[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AT THE UNIVERSITY OF PENNSYLVANIA]

α-Bromo-α-sulfonylamides[1]

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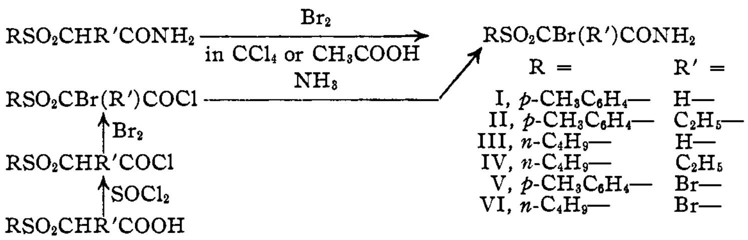
This study of α-bromo-α-sulfonylamides was undertaken for the purpose of comparing their reactions with those of the bromo derivatives of other active methylene compounds. While some reactions of the latter resemble the reactions of hypohalites ("positive halogen"[3]) rather than of halides, the ability of the sulfone group to produce this type of activation has heretofore received little attention.[4] No α-bromo-α-sulfonylamides appeared to have been prepared previously and it was first necessary to devise methods for their synthesis. Since the α-bromo-α-sulfonylamides were found to have properties identical with those of the compounds previously reported to be the isomeric N-bromoamides, the establishment of their structure constitutes a third phase of this report.

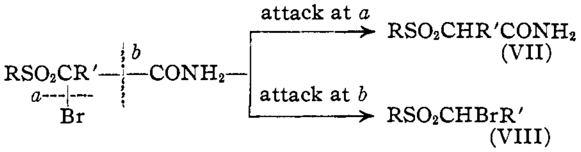
Preparation of α-Bromo-α-sulfonylamides.—Two of the α-bromo-α-sulfonylamides (I and IV) were prepared by converting α-sulfonyl acids to acid chlorides, bromination and treatment with ammonia. The method was laborious and the yields low. Much better results were obtained by treating α-sulfonylamides with bromine in moist[6] carbon tetrachloride and all of the α-sulfonylamides tested reacted readily under these conditions. Glacial acetic acid was satisfactory as a solvent for the preparation of I and III but the α-sulfonyl-*n*-butyramides were not brominated in this solvent.



$$\begin{tikzcd}
RSO_2CHR'CONH_2 \arrow[rr, "Br_2", "\text{in } CCl_4 \text{ or } CH_3COOH"'] & & RSO_2CBr(R')CONH_2 \\
RSO_2CBr(R')COCl \arrow[rru, "NH_3"] & & \\
RSO_2CHR'COCl \arrow[u, "Br_2"'] & & \\
RSO_2CHR'COOH \arrow[u, "SOCl_2"'] & &
\end{tikzcd}$$

	R =	R' =
I,	*p*-$CH_3C_6H_4$—	H—
II,	*p*-$CH_3C_6H_4$—	C_2H_5—
III,	*n*-C_4H_9—	H—
IV,	*n*-C_4H_9—	C_2H_5
V,	*p*-$CH_3C_6H_4$—	Br—
VI,	*n*-C_4H_9—	Br—

Reactions of α-Bromo-α-sulfonylamides.—The reactions of these compounds were of two types. One resulted in the oxidation of the reagent and reduction of the α-bromoamide, showing the positive character of the halogen. The other type resulted in the cleavage of the —$CONH_2$ group. The predominant reaction depended both upon the reagent and upon the structure of the α-bromo-α-sulfonylamide. For example, sodium ethoxide gave the reduction product (VII) from IV but caused elimination of the —$CONH_2$ group from I to give the α-bromosulfone (VIII). Furthermore, II was not hydrolyzed under conditions which converted I to the α-bromosulfone[7] (VIII) and which resulted in attack at both the —Br and —$CONH_2$ groups of IV.



$$\begin{tikzcd}
 & RSO_2CHR'CONH_2 \ \text{(VII)} \\
\underset{\substack{a\text{---}|\text{---} \\ Br}}{RSO_2CR'}\overset{b}{\vdots}\text{—}CONH_2 \arrow[ru, "\text{attack at } a"] \arrow[rd, "\text{attack at } b"'] & \\
 & RSO_2CHBrR' \ \text{(VIII)}
\end{tikzcd}$$

Two of the results reported in Table I are of especial importance. The liberation of two equivalents of iodine by the dibromo amides with potassium iodide in acid solution is contradictory to the report of Tröger and Hille that only one halogen atom of the dibromo amides underwent this reaction. It is also interesting to note that the time for complete reaction of the dibromo compounds with hydrazine was less than that for the corresponding monobromo compounds. It may therefore be inferred that this reaction is not stepwise and that the monobromo derivatives

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[1] This communication is constructed from a thesis submitted by William M. Ziegler in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Pennsylvania in June, 1939.

