions of Benzamides with Anilines

Reaction no.	Amide (A)	Amine (B)	Catalyst (C)	Mole ratio, A:B:C	Temp, °C	Time, hr	% Yield of benzanilide
1	Benzamide (I)	Aniline	–	1:1:0	184	2	11.1
2	I	Aniline	–	1:10:0	184	2	25.3
3	I	Aniline	–	1:10:0	184	7	61.0
4	I	Aniline	–	1:10:0	184	24	86.0
5	I	Aniline	Aniline hydrochloride	1:10:0.1	184	4	71.0
6	I	Aniline	Aniline hydrochloride	1:10:0.1	184	7	91.1
7	I	Aniline hydrochloride	–	1:2:0	210	4	80.0[a]
8	I	Aniline hydrochloride	–	1:2:0	210	8	92.0
9	I	p-Nitro aniline	–	1:2.4:0	220 250	20 5	0.0[b]
10	I	p-Nitro aniline	Zinc chloride	1:2:0.5	220	10	0.0
11	I	p-Nitro aniline	Sodium hydroxide	1:2:0.14	210	4	0.0
12	I	p-Nitroaniline hydrochloride	–	1:2.4:0	200	6	0.0

13	I	p-Chloro aniline	–	1:2:0	210	8	67.0[c]
14	N-Methyl benzamide (II)	Aniline	–	1:10:0	184	4	10.0
15	II	Aniline	Aniline hydrochloride	1:10:0.1	184	4	22.0
16	II	Aniline	Zinc chloride	1:10:0.1	184	4	10.0
17	II	Aniline hydrochloride	–	1:2:0	210	4	85.0
18	N,N-Dimethyl benzamide (III)	Aniline	–	1:10:0	184	4	10.0
19	III	Aniline	Aniline hydrochloride	1:1:0.001	184	4	27.5
20	III	Aniline	Aniline hydrochloride	1:10:0.1	184	4	50.0
21	III	Aniline	Zinc chloride	1:10:0.1	184	4	8.5
22	III	Aniline hydrochloride	–	1:2:0	210	4	96.0

[a]Benzonitrile (9%) was also isolated.
[b]Benzonitrile (10%) was isolated.
[c]Yield of p′-chlorobenzanilide (XXIII).

Table 4. Transamidation Reactions of Phthalimides with Aniline

Reaction no.	Imide (A)	Amine (B)	Catalyst (C)	Mole ratio, A:B:C	Temp, °C	Time, hr	% Yield of phthalanil
23	Phthalimide (IV)	Aniline	–	1:1:0	100	6	0.0
24	IV	Aniline	–	1:1:0	125	6	0.0
25	IV	Aniline	–	1:1:0	151	6	30.0
26	IV	Aniline	–	1:10:0	184	4	45.0[a]
27	IV	Aniline	–	1:1:0	140[b]	6	9.0
28	IV	Aniline	–	1:1:0	151[b]	8	49.7
29	IV	Aniline	–	1:1:0	151[c]	92	78.9
30	IV	Aniline	Aniline hydrochloride	1:1.0:05	184	4	45.0
31	IV	Aniline hydrochloride	–	1:1.5:0	200	2	90.0

32	N-Methyl phthalimide (V)	Aniline	–	1:1:0	100	10	0.0
33	V	Aniline	–	1:1:0	125	6	0.0
34	V	Aniline	–	1:5:0	184	4	0.0
35	V	Aniline	–	1:1:0	140[b]	6	0.0
36	V	Aniline	–	1:1:0	151[b]	24	0.0
37	V	Aniline	–	1:1:0	190[b]	24	0.0
38	V	Aniline	Aniline hydrochloride	1:1:0.025	190[b]	36	0.0
39	V	Aniline	Zinc chloride	1:1:0.025	190[b]	36	0.0
40	V	Aniline	Potassium phthalimidate	1:1:0.1	190[b]	36	0.0
41	V	Aniline hydrochloride	–	1:2:0	200	2	93.0[d]

[a]Yield of N,N'-diphenylphthalamide (XXV).
[b]Reaction was carried out in a sealed flask.
[c]Reaction was carried out in a sealed flask which was opened every 12 hr to release pressure.
[d]Starting material had sublimed from the reaction mixture. This yield is based on the amount of unrecovered starting material.

