ratio is important only with the primary mercaptan. The trisulfide is the major product (75%) obtained from the stoichiometric charge of *n*-butyl mercaptan and sulfur (1:1 mole–atom ratio). If the *n*-butyl mercaptan:sulfur mole–atom ratio is 2, *n*-butyl disulfide is formed in 71% yield. Previous reports indicate that disulfides are formed in respectable yields from the base-catalyzed reaction of sulfur with primary mercaptans.[2,3] The results from variation in charge ratios are summarized in Table I.

TABLE I
REACTION OF MERCAPTANS WITH SULFUR. ALKYL POLYSULFIDES[a]
RS_xR

	Charge, moles of RSH/ g-atom	Product[b,c]		
R	of S	% S_2	% S_3	% S_4
n-C_4H_9	1	[15.4]	[>75]	[<5]
n-C_4H_9	2	[71]	[29]	. . .
sec-C_4H_9	1	<3	>95	Trace
sec-C_4H_9	2	<3	>95	Trace
i-C_4H_9	1	[5]	[87]	[5]
t-C_4H_9	1	. . .	12.5	87.5
t-C_4H_9	2	. . .	10.6	89.4
i-C_3H_7	1	. . .	[>90]	[<10]

[a] The physical constants for all these polysulfides, except *sec*-butyl are given in ref 1. *sec*-$C_4H_9S_3C_4H_9$: bp 79–80° (0.4 mm), n^{25}D 1.5290. [b] Yields in brackets were obtained by fractional distillation; all other yields were calculated from the nmr curves and confirmed by fractionation. [c] Total yields of product represent 90 to 100% of the sulfur charge.

The reaction is carried out by adding the mercaptan slowly to a slurry of sulfur and amine in an inert solvent at room temperature. Hydrogen sulfide evolution begins immediately and the reaction is complete in 2 to 4 hr. The mixture of products was separated by careful fractionation. In addition, the crude reaction products were examined by proton nmr spectroscopy. Recent work has shown that, as x increases in the formula, RS_xR, the chemical shifts for the protons nearest the sulfur are shifted downfield.[4,5] This was confirmed by preparing synthetic blends of di-, tri-, and tetrasulfides. The chemical shifts for the polysulfides investigated are reported in Table II.

TABLE II
H^1 CHEMICAL SHIFTS[a] OF POLYSULFIDES[b]

	Values of x		
Compd	2	3	4
$CH_3CH_2CH(CH_3)S_xCH(CH_3)CH_2CH_3$	2.65	2.83	2.92
$CH_3CH_2CH_2CH_2S_xCH_2CH_2CH_2CH_3$	2.64	2.87	2.95
$CH_3CH(CH_3)CH_2S_xCH_2CH(CH_3)CH_3$	2.57	2.77	2.80
$CH_3CH(CH_3)S_xCH(CH_3)CH_3$	. . .	3.22	. . .
$(CH_3)_3CS_xC(CH_3)_3$[c]	1.28	1.35	1.38

[a] In ppm. [b] Hydrogens on carbon atom adjacent to sulfur. [c] Since there are no hydrogens on the carbon adjacent to the sulfur, these shifts are obviously those of the methyl groups.

The yields, as determined from nmr spectra, were in good agreement with the yields obtained by distillation. Polysulfides higher than tetra- were present in very small amounts.

Preliminary experiments indicate that the reaction is also applicable to the preparation of aromatic trisulfides.

Experimental Section

General Procedure for the Reaction of Mercaptans with Sulfur.—The mercaptan (1 or 2 moles) was added slowly over about 1 hr to a slurry of 1 g-atom of sulfur and *n*-propylamine (1–3 mole % of mercaptan charged) in methylene chloride at room temperature. Evolution of hydrogen sulfide began immediately and continued for 2 to 4 hr after the mercaptan addition. There was no detectable temperature change during the reaction. When hydrogen sulfide evolution ceased, the slightly hazy mixture was filtered, and the solvent was removed by vacuum distillation. A sample was removed for nmr analysis and the remainder was separated into its components by careful fractionation. Care was taken to keep the pot temperature below 140°, since disproportionation is known to occur above this temperature.[6]

Analytical Procedure.—A Varian A-60 high-resolution spectrometer was used to analyze the crude reaction mixtures after removal of methylene chloride. Semiquantitative yields were obtained from the chemical shifts for the protons nearest the sulfur. The yields were calculated from the peak heights with necessary allowance being made for the difference in molecular weights. Chemical shifts in Table II are reported with respect to tetramethylsilane with positive shifts being downfield.