[2] Harrison Fellow in Chemistry, 1938–1939.

[3] Waters, "Physical Aspects of Organic Chemistry," 2nd ed., George Routledge and Sons, London, 1937, p. 221.

[4] The results of Tröger and Hille[5] indicated that α-bromo-α-sulfonylamides do not contain positive halogen. Since our problem was begun, Samen [*Arkiv Kemi, Mineral. Geol.*, **12B**, No. 51 (1938); *Chem. Abs.*, **32**, 4520 (1938)] reported that triethylsulfonylmethyl bromide was reduced to triethylsulfonylmethane by treatment with hydrazine or hydriodic acid, and Mellander [*ibid.*, **12A**, No. 16, 32 (1937); *Chem. Abs.*, **31**, 5763 (1937)] found that α-bromo-α-sulfonyl acids were reduced by hydrazine.

[5] Tröger and Hille, *J. prakt. Chem.*, [2] **71**, 201 (1905).

[6] Water alone could not be used as a reaction medium, probably because of the insolubility of the α-sulfonylamides. Bromination occurred more slowly or not at all in dry carbon tetrachloride, suggesting that the reaction is similar to the basic catalysis in the bromination of ethyl acetoacetate [Pederson, *J. Phys. Chem.*, **38**, 601 (1934)]. However, aqueous sodium hypobromite was a less favorable reagent for halogenation of α-sulfonylamides than was bromine in moist carbon tetrachloride.

[7] The result of this hydrolysis was unexpected. According to Mossler [*Monatsh.*, **29**, 73 (1908)] α-bromoamides give aldehydes upon alkaline hydrolysis. A N-bromoamide would be expected to give an amine.[8]

are not intermediates in the reduction of the dibromo amides with hydrazine.

The reactions of the α-bromo-α-sulfonylamides with hydrazine, hydriodic acid, piperidine and mercaptides gave VII accompanied by nitrogen, iodine, piperidine hydrobromide and disulfide, respectively. Since similar results have been obtained with the bromo derivatives of active methylene compounds, it may be concluded that the sulfone group exerts upon halogen in the *alpha* position an effect similar to that of other labilizing groups.

Structure of the Bromoamides.—There seemed no reasonable doubt that the syntheses involving bromination of the acid chlorides would give α-bromo-α-sulfonylamides. However, I, prepared by this method, was identical with the product obtained by bromination of the α-sulfonylamide in glacial acetic acid by the procedure of Tröger and Hille[5] and reported by those workers to be a N-bromoamide (IX). Furthermore, IV prepared from the α-bromoacid chloride was identical with the products obtained by the method of Tröger and Hille and by bromination of the α-sulfonylamide in moist carbon tetrachloride. There seems to be little doubt, therefore, that the compounds assigned structures IX and X by Tröger and Hille are actually I and V.

p-$CH_3C_6H_4SO_2CH_2CONHBr$
IX

p-$CH_3C_6H_4SO_2CHBrCONHBr$
X

Attempts further to confirm the structures by synthesis of the isomeric N-bromoamides by bromination in the presence of alkali were unsuccessful because of the failure of the amides to react or the formation of dibromosulfones. The α-bromo-α-sulfonylamides did not react with nitrous acid and their conversion to α-bromo acids was therefore unsuccessful.