Table 5. Transamidation Reactions of Sulfonamides with Aniline

Reaction no.	Amide (A)	Amine (B)	Mole ratio, A:B	Temp, °C	Time, hr	% Yield of sulf anilide
42	Benzene sulfonamide (X)	Aniline	1:2	184	16	0.0
43	X	Aniline	1:20	184	16	0.0
44	p-Toluene sulfonamide (XI)	Aniline	1:1	184	16	0.0
45	XI	Aniline hydrochloride	1:2	190	0.5	39.1
46	XI	Aniline hydrochloride	1:2	190	1	77.6
47	XI	Aniline hydrochloride	1:2	190	2	91.2
48	N-Methyl-p-toluene sulfonamide (XII)	Aniline	1:1	184	16	0.0
49	N,N-Dimethyl-p-toluenesulfonamide (XIII)	Aniline	1:1	184	16	0.0
50	XIII	Aniline hydrochloride	1:2	190	0.5	78.0

51	**XIII**	Aniline hydrochloride	1:2	190	1	90.9
52	**XIII**	Aniline hydrochloride	1:2	190	2	92.7
53	Di-p-toluene sulfonamide (**XIV**)	Aniline	1:1	184	16	0.0
54	**XIV**	Aniline hydrochloride	1:2	190	0.5	22.9
55	**XIV**	Aniline hydrochloride	1:2	190	1	49.5
56	N-Methyl-di-p-toluenesulfonamide (**XV**)	Aniline	1:1	184	16	0.0
57	**XV**	Aniline hydrochloride	1:2	190	0.5	33.6
58	**XV**	Aniline hydrochloride	1:2	190	1	61.6
59	**XV**	Aniline hydrochloride	1:2	190	2	70.8
60	**XV**	Aniline hydrochloride	1:2	190	4	71.4

Table 6. Transamidation Reactions of Disulfonimides and Disulfonamides with Aniline

Reaction no.	Reagents	Mole ratio	Temp, °C	Time, hr	Types of products isolated (% yields)
61	o-Benzenedisulfonimide (XVI) + aniline	1:1	184	16	Starting materials only
62	XVI + aniline hydrochloride	1:1	200	1	N-Phenylsulfonimide (15.2) Alkali-soluble mixture[a] (58.3)
63	XVI + aniline hydrochloride	1:1	200	2	N-Phenylsulfonimide (31.8) Alkali-soluble mixture[a] (43.2)
64	XVI + aniline hydrochloride	1:2	200	1	N-Phenylsulfonimide (19.3) Alkali-soluble mixture[a] (56.1)
65	XVI + aniline hydrochloride	1:2	200	2	N-Phenylsulfonimide (35.6) Alkali-soluble mixture[a] (30)
66	Anilinium-o-benzenedisulfonimidate (XVII)	–	190	24	Starting material (43.5) N-Phenylsulfonimide (9.3) Alkali-soluble mixture[a] (23.6)
67	XVII	–	230	24	Starting material (33.0) N-Phenylsulfonimide (20.2) Alkali-soluble mixture[a] (25.2)
68	XVII	–	260	24	Starting material (25.0) N-Phenylsulfonimide (25.1) Alkali-soluble mixture[a] (30.7)
69	N-methyl-o-benzene disulfonimide (XVIII)	1:1	130	4	Starting materials only