---

(2) F. H. McMillan and J. A. King, *J. Am. Chem. Soc.*, **70**, 4143 (1948).

(3) J. F. Olin, U. S. Patent 2,237,625 (April 8, 1941).

(4) D. Grant and J. R. VanWazer, *J. Am. Chem. Soc.*, **86**, 3012 (1964).

(5) I. B. Doughlas, presented at the Symposium on Fossil Fuels: Critical Discussion of Origin, Composition and Related Chemistry, sponsored by the American Petroleum Institute (Research Projects 48 and 52), University of Wyoming Science Camp, Laramie, Wyo., July 28–Aug 1, 1964.

(6) G. F. Bloomfield, *J. Chem. Soc.*, 1547 (1947).

The Reaction of *o*-Chlorobenzoic Acid with Certain Active Hydrogen Compounds and Sodamide in Liquid Ammonia[1]

EDWARD R. BIEHL AND HSUEH-MING LI[2]

Southern Methodist University, Dallas, Texas

Received August 2, 1965

As an extension of the general benzyne–carbanion phenylation reaction,[3–4] the reaction of *o*-chlorobenzoic acid with certain nitriles and mercaptans and sodamide has been investigated. This paper represents the first time halobenzoic acids have been subjected to such treatment and the first time that benzynecarboxylate has been detected under these conditions. Thus, it has been found that this reaction yields exclusively the corresponding *m*-carboxyphenylated active hydrogen compound I (49–71%) and a mixture of *o*- and *m*-aminobenzoic acids (10–20%). Mercaptans also gave the *meta*-substituted benzoic acids, II. In

---

(1) We gratefully acknowledge support of the Robert A. Welch Foundation, Houston, Texas, Grant No. N-118.

(2) Robert A. Welch Predoctoral Fellow.

(3) For reviews, see J. F. Bunnett, *J. Chem. Educ.*, **38**, 278 (1961); H. Heanly, *Chem. Rev.*, **62**, 81 (1962).

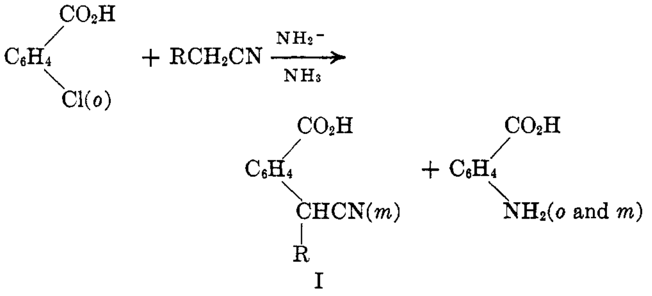
(4) (a) F. W. Bergstrom and R. J. Agostinho, *J. Am. Chem. Soc.*, **67**, 2152 (1945); (b) P. H. Dirstini and F. W. Bergstrom, *J. Org. Chem.*, **11**, 55 (1946); (c) R. A. Seibert and F. W. Bergstrom, *ibid.*, **10**, 544 (1945); (d) W. W. Leake and R. Levine, *Chem. Ind.* (London), 1160 (1955); *J. Am. Chem. Soc.*, **81**, 1627, 1169 (1959).

Table I

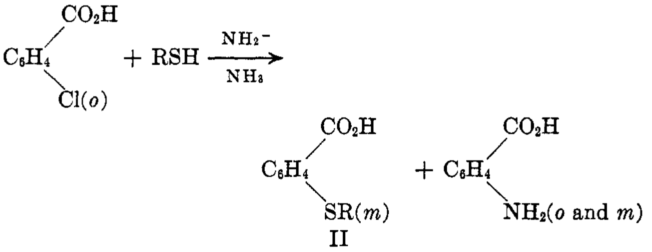
Reaction of *o*-Chlorobenzoic Acid and Active Hydrogen Compounds

Active hydrogen compd.	M.p., °C.[a]	I or II, % yield	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found
CH_3CN	176–177	70	67.07	66.70	4.38	4.34	8.69	8.47
CH_3CH_2CN	134–135	49	68.55	68.61	5.17	5.27	7.99	7.80
$CH_3(CH_2)_3CN$	130–131	71	70.91	70.77	6.44	6.42	6.89	6.87
C_6H_5SH	107–108[b]	56						
CH_3SH	126–127[c]	62						
C_2H_5SH	98[d]	61						

[a] Melting points are uncorrected. [b] Lit.[6] m.p. 107–109°. [c] C. C. Price and J. J. Hydock [*J. Am. Chem. Soc.*, **74**, 1943 (1952)] reported m.p. 126–127°. [d] J. J. Donleavy and J. English, Jr. [*ibid.*, **62**, 221 (1940)] reported m.p. 98–99°.



no case has any *o*-carboxyphenylated active hydrogen compound been isolated. The isomeric aminobenzoic acids were separated, identified, and quantitatively analyzed. The isomeric aminobenzoic acid distribution in all reactions was approximately 1:2 *ortho*:*meta*. Table I shows the yields of the compounds I and II that have been prepared using a reaction time of 1 hr. and a molar ratio of 0.6 mole of sodamide to 0.3 mole of active hydrogen compound to 0.1 mole of *o*-chlorobenzoic acid.