It should be pointed out that the arguments of Tröger and Hille for a N-bromo structure for these compounds were based largely upon the statement that the dibromoamides reacted with only one equivalent of iodide, a statement now shown to be incorrect. If further evidence for the attachment of bromine to carbon is necessary it may be gained from the following. (a) The compounds are stable toward boiling water.[8] (b) The difference in the ease of bromination of the acetamides and butyramides would not be expected to be so great if it depended upon the influence of an *alpha* ethyl group upon the reactivity of —$CONH_2$. (c) The conversion of I to an α-bromosulfone (VIII) by hydrolysis further establishes the position of the halogen.[9]

Experimental Part[10]

Reactions of α-Sulfonylamides[11] with Sodium Hypobromite.—To 21.4 g. of α-p-tolylsulfonylacetamide[12] was added 5.4 ml. (16 g.) of bromine, and the mixture shaken until about three-fourths of the amide had dissolved. The mixture was cooled in an ice-bath at −15° and a cold solution of 50% sodium hydroxide added dropwise with stirring until 10% more than the theoretical amount required to react with the bromine had been used. After standing in the ice-bath for one hour, cold water was added, the product removed by filtration and recrystallized from alcohol. The yield of p-tolylsulfonyldibromomethane, m. p. 116–117°,[9] was 2.9 g. (18% based on the bromine).

In another experiment 10.3 g. of α-n-butylsulfonyl-n-butyramide was mixed with 5.4 ml. (16 g.) of bromine and treated as described above. Unchanged starting material was the only product isolated.

Preparation of α-Bromoamides from Acid Chlorides

α-Bromo-α-p-tolylsulfonylacetamide (I).—To 21.4 g. of p-tolylsulfonylacetic acid[13] in 75 ml. of carbon tetrachloride, 13 g. of thionyl chloride in 25 ml. of carbon tetrachloride was added slowly. After refluxing for one hour and cooling, 6 ml. (18 g.) of bromine was added and the mixture then refluxed for ten hours, cooled, and poured into excess concentrated ammonia water at −15°. The lump that formed on stirring was removed and extracted several times with the same 200 ml. of water, cooling and removing the crystals between extractions. The crystals thus removed were recrystallized from water with the aid of charcoal. The yield was 2.40 g. (8%), m. p. 172–174°.

Anal. Calcd. for $C_9H_{10}O_3NSBr$: Br, 27.3. Found: Br, 27.2, 27.5.

α-Bromo-α-n-butylsulfonyl-n-butyramide (IV).—From 136.5 g. of ethyl α-bromo-n-butyrate and the mercaptide from 54.6 g. of n-butyl mercaptan under the conditions previously used for the preparation of the amides,[11] there was obtained 105 g. (74%) of crude ethyl α-n-butylthio-n-butyrate which was oxidized[11] in acetic acid–acetic anhydride mixture to the α-sulfonyl ester. The ester could not be crystallized and decomposed upon attempted dis-

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[8] Hofmann [*Ber.*, **15**, 411 (1882)] reported that N-bromoamides are decomposed by boiling water.

[9] The formation of VIII might be considered possible from a N-bromoamide by hydrolysis of the latter to sodium hypobromite, followed by the action of the hypobromite upon the other hydrolysis products. This explanation of the hydrolysis result was eliminated by showing that none of the hydroylsis products were converted to VIII by sodium hypobromite.

[10] All melting points are corrected unless otherwise specified.

[11] The α-sulfonylamides were prepared by the methods described by d'Ouville and Connor, THIS JOURNAL, **60**, 33 (1938), and Pomerantz and Connor, *ibid.*, **61**, 3386 (1939).

[12] Similar results were obtained when sodium p-tolylsulfonylacetate was used but methyl p-tolyl sulfone did not react under these conditions.

[13] Gabriel, *Ber.*, **14**, 833 (1881).

tillation. The crude material was hydrolyzed with 400 ml. of 8% sodium hydroxide solution, acidified and extracted with ether. The acid obtained (93.6 g.) was converted to the acid chloride under the conditions described above, refluxed with bromine (71 g.) for twenty-five hours and treated with an excess of dry ammonia. The solvent was decanted, the residue extracted with alcohol and the alcohol solution treated with decolorizing charcoal. Removal of the solvent gave an oil which was crystallized with considerable difficulty. The solid was recrystallized several times from ether, seeding each time. The yield was 10.75 g. (6% based on the mercaptan), m. p. 56–57°. This was slightly less pure than the material obtained as described below.

Anal. Calcd. for $C_8H_{16}O_3NSBr$: Br, 27.9. Found: Br, 27.1, 27.2.