70	**XVIII** + aniline	1:1	150	8	Starting materials only
71	**XVIII** + aniline	1:1	184	12	Starting materials only
72	**XVIII** + aniline	1:1	184	16	Starting materials only
73	**XVIII** + aniline + aniline hydrochloride	1:1:0.1	200	24	Recovered **XVIII** (80) N-Methyl-N′-phenyldisulfonamide (5)
74	**XVIII** + aniline + aniline hydrochloride	1:1:0.1	230[b]	24	Recovered **XVIII** (70) N-Methyl-N′-phenyldisulfonamide (10)
75	**XVIII** + aniline hydrochloride	1:1	200	1	N-Phenyldisulfonimide (25.1)
76	**XVIII** + aniline hydrochloride	1:1	200	2	N-Phenyldisulfonimide (42.2)
77	**XVIII** + aniline hydrochloride	1:1	200	4	N-Phenyldisulfonimide (60.5)
78	**XVIII** + aniline hydrochloride	1:1	200	24	N-Phenyldisulfonimide (68.2)[c]
79	**XVIII** + aniline hydrochloride	1:2	200	1	N-Phenyldisulfonimide (30.8) Alkali-soluble mixture[d] (45)
80	**XVIII** + aniline hydrochloride	1:2	200	2	N-Phenyldisulfonimide (48.6) Alkali-soluble mixture[d] (39)
81	N,N′-Dimethyl-o-benzenedisulfonamide **(XIX)** + aniline	1:1	184	8	Starting materials only
82	**XIX** + aniline + aniline hydrochloride	1:1:0.1	230[b]	24	Starting materials only

(continued)

Table 6 (continued)

Reaction no.	Reagents	Mole ratio	Temp, °C	Time, hr	Types of products isolated (% yields)
83	**XIX** + aniline + aniline hydrochloride	1:1:0.1	250[b]	24	Recovered **XIX** (70) N-Methyldisulfonimide (10) N-Methyl-N′-phenyldisulfonamide (10)
84	**XIX** + aniline hydrochloride	1:1	250	1	N-Phenyldisulfonimide (45.3)
85	**XIX** + aniline hydrochloride	1:1	250	2	N-Phenyldisulfonimide (61.8)
86	**XIX** + aniline hydrochloride	1:2	250	0.5	N-Phenyldisulfonimide (35) Alkali-soluble mixture[e] (45)
87	**XIX** + aniline hydrochloride	1:2	250	1	N-Phenyldisulfonimide (51) Alkali-soluble mixture[e] (39)

[a] These mixtures contained o-benzenedisulfonimide, N-phenyl-o-benzenedisulfonamide, and N,N′-diphenyl-o-benzenedisulfonamide.

[b] Reaction was carried out in a sealed flask.

[c] As for all yields, this value is for recrystallized product. Based on the amount of unreacted aniline hydrochloride determined by titration, the reaction was 96.5% complete.

[d] These mixtures contained N-methyl-N′-phenyl-o-benzenedisulfonamide and N,N′-diphenyl-o-benzenedisulfonamide.

[e] These mixtures contained N,N′-dimethyl-o-benzenedisulfonamide, N-methyl-N′-phenyl-o-benzenedisulfonamide, and N,N′-diphenyl-o-benzenedisulfonamide.

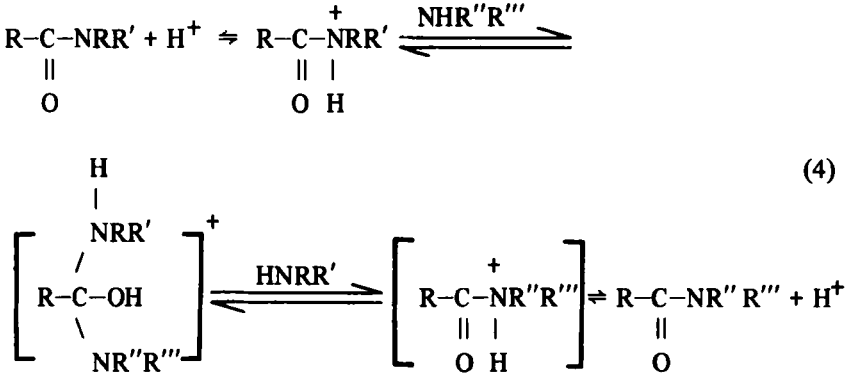
Table 7. Transamidation Reactions of Saccharins with Aniline

