hot solution was filtered and, on cooling, 2.19 g. (79%) of light orange crystals separated, m. p. 151–155° with dec. Recrystallization from 5 cc. of dioxane yielded 1.79 g. (63%) of product which, after drying several days *in vacuo* over sulfuric acid, melted at 163–164° with dec.

*Anal.* Calcd. for $C_{24}H_{23}AsN_2O_3S$: C, 58.30; H, 4.69; N, 5.67; As, 15.15. Found: C, 58.29; H, 4.35; N, 5.54; As, 15.15.

**Tri-*p*-tolylarsinehydroxy-*p*-aminobenzenesulfonamide (X).**—This product was obtained by the above method in 63% yield, from tri-*p*-tolylarsine dihydroxide and sulfanilamide. The product was recrystallized from 10 cc. of dioxane and dried over sulfuric acid, then a day at 85°; m. p. 149–150° with dec.

*Anal.* Calcd. for $C_{27}H_{29}AsN_2O_3S$: C, 60.44; H, 5.45; N, 5.22. Found: C, 60.17; H, 5.42; N, 4.88.

**Tri-*o*-tolylarsinehydroxy-*p*-aminobenzenesulfonamide (XI).**—This compound was prepared from tri-*o*-tolylarsine dihydroxide and sulfanilamide; after recrystallization from dioxane and drying over sulfuric acid *in vacuo*, it melted at 186–187°.

*Anal.* Calcd. for $C_{27}H_{29}AsN_2O_3S$: C, 60.44; H, 5.45; N, 5.22; As, 13.96. Found: C, 60.20; H, 5.60; N, 5.07; As, 14.03.

**Triphenylarsinehydroxy-*p*-acetylaminobenzenesulfonamide (VIII).**—Triphenylarsine dihydroxide and $N^4$-acetylsulfanilamide condensed in boiling dioxane to yield 86% of product, m. p. 148–153° with dec. Recrystallization from dioxane yielded material of m. p. 158–159° with dec.

*Anal.* Calcd. for $C_{26}H_{25}AsN_2O_4S$: C, 58.21; H, 4.70; N, 5.22; As, 13.96. Found: C, 58.13; H, 4.71; N, 5.47; As, 14.25.

**Attempted Condensations: Tri-*p*-tolylarsine dihydroxide** and acetylsulfanilamide failed to condense in boiling dioxane: both starting materials were recovered. The reaction was also unsuccessful in acetic anhydride solution.

**Tri-*o*-tolylarsine dihydroxide** failed to condense with acetylsulfanilamide in boiling dioxane.

**Hydrolysis of Tri-*o*-tolylarsinehydroxy-*p*-acetylaminobenzenesulfonamide (IX).**—The compound was unchanged by heating on the steam-bath for thirty minutes in 5% sodium hydroxide.

A 0.5-g. sample was heated for thirty minutes on the steam-bath with 5% hydrochloric acid, which gave a clear solution. On standing overnight, large white crystals of tri-*o*-tolylarsine hydroxychloride (XIV), m. p. 222–225°, separated. This product was synthesized as described below. After neutralizing the filtrate from this compound with sodium hydroxide, a small amount of material was obtained by ether extraction and recrystallization from dilute alcohol. This was shown to be sulfanilamide by mixed m. p. determination with an authentic sample.

**Tri-*o*-tolylarsine Hydroxychloride (XIV).**—A suspension of 1.0 g. of tri-*o*-tolylarsine dihydroxide in 20 cc. of 5% hydrochloric acid was warmed on the steam-bath until solution was complete. After filtration and cooling a few drops of concentrated hydrochloric acid were added to promote crystallization; the product (0.88 g., 84%) separated as well-formed colorless crystals, m. p. 224–226°. This product was shown to be identical by mixed m. p. with that formed by hydrolysis of the arsinimine IX. The compound is only slightly soluble in cold water, very soluble in alcohol, and gives a positive test for chloride ion.