Preparation of α-Bromo-α-sulfonylamides from α-Sulfonylamides.—Five hundredths mole of the amide[11] was mixed with 100 ml. of carbon tetrachloride and 2.66 ml. (8 g.) of bromine added. With the acetamides the moisture present in unpurified carbon tetrachloride was adequate but the bromination of the butyramide was accomplished more readily by the addition of 2 ml. of water. After refluxing until the bromine color had disappeared, the solvent was removed quickly and the oil recrystallized. Slow removal of the solvent resulted in hydrolysis. A prolonged reaction period in the presence of excess water gave the dibromosulfonylmethane as shown below under the preparation of I.

α-Bromo-α-*p*-tolylsulfonylacetamide (I).—The mixture, without additional water, was refluxed for one hour and the solvent removed over a period of twenty minutes. The oil was dissolved in alcohol and allowed to crystallize. The solid was recrystallized from alcohol. From 10.7 g. of the amide there was obtained 6 g. (42%) of the product, m. p. 172–174°. The same product (51%) was obtained by the method of Tröger and Hille.[5] Neither sample lowered the melting point of the amide prepared from the α-bromo-α-sulfonyl acid chloride.

Anal. Calcd. for $C_9H_{10}O_3NSBr$: Br, 27.3; N, 4.80. Found: Br, 27.4, 27.6; N, 4.85, 4.80.

Ten and seven-tenths grams of α-*p*-tolylsulfonylacetamide in 100 ml. of carbon tetrachloride and 4 ml. of water was treated with 2.66 ml. (8 g.) of bromine and refluxed for one-half hour. The solution was then poured into a beaker and evaporated on a water-bath over a period of four hours. The sirup was dissolved in ether and filtered, the ether was then evaporated and the oil well chilled. After several hours chilling the paste that formed was mixed with enough very cold ether to dissolve the oily impurities and the material was filtered. The crystals were recrystallized from ligroin (b. p. 70–90°) and then from alcohol. The yield was 2.3 g. (28% based on the bromine) of product melting 116–117°, reported by Tröger and Hille[5] to be the melting point of *p*-tolylsulfonyldibromomethane.

α-Bromo-α-*p*-tolylsulfonyl-*n*-butyramide (II).—Two milliliters of water was added and the mixture refluxed for two and one-half hours. Half the solvent was removed and the material chilled. The product was recrystallized four times as follows: it was dissolved in a hot mixture of 75% carbon tetrachloride–25% ether, cooled and filtered. Then it was dissolved *immediately* in ether; failure to do so resulted in a product insoluble in ether. Just as solution was complete the product precipitated. It was removed by filtration and the process repeated. Twelve grams of amide gave 6.8 g. (43%) of product, m. p. 115–116°.

Anal. Calcd. for $C_{11}H_{14}O_3NSBr$: Br, 25.0; N, 4.38. Found: Br, 25.3, 25.0; N, 4.45, 4.44.

α-Bromo-α-*n*-butylsulfonylacetamide (III).—The mixture, without additional water, was heated for three-fourths hour and the solvent removed in twenty minutes. The oil was dissolved in alcohol, cooled and the product recrystallized once from benzene and twice from water. Nine grams of amide gave 5.75 g. (44%) of product, m. p. 130–131°. The procedure of Tröger and Hille[5] gave a 31% yield of the same material.

Anal. Calcd. for $C_6H_{12}O_3NSBr$: Br, 31.1; N, 5.45. Found: Br, 31.1, 31.0; N, 5.46, 5.50.

α-Bromo-α-*n*-butylsulfonyl-*n*-butyramide (IV).—The mixture with 2 ml. of water was refluxed for two hours and the solvent removed in twenty minutes. The oil was cooled and a seed crystal added. Seeding was also necessary in recrystallizing the product from ether. To obtain a seed crystal, a little of the oil was dissolved in ether and ligroin added to turbidity, then cleared with ether. The solution was allowed to stand open for three days, when the oil which first precipitated was crystallized. From 10.3 g. of the amide, 8.3 g. (58%) of product, m. p. 57–58°, was obtained. A mixed melting point with the product from the acid chloride was 56–58°.

Anal. Calcd. for $C_8H_{16}O_3NSBr$: Br, 27.9; N, 4.89. Found: Br, 27.7, 27.8; N, 4.74, 4.75.