Reaction no.	Reagents	Mole ratio	Temp, °C	Time, hr	Types of products isolated (% Yield)
88	Saccharin (VI) + aniline	1:1	150	6	o-Sulfamidobenzanilide (60)
89	VI + aniline	1:1	100–130	24	o-Sulfamidobenzanilide (93)
90	VI + aniline	1:1	150[a]	24	o-Sulfamidobenzanilide (94)
91	Anilinium saccharinate (VII)	–	150	6	o-Sulfamidobenzanilide (60)
92	N-Methylsaccharin (VIII) + aniline	1:1	125	11	Starting materials only
93	VIII + aniline	1:1	160[a]	4	Starting materials only
94	VIII + aniline	1:1	190[a]	12	Starting materials only
95	VIII + aniline hydrochloride	1:1	190[a]	36	Recovered VIII (45) N-Methylphenylpseudo saccharin (6)
96	N-Butylsaccharin (IX) + aniline	1:1	190[a]	40	Starting materials only
97	o-Sulfamidobenz-anilide (XXIX)	–	225/30 mm	2.5	Saccharin (68) Phenylpseudosaccharin (12) Aniline (75)
98	XXIX	–	225	2	Saccharin (9.9) Phenylpseudosaccharin (81) Aniline (13)

[a]Reaction was carried out in a sealed flask.

when a small amount of aniline hydrochloride was added to the system, the yield of benzanilide was raised to 50%. It is not surprising, then, that the best yields of benzanilide were obtained when aniline hydrochloride was used in place of aniline. Aniline hydrochloride and benzamide gave an 80% yield of benzanilide after 4 hr at 210°C, aniline hydrochloride and N-methylbenzamide gave an 85% yield under the same conditions, and aniline hydrochloride and N,N-dimethylbenzamide gave a 96% yield.

For reactions of this type, the mechanism shown in Eq. (4) has been proposed by Klamann [6].



(4)

On the basis of this mechanism, the more easily protonated amide would be expected to undergo transamidation more readily. Our results are consistent with this conclusion. The increasing yields of transamidated product parallel the increasing values reported by Edwards and co-workers [29] for the basicities of benzamide (pK_B = 16.16), N-methylbenzamide (pK_B = 16.13), and N,N-dimethylbenzamide (pK_B = 15.62). These workers also report that protonation of these amides occurs at the nitrogen and not on oxygen.

In contrast to the reactions involving aniline hydrochloride, transamidations with aniline alone gave decreased yields when the benzamide was methyl-substituted. When aniline and benzamide were allowed to react at 184°C for 2 hr, a 25.3% yield of benzanilide was obtained. When benzamide was replaced in the reaction by N-methylbenzamide or N,N-dimethylbenzamide, the yield of benzanilide was, at most, 10% after 4 hr at 184°C. The transamidation reaction has been shown to be catalyzed by acid, and it is possible that even though benzamide is a weak acid (pK_A = 14 or 15) [30], it may exert some catalytic effect on the reaction. The acidity constant of N-methylbenzamide could not be found in the literature, but the

presence of the methyl group would be expected to result in a higher pK_A. In the case of N,N-dimethylbenzamide, there is no proton available to catalyze the reaction.

The data in Table 3 also show that zinc (II) chloride had no catalytic effect on the transamidation reaction. It can also be seen that benzamide failed to undergo transamidation when treated with p-nitroaniline, while with p-chloroaniline, a 67% yield of 4′-chlorobenzanilide was obtained. It is likely that the failure of p-nitrobenzaniline to react is due to its very low basicity and reluctance to enter into the nucleophilic addition to the carbonyl compound.

In the reaction of benzamide and aniline hydrochloride, a small amount of benzonitrile was produced via dehydration of the benzamide. In a polymerization system, such a side reaction would lead to a monofunctional unit, thereby drastically limiting the molecular weight of the resultant polymer. With N-methylbenzamide and N,N-dimethylbenzamide, dehydration cannot occur, and the corresponding elimination of an alcohol or ether molecule is not likely under the conditions used.

On the basis of the foregoing data, the most efficient transamidation reaction in a comparable polymerizing system would involve an N,N-disubstituted amide and an aromatic amine hydrochloride.

The second group of model compounds chosen for the transamidation studies was the phthalimides. The results of the reactions of the phthalimides and aniline are shown in Table 4.