*Anal.* Calcd. for $C_{21}H_{22}ClAsO$: C, 62.93; H, 5.53; As, 18.69. Found: C, 61.94; H, 5.76; As, 18.32.

## Summary

1. Triphenylarsine and tri-*o*-tolylarsine have been condensed with $N^1$-potassiochloro-$N^4$-acetylsulfanilamide to yield the corresponding hydrated arsinimines, while tri-*p*-tolylarsine yields the unhydrated arsinimine.

2. Several triarylarsine dihydroxides (arsine oxide hydrates) have been condensed with sulfanilamide or $N^4$-acetylsulfanilamide to yield hydrated arsinimines.

3. Tri-*o*-tolylarsinehydroxy-*p*-acetylaminobenzenesulfonamide is much more stable to alkaline than to acidic hydrolysis; the latter leads to sulfanilamide and tri-*o*-tolylarsine hydroxychloride, which has been synthesized and characterized.

ROCHESTER, NEW YORK RECEIVED AUGUST 15, 1944

---

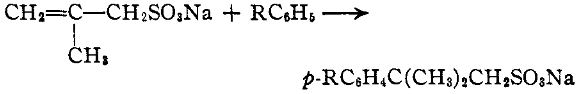
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

# The Condensation of Sodium 2-Methyl-2-propenesulfonate with Aromatic Hydrocarbons

BY S. ARCHER,[1] J. D. MALKEMUS[2] AND C. M. SUTER[1]

A convenient preparation and the proof of structure of sodium 2-methyl-2-propenesulfonate were presented in a previous paper.[3] In this communication there is described the reaction of this salt with aromatic hydrocarbons.

The catalytic alkylation of aromatic substances with olefinic compounds has been thoroughly investigated in recent years. Catalysts which have been used successfully to effect such condensations include aluminum chloride, sulfuric acid, boron fluoride and hydrogen fluoride.[4,5] It has now been found that the reaction



$$CH_2{=}\underset{\substack{|\\ CH_3}}{C}{-}CH_2SO_3Na + RC_6H_5 \longrightarrow p\text{-}RC_6H_4C(CH_3)_2CH_2SO_3Na$$

may be carried out in the presence of sulfuric acid or, better, with boron fluoride–sulfuric acid as the condensing agent.

Thus, when a suspension of sodium 2-methyl-2-propenesulfonate in excess toluene is stirred with sulfuric acid at low temperatures, there may be

---

(1) Present address: Winthrop Chemical Company, Inc., Rensselaer, N. Y.

(2) Present address: Colgate-Palmolive-Peet Company, Jersey City, N. J.

(3) Suter, Malkemus and Archer, THIS JOURNAL, 63, 1594 (1941).

(4) Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Company, New York, N. Y., 1941.

(5) Ipatieff, Pines and Schmerling, *J. Org. Chem.*, 5, 253 (1940), give a sizable bibliography.

isolated in fair yield the expected product, sodium 2-(*p*-tolyl)-2-methylpropanesulfonate. When higher hydrocarbons are used the yields of purified material fall off rather sharply. The contamination of the condensation product with sodium sulfate, formed by neutralization of the catalyst, and with aromatic sulfonic acids formed by direct sulfonation, is partly responsible for the purification difficulties. Another factor which affects the yield is the insolubility of the olefin sulfonic acid in the aromatic hydrocarbon.

By using an amount of sulfuric acid just in excess of that necessary to convert the sodium salt to the free sulfonic acid and then bubbling boron fluoride into the rapidly-stirred reaction mixture, the yields of condensation product are markedly improved in the case of the lower alkylbenzenes. However, the higher members of the series react very poorly or not at all.

At this point our attention was directed to finding a suitable reaction medium for the condensation. This was important for two reasons: first, to improve the yield if possible and second, to conserve the higher alkylbenzenes which were available in limited quantities.

