peatedly at 80 to 55° there was finally obtained 54 g. of pure *d*B*d*A salt. The intermediate crops were not further fractionated since this base can be much more easily resolved by means of *d*-camphoric acid.[1d]

***d*-α-*p*-Tolylethylamine-*d*-α-bromocamphor-π-sulfonate.**—This salt crystallized as monohydrate in transparent prisms; solubility 2.12 g. per 100 g. of water at 25°; m. p. (anhydrous) 165° (corr.).

Anal. Calcd. for $C_{19}H_{28}O_4NSBr \cdot H_2O$; H_2O, 3.87. Found: H_2O, 3.89.

Rotation. Subs., 0.9280 g. (hydrated) made up to 50 cc. in water gave $[\alpha]_D^{25}$ +2.32° in 2 dm.; $[\alpha]_D^{25}$ +62.5°, $[M]_D$ +290°(10)².

***dl*-α-*p*-Tolylethylamine-*dl*-α-bromocamphor-π-sulfonate.**—This salt was prepared from the inactive components. It first separated as an oil, which solidified. It crystallized from water in anhydrous needles, m. p. 161° (corr.). The solubility was 3.38 g. per 100 g. of water at 25°.

Summary

1. The resolution of *dl*-mandelic acid by an improvement of the method of Smith[6] has been described.

2. All of the stable isomeric mandelates and α-bromocamphor-π-sulfonates of α-phenylethylamine and α-*p*-tolylethylamine have been described and classified according to their stabilities and relative solubilities.

3. The significance of these factors for the separation of mixtures of optically isomeric salts has been discussed.

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The Acetoacetic Ester Condensation. IV. The Reaction Product of Certain Aliphatic Esters and Sodium Ethoxide

BY JOHN M. SNELL AND S. M. MCELVAIN

During the course of a study of the reaction of metallic sodium on various aliphatic esters[1] a product, which from its boiling point and method of isolation was thought at first to be ketene acetal,[2] was obtained in a small yield from the reaction of sodium and ethyl acetate in absolute ether. Further investigation of this product, however, showed it to be merely a mixture of alcohol and xylene. The latter compound had been used to powder the sodium for the reaction and, presumably, had not been completely removed from the metal by ether washing, for in subsequent experiments when the powdered sodium, after decantation of the xylene, was washed more thoroughly with ether no product was obtained at the point

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(1) Snell and McElvain, THIS JOURNAL, **53**, 750 (1931); John M. Snell, Ph.D., Thesis, University of Wisconsin, 1932.

(2) (a) Scheibler and Zeigner, *Ber.*, **55**, 801 (1922); (b) Scheibler and Marhenkel, *Ann.*, **458**, 15 (1927).

where ketene acetal should appear. It was decided then to attempt the preparation of a ketene acetal by the improved method described by Scheibler, Marhenkel and Nikolic.[3] Several attempts, in which the directions of these authors were followed in every detail, to duplicate this preparation were unsuccessful.

In the view of these failures to obtain ketene acetal it seemed advisable to examine Scheibler's so-called "primary reaction product," *i. e.*, the residue left after evaporation of the ester and ether from the sodium ethoxide. This was done using ethyl acetate and ethyl isobutyrate as representative esters.

Experimental Part

Materials Used.—The sodium ethoxide was prepared as recommended by Scheibler, Marhenkel and Nikolic[3] by treating powdered sodium under ether with the theoretical amount of absolute alcohol. The product obtained was white and granular and contained 33.75% Na; calcd. for C_2H_5ONa, 33.80. The ether and esters were purified by washing with water, drying over calcium chloride (in the case of ether) or potassium carbonate (in the cases of the esters). Each of these materials was then allowed to stand over phosphorus pentoxide for twenty-four hours and then distilled directly from this reagent.

An Attempted Preparation of Ketene Acetal.—The following procedure describes in detail a representative attempt to prepare ketene acetal from ethyl acetate and sodium ethoxide according to the procedure described in the literature.[3] Twenty-three grams (1 atom) of sodium was finely powdered in a 1-liter round-bottomed flask by shaking under heated xylene. After cooling and decantation of the xylene the powdered metal was washed thoroughly with four or five portions of absolute ether, and then covered with 500 cc. of fresh ether. A reflux condenser was fitted to the flask and 50 g. (1.1 mole) of absolute alcohol was slowly run in from a dropping funnel at the top of the condenser. The reactants were protected by calcium chloride tubes from atmospheric moisture. After all the alcohol had been added the mixture was allowed to stand for fifteen hours or longer. Then 200 g. (2.2 moles) of ethyl acetate was added. At this point cooling the flask, as recommended by the original investigators,[3] was unnecessary as no perceptible heat was generated. The mixture was allowed to stand with occasional shaking for twenty-four hours, and then was poured into a shallow dish and placed in an empty vacuum desiccator. The volatile substances were removed by evacuation with a water pump, a calcium chloride tower being interposed to prevent backward diffusion of water vapor. The dry residue (which generally weighed 90–100 g. as compared to 125 g., the weight of reaction product obtained by the original investigators[3]) was scraped from the walls of the dish and the desiccator, pulverized in a porcelain mortar, and triturated with 125 g. of ice water. The resulting solution was extracted with ether in a continuous extraction apparatus[4] for twelve hours, the solvent vapors passing through a 25-cm. spiral Widmer column on the return path to the extraction vessel. The ether solution was shaken intermittently for three or four hours with three successive portions of powdered calcium chloride and then washed with a small volume of a saturated solution of calcium chloride. After standing overnight with anhydrous sodium sulfate the ethereal extract was distilled through the Widmer fractionating column mentioned above. It all passed over at 34–35°. Ketene acetal was reported[3] as boiling at 77–78°.