Spring and Woods [5] had previously reported the reaction of phthalimide and methylamine. This reaction was found to proceed readily at 5°C, and a 63% yield of N,N′-dimethylphthalamide was obtained. A similar reaction occurred when phthalimide was treated with a 10-fold excess of aniline. After 4 hr at 184°C, a 45% yield of N,N′-diphenylphthalamide was obtained. However, when a small amount of aniline hydrochloride was added to this reaction mixture, a 45% yield of N-phenylphthalimide was obtained after 4 hr at 184°C.

When phthalimide and aniline were allowed to react in a closed system at 151°C for 8 hr, the product mixture was found to be 50% N-phenylphthalimide and 50% unreacted phthalimide. By periodically opening the reaction flask to release ammonia, the reaction could be carried to at least 80% completion.

The transamidation reaction of N-methylphthalimide and aniline was not achieved under any of the conditions used. Even when equimolar quantities of aniline and N-methylphthalimide were heated to 190°C for 24 hr in a closed system, at least 97% of the aniline remained unreacted.

However, N-methylphthalimide and aniline hydrochloride did react, and a 93% yield of N-phenylphthalimide was obtained after 2 hr at 200°C. A similar yield of N-phenylphthalimide (90%) was obtained when phthalimide and aniline hydrochloride were allowed to react for 2 hr at 200°C. As with the benzamides, the transamidation reactions of the phthalimide series were found to proceed more readily with aniline hydrochloride than with aniline alone. This is consistent with the acid catalysis proposed by Klamann [6] for the transamidation reactions of phthalimide.

That phthalimide and aniline reacted under conditions such that N-methylphthalimide and aniline failed to react may also be explained in light of Klamann's proposed acid catalysis. It would be possible for phthalimide ($pK_A = 8.31$) [31] to catalyze the transamidation reaction. Such autocatalysis is not possible in the case of N-methylphthalimide.

The reactions of difunctional molecules analogous to phthalimide or N-methylphthalimide with difunction aromatic amine hydrochlorides would be suitable for condensation polymerizations. These prototype studies also indicate that it may be possible to produce high-molecular-weight polymers by means of the polycondensation of a diamine with a diimide, or of an aminoimide, provided that the acidic imide-hydrogen is not replaced.

Table 5 summarizes the results of prototype transamidation reactions involving sulfonamides in which the sulfonyl moiety is monofunctional.

These sulfonamides, both substituted and unsubstituted, failed to undergo transamidation reactions with aniline, when this latter reagent was added as the free amine. Only starting materials were isolated from these reactions even when a long reaction time (16 hr) and a large excess of aniline (20:1 mole ratio) were used. However, the transamidation reaction proceeded readily when the amine was added in the form of its hydrochloride salt. After only 30 min at 190°C, p-toluenesulfonamide yielded 39.1% of the corresponding anilide. After 2 hr, the yield of crystallized product was 91.2%.

These results are consistent with the acid-catalyzed mechanism for cleavage of sulfonamides proposed by Klamann and Hofbauer [32].

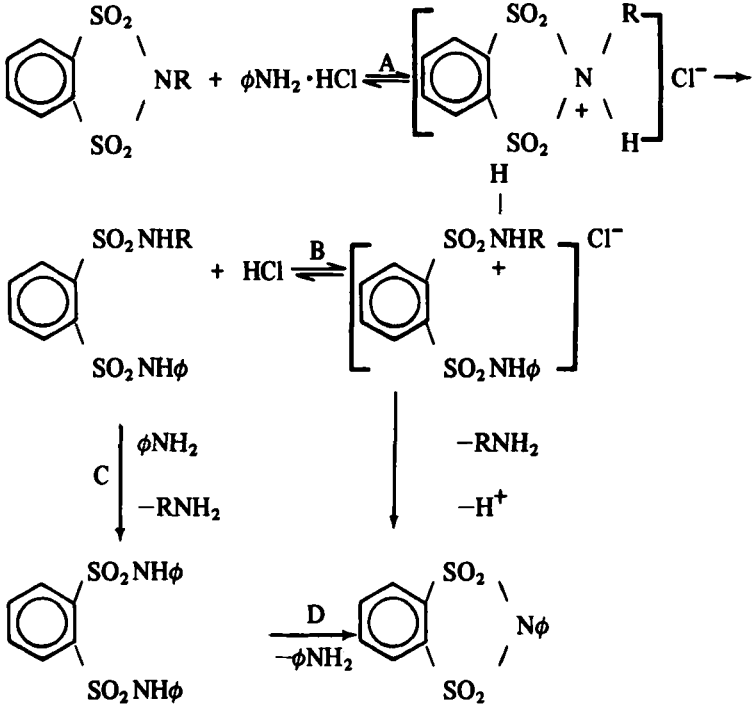
A comparison of the reactions of substituted sulfonamides also supports a mechanism involving initial protonation of the sulfonamide nitrogen. N,N-dimethyl-p-toluenesulfonamide would be expected to be protonated more readily than the unsubstituted compound since the electron-donating properties of the methyl group would enhance the electron density around the nitrogen atom. The reaction of the disubstituted amide with aniline hydrochloride gave a 78% yield of p-toluenesulfanilide after 30 min compared to the 39.1% yield obtained with the unsubstituted compound.