It was found that chloroform was a good solvent and that 1,1,2-trichlorethane, methylchloroform and methylene chloride were only fair. Ethylene chloride proved to be the most effective; the results are summarized in Table I. It was noted that in the case of *t*-amylbenzene a higher reaction temperature decreased rather than increased the yield of desired product. This is undoubtedly caused by the poorer solubility of the catalyst at this higher temperature.

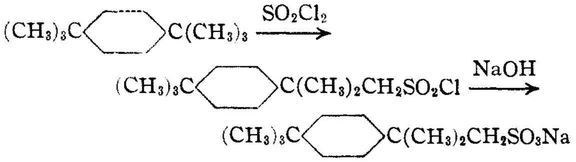
Table I

2-(Alkylphenyl)-2-methylpropanesulfonic Acids[a]

| Alkyl-benzene | Yield, % of sodium salt | Anal. sodium salt, % Na Calcd. | Anal. sodium salt, % Na Found | M. p. B. T.[b] salt, °C. | Anal. B. T.[b] salt, % N Calcd. | Anal. B. T.[b] salt, % N Found |
|---|---|---|---|---|---|---|
| Methyl | 73 | 9.19 | 9.11 | 159.5–160.3 | 7.13 | 7.09 |
| Ethyl | 77 | 8.70 | 8.76 | 135–137 | 6.90 | 6.64 |
| *n*-Propyl[c] | 61 | 8.28 | 7.47 | 89–91 | 6.67 | 6.43 |
| Isopropyl[c] | 30 | 8.28 | 7.74 | 145–147 | 6.67 | 6.85 |
| *n*-Butyl | 47 | 7.87 | 7.97 | 142–143 | 6.42 | 6.31 |
| *t*-Butyl | 55 | 10.93[d] | 10.86 | 196.5–197.5 | 6.42 | 6.19 |
| *t*-Amyl | 85 | 7.57 | 7.87 | 151–152 | 6.25 | 6.41 |
| *n*-Hexyl | 52 | 7.18 | 6.82 | 126–127 | 6.06 | 6.37 |
| *n*-Octyl | 48 | 6.61 | 6.57 | 115–117 | 5.80 | 6.64 |
| *n*-Decyl | 38 | 6.11 | 6.08 | 124–125 | 5.48 | 5.39 |
| *n*-Undecyl | 44 | 5.90 | 5.66 | 125–127 | 4.94 | 5.08 |
| *n*-Tridecyl | 48 | 5.48 | 5.08 | 124–125[e] | 4.80 | 4.90 |

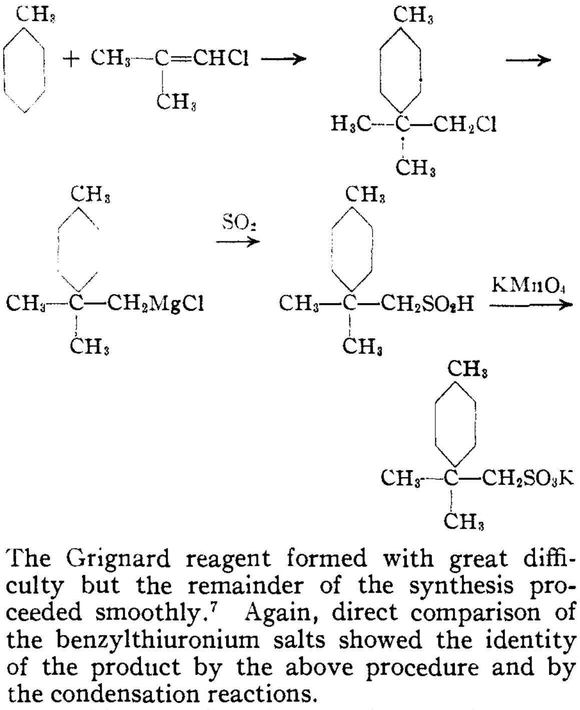
[a] All reactions listed in this table were run in ethylene chloride except where otherwise noted. [b] B. T. is benzylthiuronium salt. [c] No solvent was used. [d] Sulfur analysis. [e] *p*-Chlorobenzylthiuronium salt.