α,α-Dibromo-α-*p*-tolylsulfonylacetamide (V).—The mixture without water but with 5.3 ml. of bromine was heated for two and one-half hours and the solvent removed in twenty minutes. The oil was taken up in alcohol and crystallized by cooling. It was then recrystallized from alcohol. The product from 10.7 g. of amide was 2.1 g. (11%), m. p. 134–135°.

Anal. Calcd. for $C_9H_9O_3NSBr_2$: Br, 43.1; N, 3.77. Found: Br, 43.3, 43.3; N, 3.65, 3.68.

α,α-Dibromo-α-*n*-butylsulfonylacetamide (VI).—This was obtained as a by-product in the preparation of III by the method of Tröger and Hille as mentioned above. The reaction mixture from 9 g. of α-*n*-butylsulfonylacetamide in 35 ml. of glacial acetic acid with 8 g. of bromine for one hour at room temperature was poured onto cracked ice and the III removed by filtration. The filtrate, after standing for three hours, gave a precipitate of VI which was recrystallized from dilute alcohol. The yield of VI was 1.8 g. (19%), m. p. 106–107°.

Anal. Calcd. for $C_6H_{11}O_3NSBr_2$: Br, 47.6; N, 4.17. Found: Br, 47.4, 47.6; N, 4.25.

Reactions of α-Bromo-α-sulfonylamides

With Sodium *n*-Butyl Mercaptide.—Four-tenths gram of sodium was dissolved in 30 ml. of absolute alcohol, and 1.7 ml. of *n*-butyl mercaptan added. This was cooled in a salt–ice-bath and a suspension prepared by dissolving 5.4 g. of II in 10 ml. of absolute alcohol and chilling, was added. The mixture was allowed to come to room temperature as the bath melted and then stand for five days.

The alcohol was evaporated to a small volume and the product poured onto chipped ice. The crystalline material was removed by filtration and recrystallized from water. The product was 2.45 g. (60%) of *α*-*p*-tolylsulfonyl-*n*-butyramide, m. p. 170–171°.

With Sodium *n*-Thiocresolate.—To 0.23 g. of sodium in 25 ml. of absolute alcohol was added 1.25 g. of *p*-thiocresol, then 2.85 g. (0.01 mole) of IV. The mixture was allowed to stand for five days and was then evaporated under reduced pressure until crystals separated. The residue was poured onto cracked ice, the product removed by filtration and recrystallized from alcohol. The product, 1 g. (80%), m. p. 45–46°, was ditolyldisulfide. Evaporation of the alcoholic and aqueous mother liquors gave, on recrystallization from water, 1.5 g. (73%) of *α*-*n*-butylsulfonyl-*n*-butyramide.[14]

This experiment was repeated using dioxane as a solvent and preparing the thiocresolate by the reaction of powdered sodium with *p*-thiocresol. There were isolated 0.75 g. (60%) of ditolyldisulfide, 0.72 g. (35%) of *α*-*n*-butylsulfonyl-*n*-butyramide and an oil from which nothing could be separated.

With Hydriodic Acid and with Hydrazine.—See Table I.

With Piperidine.—Six milliliters of piperidine dissolved in 10 ml. of dry dioxane was added to 6.25 g. of I dissolved in 40 ml. of dry dioxane and the mixture refluxed for seven hours. The crystalline precipitate was removed by filtration and washed with a little dioxane. The filtrate was evaporated to a smaller volume, removing both dioxane and piperidine, cooled and again filtered. The residue was washed with a little dioxane and added to the first one. The yield was 2.15 g. (60%) of piperidine hydrobromide,[15] m. p. 233–235°. Further evaporation of the filtrate resulted, on cooling and filtering, in a 2 g. (45%) yield of *α*-*p*-tolylsulfonylacetamide, m. p. 166–167°. Evaporation of this filtrate resulted in an oil from which nothing separated.

With Sodium Ethoxide.—To 50 ml. of absolute alcohol was added 0.23 g. of sodium. After the reaction was completed, the solution was cooled and 2.92 g. (0.01 mole) of I was added. The mixture was allowed to stand for two days at room temperature. Most of the alcohol was removed by distillation and a volume of water equal to the residue was added. On cooling and filtering 2.10 g. (84%) of *p*-tolylsulfonylmethyl bromide, m. p. 87–88°, was obtained. The identity of this compound was established by a mixed melting point with a sample prepared by a method to be described in a later paper.