To show that no *ortho* isomer was present, authentic samples of both the *ortho* and *meta* isomer were prepared and a comparison was made of the respective infrared spectra. In all cases, the infrared spectra of the products were identical in all respects with the spectra of the corresponding known *meta* isomer.

From these results it appears that this reaction is an excellent method for substituting the active hydrogen atom by a *m*-carboxyphenyl group.[5] Thus, in the single previously reported synthesis of *m*-carboxydiphenyl sulfide,[6] the von Richter reaction provided a yield of only 5%. We are currently trying to extend this reaction to other active hydrogen compounds.

Experimental Section

General Procedure for the Reaction of *o*-Chlorobenzoic Acid with Active Hydrogen Compounds and Sodamide in Liquid Ammonia.—Sodamide (0.6 mole) was prepared by adding 0.6 g.-atom (18.2 g.) of cleanly cut sodium to a 1-l. flask equipped with a stirrer and Dry Ice condenser and containing about 600 ml. of liquid ammonia and 0.1 g. of ferric nitrate. The active hydrogen compound (0.3 mole) was added over a period of 5 min. and allowed to react for 30 min. to ensure anion formation. Then 0.1 mole (15.6 g.) of *o*-chlorobenzoic acid was added portionwise over a period of 5–7 min., and the solution was stirred for 1 hr. At this time, 0.65 mole of ammonium chloride was added and the ammonia was removed by heating with a steam bath. The residue was slurried with a little ether and poured into about 150 ml. of ice–water slurry. The basic mixture was treated with charcoal, filtered, and added to 50 ml. of concentrated hydrochloric acid. The solid material was recovered by filtration and purified by recrystallization from a water-methanol mixture. Table I summarizes pertinent physical data for the compounds.

The isomeric aminobenzoic acids were separated and the ratio of the isomers was estimated by paper chromatography.

---

[5] The reactions of *m*- or *p*-chlorobenzoic acid with active hydrogen compounds yield a mixture of *m*- and *p*-carboxyphenylated active hydrogen compounds in a ratio of approximately 1:1 *meta*:*para*, as determined by infrared analysis.

[6] J. F. Bunnett and M. M. Rauhut, *J. Org. Chem.*, **21**, 934 (1956).

The Isomerization and Disproportionation of 8-*t*-Butylchroman and Related *t*-Butyl phenyl Ethers[1]

Irving J. Borowitz and Gregory J. Williams

Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania

Received August 17, 1965

In relation to our recent syntheses of 6-ketononanolides from tetrahydrochromans,[2] it was desired to prepare the 6- and 8-*t*-butyl derivatives of chroman. A standard synthesis of chromans substituted in the aromatic ring involves the alkylation of the appropriate sodium phenoxide with 3-chloro-1-propanol to give the corresponding 3-phenoxy-1-propanol which is then cyclized by dehydration in boiling benzene with phosphorus pentoxide followed by direct distillation.[3] We have utilized this method previously to synthesize several monomethylchromans and 5,8-dimethylchroman.[2b] Application of this method to 4-*t*-butylphenol (**1**) gave 3′-hydroxypropyl 4-*t*-butylphenyl ether (**2**) which was cyclized to 6-*t*-butylchroman (**3**).

Similar reaction of 2-*t*-butylphenol (**4**) gave 3′-hydroxypropyl 2-*t*-butylphenyl ether (**5**). Cyclization of **5** with phosphorus pentoxide by the previously utilized procedure (method B) gave a mixture which

---

[1] This investigation was supported in whole by Public Health Service Research Grant AI 06303-01 to I. J. B. from the National Institute of Allergy and Infectious Diseases.

[2] (a) I. J. Borowitz and G. Gonis, *Tetrahedron Letters*, **No. 19**, 1151 (1964); (b) R. Kelsey, Lehigh University, unpublished results.

[3] R. E. Rindfusz, *J. Am. Chem. Soc.*, **41**, 667 (1919); (b) R. E. Rindfusz, P. M. Gennings, and V. L. Harnack, *ibid.*, **42**, 157 (1920).