The structures of the condensation products were proved by two independent methods. Since all the aliphatic hydrogens are equivalent in di-*t*-butylbenzene, it was thought that the application of Kharasch's photosulfonation procedure[6] would yield a compound identical with that obtained from *t*-butylbenzene and sodium 2-methyl-2-propenesulfonate according to the following equations



The products from both the sulfonation and condensation reactions showed the same solubility behavior (sodium salts insoluble in water), and the benzylthiuronium salts were identical as shown by mixed melting points.

Potassium 2-*p*-tolyl-2-methylpropanesulfonate was synthesized by the following procedure



The Grignard reagent formed with great difficulty but the remainder of the synthesis proceeded smoothly.[7] Again, direct comparison of the benzylthiuronium salts showed the identity of the product by the above procedure and by the condensation reactions.

The identification of the various products was greatly facilitated by the fact that nearly all the compounds formed crystalline benzylthiuronium salts on treatment with a solution of benzylthiuronium chloride. Although the derivatives tended to form hydrates and some melted close to each other, they proved invaluable for direct comparison of compounds formed by the various procedures.

## Experimental

**Preparation of Materials.**—Sodium 2-methyl-2-propenesulfonate was made by the previously described procedure. The higher monoalkylbenzenes containing an even number of carbon atoms were prepared by reduction of the corresponding phenones.[8] The straight chain odd-

---

[6] Kharasch and Read, This Journal, **61**, 3089 (1939).

[7] *Cf.* Kharasch and Brown, *ibid.*, **61**, 2148 (1939), report in a footnote that *β*-chloro-*t*-butylbenzene reacts with magnesium very slowly.

[8] Myristophenone was prepared in 81% yield from myristoyl chloride and excess benzene in the presence of aluminum chloride. After crystallization from ligroin it melted at 50–52° and gave a semi-

carbon members of the series were prepared from the action of the proper Grignard reagent on benzaldehyde followed by dehydration of the carbinol and reduction of the olefin thus formed. The lower homologs were prepared by conventional methods.

### Procedures for the Condensation Reactions

A. **Sulfuric Acid.**—A mixture of one mole of the hydrocarbon, 26 cc. of 96% sulfuric acid and 20 g. of sodium 2-methyl-2-propene-sulfonate was stirred at 0° for five hours. The organic liquid was removed by decantation and the residue neutralized with sodium hydroxide solution. The solution was then evaporated to dryness. The salts were thoroughly extracted with boiling alcohol. On cooling the desired product crystallized.

**B. Boron Fluoride: Preparation of Sodium 2-*p*-Ethylphenyl-2-methylpropanesulfonate without Solvent.**—Eighty-five milliliters of ethylbenzene was mixed with 5 ml. of 96% sulfuric acid and 10 g. of sodium 2-methyl-2-propenesulfonate and stirred for several minutes. Boron fluoride was then bubbled through the stirred mixture for about one-half hour. The temperature rose from 25 to 41° during the course of the addition of the catalyst and then fell. After stirring for an additional two hours, the reaction mixture was aerated to remove the boron fluoride. Dilute sodium hydroxide was added to neutralize the acids and after removal of the hydrocarbon the aqueous solution was taken to dryness. Extraction of the salts with hot alcohol gave 7.7 g. of shiny plates of the desired condensation product.

**Preparation of Sodium 2-*p*-Decylphenyl-2-methylpropanesulfonate with a Solvent.**—After stirring a mixture of 100 ml. of ethylene chloride, 45 ml. of *n*-decylbenzene, 5 ml. of 96% sulfuric acid and 10 g. of sodium 2-methyl-2-propenesulfonate for about one-half hour, boron fluoride was bubbled slowly through the mixture for the same length of time. After stirring for two additional hours the desired product was isolated as immediately above.