To 25 ml. of absolute alcohol was added 0.23 g. of sodium. After the reaction was completed, the solution was cooled and 2.86 g. of IV was added. This was allowed to stand for four days, then most of the alcohol was evaporated, the residue poured into water and the mixture chilled. The resulting paste was recrystallized from alcohol and then water and gave 1.25 g. (61%) of *α*-*n*-butylsulfonyl-*n*-butyramide, m. p. 120–122°. The filtrates on evaporation gave a small quantity of oil.

TABLE I

REACTIONS OF *α*-BROMO-*α*-SULFONYLAMIDES

	With HI,[a] % Br		With H_2NNH_2[b] N_2 (ml.)			
Amide	Calcd.	Found	Calcd.	Found	Reaction time (hr.)	IX isolated %
I	27.4	28.2	44.8	45.0	5	82
II	25.0	24.3	39.5	39.0	4	87
III	31.1	32.2	47.5	46.5	2	80
IV	27.9	27.6	40.8	31.0	6	82
V	43.1	38.6	29.5[c]	30.0	1	83
VI	47.6	47.0	32.6[d]	33.0	1	47[d]

[a] Ten drops of 16 *N* sulfuric acid and 2 ml. of saturated potassium iodide solution were added to a solution of about 0.1 g. of the *α*-bromoamide in 15 ml. of glacial acetic acid. The flasks were stoppered and allowed to stand for thirty minutes with occasional shaking. The mixture was then titrated with 0.1 *N* sodium thiosulfate solution, using the disappearance of iodine color as an end-point and confirming by the addition of 0.5 ml. of 1% starch solution. Blanks were run in all experiments and, since they amounted to 10–15% of the total readings, the results reported are not considered to be quantitative. The data do show, however, that at least 90–95% of the total bromine in the compounds is able to oxidize hydriodic acid and that the observations of Tröger and Hille on the dibromo-*p*-tolylsulfonylacetamide were in error. [b] Except as otherwise indicated, about 1.00 g. of the *α*-sulfonyl-*α*-bromoamide was added to 15 ml. of water in a 50-cc. flask and a small tube containing 3.0 ml. of 10% hydrazine hydrate solution placed upright in the flask. This was then put in a water-bath at 75 ± 2°, allowed to come to this temperature, connected to a gas measuring apparatus, and the contents mixed. The mixture was kept at 75° and shaken occasionally until the evolution of nitrogen ceased. The contents of the flask were concentrated, chilled and the *α*-sulfonylamide removed by filtration, dried and weighed. [c] The sample weighed 0.45 g. [d] The sample weighed 0.50 g. The low recovery may be attributed to the difficulty of isolation of a rather small amount of a fairly soluble product.

With Nitrous Acid.[16]—To 5.4 g. of I dissolved in 50 ml. of alcohol–acetic acid (1:4) and kept cool, 2.6 cc. of *n*-butyl nitrite was added. The mixture was allowed to stand for twenty-four hours. Then hydrochloric acid was added and the mixture again allowed to stand for twenty-four hours; 80% of the bromoamide was recovered.

Addition of a solution of sodium nitrite to a solution of the bromoamide in acetic acid in the cold gave a 70% recovery. When the mixture was heated to 60° after one hour of standing the recovery was 85%.

Hydrolysis.—Two grams of I was sprinkled into 80 ml. of boiling 5% sodium hydroxide solution and the mixture boiled for two and one-half minutes. The material was chilled and filtered. The product was recrystallized from alcohol and yielded 0.78 g. (45%) of material melting at 89–90°. A mixed melting point with a sample of *p*-tolylsulfonylbromomethane (m. p. 90–91°) was 89–91°. This hydrolysis was carried out on the bromoamide pre-

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(14) These reactions are comparable to the formation of di-*p*-tolyldisulfide and tribenzoylmethane from the sodium salt of *p*-thiocresol and tribenzoylmethyl chloride as reported by Kohler and Potter, THIS JOURNAL, **58**, 2168 (1936).

(15) Similar dehalogenations have been observed frequently; for example, Cope, *ibid.*, **54**, 1250 (1932).