When the nitrogen atom was substituted with an electron-withdrawing group such as the additional p-toluenesulfonyl moiety in di-p-toluenesulfonamide, the yield of sulfanilide dropped to 22.9%. The addition of a methyl group, as in N-methyl-di-p-toluenesulfonamide, would be expected to mitigate somewhat the electron-withdrawing effect of the sulfonyl group. This conclusion was supported by the increase in yield of sulfanilide (33.6%) obtained in the reaction of N-methyl-di-p-toluenesulfonamide compared to the 22.9% yield obtained with di-p-toluenesulfonamide.

A desirable feature of transamidation reactions designed to ultimately yield polysulfimides is the intermediate formation of isolatable sulfamide hemipolymers. The prototype studies involving disulfonamides and disulfonimides were expected to provide information regarding the conditions required for isolation of sulfonamide intermediates and for subsequent ring closure to sulfonimides.

As was the case with linear sulfonamides (Table 5), the difunctional sulfonyl compounds (Table 6) failed to undergo transamidations with aniline. However, when aniline hydrochloride was used as a catalyst or was the principal reagent, transamidated products were obtained.

The transamidation of cyclic imides with aniline hydrochloride proceeds by ring opening followed by ring closure.



The ease with which the nitrogen can undergo protonation in both step A and step B should be influenced by the electron density at the nitrogen. This is essentially the same argument invoked in the case of linear sulfonamides. In addition, the reaction may be facilitated by the release of steric strain in the cyclic quaternary ammonium species after attack by aniline.

If the effect of ring opening is ignored, a correlation can be made between higher yields of transamidated products and increased electron density at nitrogen. This correlation parallels the trend noted in the case of linear sulfonamides. For example, after 1 hr at 200°C, a 1:1 mole ratio of o-benzenedisulfonimide and aniline hydrochloride gave 15.2% of N-phenyl-o-benzenedisulfonimide, whereas N-methyl-o-benzenedisulfonimide under these same conditions gave 25.1% of the product.

It is somewhat more difficult to evaluate the influence of the ring opening requirement for sulfonimide starting mateials compared to their open-chain counterparts. The nitrogen atoms in N-methyl-di-p-toluenesulfonamide and N-methyl-o-benzenedisulfonimide carry similar substituents, two electron-withdrawing sulfonyl groups and one electron-donating alkyl group. Thus, electronic effects in these two compounds could be considered comparable. The products obtained in transamidation reactions involving these compounds are different, but in general, the relative total yields of transamidated products are in agreement with results expected if the ring opening provides an additional driving force in these reactions. The imide gave 88% of transamidated products, whereas under comparable conditions the amide gave a 70.8% yield of transamidated product.

The reactions of N,N′-dimethyl-o-benzenedisulfonamide gave results which approximated those from sulfonimides. A significant variation in products was noted only in the case of the reaction of the diamide with aniline in the presence of a catalytic amount of aniline hydrochloride. After 24 hr at 250°C in a sealed flask, these reagents gave a 10% yield of N-methyl-o-benzenedisulfonimide. This product probably arose from the cyclization of the starting material under the vigorous reaction conditions employed. A transamidated product, N-methyl-N′-phenyl-o-benzenedisulfonamide, was also isolated from this reaction. The same transamidated product was also isolated from the reaction of N-methyl-o-benzenedisulfonimide under similar conditions.