**Preparation of 2-Methyl-2-*p*-tolylpropyl Chloride.**—Twenty-three grams (0.25 mole) of isocrotyl chloride was slowly added to a well-stirred mixture of 50 ml. of 96% sulfuric acid and 125 ml. of dry toluene over a period of one-half hour. After one hour more the mixture was poured onto ice-water, the oil removed and the water shaken with ether. After shaking with dilute sodium hydroxide and drying, the organic layers were distilled. The product which weighed 34 g. boiled at 118–119° (17 mm.). The yield was 76% of the theoretical.

**Preparation of Potassium 2-Methyl-2-*p*-tolylpropanesulfonate.**—A Grignard reagent was prepared from 30 g. of the halide and 4.5 g. of magnesium in 150 ml. of dry ether. Iodine and a few ml. of a solution of amylmagnesium bromide were needed as catalysts to prepare the reagent. The passage of dry sulfur dioxide over the surface of the ether for one-half hour caused a heavy precipitate to separate. This complex was decomposed with dilute sulfuric acid. The ether layer was removed on the steam-bath and the residue then taken up in dilute sodium hydroxide. The basic solution was shaken with ether and then acidified. The sulfinic acid that had separated was taken up in ether and dried. The residue after removal of solvent weighed 22.5 g.

The acid was dissolved in 50 ml. of water containing 5.8 g. of potassium hydroxide and then added with stirring to a dilute solution of 12.6 g. of potassium permanganate. When the addition was complete the mixture was warmed on the steam-bath for an hour to complete the oxidation. After filtration the filtrate was evaporated to dryness and the residue extracted with boiling alcohol. The liquors deposited 23 g. of the potassium salt. The yield was 52% of the theoretical based on the propyl chloride. .

A portion of the above compound was converted to the benzylthiuronium salt which melted at 153–154.5° after two recrystallizations from alcohol. It did not depress the melting point of the derivative of the material prepared by the condensation reaction.

**Photosulfonation of *p*-Di-*t*-butylbenzene.**—To a solution of 36 g. of the hydrocarbon in 150 cc. of benzene containing 0.5 cc. of pyridine (C. P.) there was added dropwise 19 cc. of redistilled sulfuryl chloride. The stirred solution was illuminated with a 200-watt bulb kept 6 inches away from the flask. After ten hours the reaction appeared to be over. Half the solvent was removed and 20 g. of sodium hydroxide in 150 cc. of water was added and the mixture refluxed with stirring for one-half hour. The heavy precipitate was filtered, washed with ether and dried. Thirty-nine grams of salt was formed. It was recrystallized from ethanol and converted to its benzylthiuronium salt which melted, when pure, at 195–197°. A mixed melting point with the salt obtained from the boron fluoride reaction showed no depression.

## Summary

1. A procedure has been developed for condensing sodium 2-methyl-2-propenesulfonate with alkylbenzenes.

2. An independent synthesis of potassium 2-*p*-tolyl-2-methylpropanesulfonate from 2-*p*-tolyl-2-methylpropyl chloride via the Grignard reagent and sulfinic acid is presented.

3. Sodium 2-*p*-*t*-butylphenyl-2-methylpropanesulfonate was synthesized by chlorosulfonating *p*-di-*t*-butylbenzene and hydrolyzing the sulfonyl chloride derivative thus formed.

EVANSTON, ILLINOIS RECEIVED FEBRUARY 10, 1944

---

carbazone which melted at 97.8–98.4° (corr.) after two recrystallizations from ethanol. Since this melting point is considerably higher than that reported by Sabatier (*C. A.*, **8**, 2673 (1914)), it was analyzed. *Anal.* Calcd. for $C_{21}H_{33}N_3O$: N, 12.16. Found: N, 12.23.