(16) These experiments were carried out in an attempt to convert the amides to *α*-bromoacids as additional confirmation of their structure.

pared from the bromoacid chloride as well as that from the bromination of the amide in carbon tetrachloride. No trace of the α-sulfonyl acid was observed when the filtrate from the reaction mixture was acidified. Addition of silver nitrate solution gave silver bromide, indicating some hydrolysis of the halide.

Into 50 ml. of boiling 5% sodium hydroxide solution was sprinkled 2.86 g. of IV. The mixture was boiled about five minutes until only a faint test for ammonia was obtained. It was then chilled, acidified with nitric acid and extracted with ether. The aqueous portion gave a heavy precipitate with silver nitrate, indicating a large removal of bromine. The ether extracts were evaporated and gave a small quantity of oil that did not solidify at −15°. The amount of oil was less than 1 ml.

Two grams of II was sprinkled into 50 ml. of boiling 5% sodium hydroxide solution. The material formed opaque globules and only traces of ammonia were evolved. The mixture was refluxed for five minutes, chilled and filtered. The entire residue was unchanged amide.

Summary

Compounds reported to be N-bromo-α-sulfonylamides by Tröger and Hille have been shown to be α-bromo-α-sulfonylamides. The most satisfactory method of preparation of α-bromo-α-sulfonylamides was by direct bromination of α-sulfonylamides in moist carbon tetrachloride. Members of this series were also prepared by direct bromination of the amides in glacial acetic acid and by bromination of α-sulfonyl acid chlorides, followed by reaction with ammonia. The reactions of α-bromo-α-sulfonylamides showed that the sulfone group was similar to other labilizing groups in causing hypohalite characteristics in α-halo derivatives.

PHILADELPHIA, PENNA. RECEIVED OCTOBER 26, 1939

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, CALCO CHEMICAL DIVISION, AMERICAN CYANAMID COMPANY]

The Polyhydric Alcohol–Polybasic Acid Reaction. V. The Glyceryl Succinate and Glyceryl Maleate Polyesters

BY R. H. KIENLE AND F. E. PETKE

Although the glycol succinate reaction has been studied in some detail, no quantitative data have been published for the glyceryl succinate and the glyceryl maleate polymerization reactions. Glyceryl succinate was first prepared by Van Bemmelen.[1] It has been referred to frequently in resin literature[2] but the only published quantitative data on the polyester seem to be those of Hönel.[3] No such data appear to have been published for glyceryl maleate. In the present investigation, data are presented for the formation of these polyesters, succinic acid and succinic anhydride being used to prepare glyceryl succinate, and maleic anhydride to prepare glyceryl maleate.

The apparatus and technique used have already been fully described.[4] The purification and chemical constants of the glycerol employed similarly have been given. The maleic anhydride used was American Cyanamid Company chemically pure material, redistilled. The succinic acid and succinic anhydride were the chemically pure grade of Selden Division, American Cyanamid Company. The glycerol–succinic acid reaction was carried out at 190° in order that the data might be comparable with the recently published glyceryl phthalate (acid) investigation. The glycerol–maleic anhydride and glycerol–succinic anhydride reactions were carried out at 160°, since the reactions proceeded too rapidly at 190°.

Experimental Data

The detailed data obtained for the glycerol–maleic anhydride, glycerol–succinic anhydride, and glycerol–succinic acid reactions are listed in Figs. 1, 2 and 3, respectively.

Figure 4 gives the acid value–water evolved relationship for all three reactions. When the theoretical acid value–water evolved curves are inserted in this plot, assuming only interesterification has occurred, it is found, in the case of glyceryl maleate, that the water evolved experimentally was at all times greater than theory, while in the case of both the glyceryl succinate reactions, the water evolved was at all times less than the theoretical. The equation for determining this theoretical relationship is

$$A_t = \frac{56.1(V_f - V_t)}{18(W - V_t)}$$

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(1) Van Bemmelen, *J. prakt. Chem.*, **69**, 84 (1856).

(2) Ellis, "The Chemistry of Synthetic Resins," Vol. I and II, Reinhold Publishing Corp., New York, N. Y.

(3) Hönel, *Paint Oil Chem. Rev.*, **91**, 19 (1931).

(4) Kienle, van der Meulen and Petke, THIS JOURNAL, **61**, 2258 (1939).