When N,N′-dimethyl-o-benzenedisulfonamide was allowed to react with molar amounts of aniline hydrochloride, the yields of transamidated imide and diamides were comparable to those obtained in the case of sulfonimide starting materials. Detailed comparisons are not possible since the temperature required to obtain a melt with the diamide starting material

was higher than that needed for the imide. Reaction temperatures were, therefore, higher in the case of diamides, and product yields were correspondingly higher than for reactions with sulfonimides employing the same conditions with regard to time and concentration.

In addition to supporting the use of aromatic amine hydrochlorides in polymeric transamidations of sulfonamides and sulfonimides, these prototype studies clearly indicated that the polymerization would be difficult to perform in two distinct steps. Thus, while it would be desirable to be able to isolate a polyamide hemipolymer, and later force the cyclization to the final polyimide, the data presented in Table 6 indicate that the imide is formed in significant amounts under the conditions necessary for the preparation of the transamidated sulfonamide. It should also be added, however, that the studies discussed to this point also indicate that, while it would probably not be possible to isolate pure hemipolymer in the sulfonyl system, the degree of imidization in the product would be more readily controlled than in the case of carbonyl systems. Prototype studies involving phthalimides suggested that both transamidation and transimidation steps proceed so rapidly that one should expect the products isolated in corresponding polymerizing systems to be cyclized extensively.

Finally, the transamidation reactions of saccharin and aniline were investigated. The results of these studies are shown in Table 7.

Mannessier-Mameli [7] had previously studied the reaction of saccharin and aniline but did not give the yields obtained in these reactions. It was reported [7] that saccharin and aniline reacted at room temperature to produce the anilinium salt of saccharin, while at higher temperatures, 130-150°C, o-sulfamidobenzanilide was obtained. The same results were observed in the present investigation. When the reaction time at 150°C was extended to 24 hr in a closed system, less than 1% of the aniline remained unreacted, and o-sulfamidobenzanilide was isolated in 94% yield. This type of reaction would seem to be very suitable as a polycondensation reaction.

It was found that aniline and N-methylsaccharin did not react, even when heated in a closed system at 190°C for 36 hr. The same result was obtained with N-n-butylsaccharin. Again, this may be explained by the absence of an acidic proton in both of the N-alkylsaccharins. Saccharin (pK_A = 1.61) [33] could catalyze the transamidation reaction. When N-methylsaccharin and aniline hydrochloride were allowed to react in a closed system at 190°C for 36 hr, 45% of the N-methylsaccharin was recovered and 6% of N-methylphenylpseudosaccharin (XXXI) was obtained.

When o-sulfamidobenzanilide was heated at 225°C for 2.5 hr under

atmospheric pressure 81% of phenylpseudosaccharin (XXX) was obtained. At reduced pressure, a 75% yield of aniline was distilled from the system and the yield of N-phenylpseudosaccharin was reduced to 12%. This reaction was also reported by Mannessier-Mameli [7].

Kogan and Dziomko [8] reported a 56% yield of N-phenylpseudosaccharin when saccharin and aniline hydrochloride were allowed to react in a sealed tube at 200°C for 15 min.

On the basis of the foregoing data, it was concluded that appropriate analogs of the saccharins, rather than N-substituted derivatives, should be the first choice for monomers in the proposed polymerization studies. It was also concluded that the hemipolymers would be more easily isolated from reactions of saccharin-type monomers than from either the phthalimide- or sulfonimide-type monomers. This evaluation is based on the ease of isolation of o-sulfamidobenzanilide from the reaction of equimolar quantities of aniline and saccharin. The difference in reactivity of the carbonyl and the sulfonyl groups in saccharin is such that the initial attack of the amine occurs at the carbonyl group under conditions such that the sulfonyl group is not attacked. Of the three systems studied, therefore, the saccharin or mixed acid system appears to offer the best possibility for obtaining a high degree of polymerization before extensive imidization results in a loss of solubility and fabricability.

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