Preparation of the "Primary Reaction Product" from Ethyl Acetate.—Seventeen

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[3] Scheibler, Marhenkel and Nikolic, *Ann.*, **458**, 28 (1927).

[4] "Organic Syntheses," 1923, Vol. III, p. 88.

grams (0.25 mole) of sodium ethoxide (33.75% Na), under 200–225 cc. of dry ether was treated with 55 g. (0.625 mole) of ethyl acetate and the mixture allowed to stand in a stoppered flask under nitrogen for a period of two to three days with occasional shaking. The ether and ester were then evaporated off under reduced pressure and the residue allowed to stand in a vacuum desiccator over sulfuric acid until it attained a constant weight.

Method of Examination.—The sodium content of the reaction product was determined in the following manner. A sample of approximately 0.25 g. was accurately weighed into a tared porcelain crucible and treated with 0.2 cc. of concentrated sulfuric acid added from a graduated 1-cc. pipet. The crucible was heated gently until most of the volatile matter was expelled and then ignited for thirty minutes in the full flame of a Bunsen burner. The residue was weighed as Na_2SO_4.[5]

In the case of ethyl acetate the only other constituent of the reaction product determined was the sodium derivative of acetoacetic ester. This was estimated by adding about 1 g. of the reaction product to 10 g. of ice, acidifying the resulting solution with acetic acid and extracting with ether. The ether extract was washed until neutral with sodium bicarbonate solution and then made up to 100 cc. with 95% alcohol. A 10-cc. aliquot was treated with 4 drops of a 10% ferric chloride solution and the color compared in a Duboscq colorimeter with that produced by a standard solution of acetoacetic ester in 95% alcohol. This method is accurate to 2–3% if the following precautions are observed, (a) the solutions being compared should be of about the same concentration, (b) the same amount of ferric chloride should be added to equal volumes of the two solutions, (c) the comparisons should be made as soon as possible after the addition of the ferric chloride. A rather imperfect check on this method of estimation was the determination of the amount of 1-*p*-nitrophenyl-3-methyl-5-pyrazolone[6] obtained from an aliquot of the acetoacetic ester solution by the action of *p*-nitrophenylhydrazine. This value was about 70% of that obtained by the colorimetric estimation.

Preparation of the Primary Reaction Product from Ethyl Isobutyrate.—To 6.8 g. (0.1 mole) of sodium ethoxide under 90 cc. of ether was added 29 g. (0.25 mole) of ethyl isobutyrate, and the procedure described above for ethyl acetate followed. In the case of ethyl isobutyrate, however, it was necessary to heat the residue from the evaporation of the ether and ester to a temperature of 100° on a steam-bath for one hour under diminished pressure in order that the excess ester might be completely removed and the residue attain constant weight.

A reaction product was also prepared from ethyl isobutyrate by heating 6.8 g. of sodium ethoxide with 29 g. of the ester alone on a steam-bath for twenty-four to forty-eight hours. The ester was removed by distillation and the residue heated for three hours at 100–150° under diminished pressure. During the distillation of the ester and the heating of the residue the side arm of the receiving flask was connected to a coil condenser cooled in a mixture of ether and solid carbon dioxide. About 1 g. of a mixture of alcohol and ethyl isobutyrate was condensed in this trap.

In addition to the determination of the sodium content of the reaction product, the amount of sodium isobutyrate present was estimated by treating a 5–7 g. sample of the dry reaction product with 50 cc. of water, acidifying with phosphoric acid and distilling the isobutyric acid. This distillate was then titrated with standard alkali. The identity of the isobutyric acid was established by converting it into the *p*-phenylphenacyl ester by the method of Drake and Bronitsky.[7] This ester, which has not been described previously, melts at 88.5°. Calcd. for $C_{18}H_{18}O_3$: C, 76.60; H, 6.38. Found: C, 76.61; H, 6.38.

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[5] *Cf.* Adickes, *Ber.*, **60**, 274 (1927).

[6] Altschul, *ibid.*, **25**, 1853 (1892).

[7] Drake and Bronitsky, THIS JOURNAL, **52**, 3715 (1930).

The results which were obtained from the examination of the various reaction products, prepared as described above, are summarized in the table. The values of sodio-acetoacetic ester in column 5 are calculated from the colorimetric estimation of acetoacetic ester and the percentages of sodium isobutyrate in column 6 are calculated from the amount of isobutyric acid found by titration. The corresponding values for sodium acetate were not determined. Column 7 represents the calculated percentage of sodium which would be present in the reaction product if it consisted only of the product determined (sodio-acetoacetic ester or sodium isobutyrate) and sodium ethoxide.

ANALYSES OF THE REACTION PRODUCTS FROM ETHYL ACETATE AND ISOBUTYRATE WITH SODIUM ETHOXIDE

Run	Ester ethyl	Solvent	Total % Na in reaction product	% Na acetoacetic ester in reaction product	% RCOONa in reaction product	Total % Na calcd. as $NaOC_2H_5$ and determined component
1	Acetate	Ether	30.24	12.0	?	31.56
2	Acetate	Ether	32.35	5.5	?	32.77
3	Isobutyrate	Ether	33.50	...	0.50	33.74
4[a]	Isobutyrate	None[c]	32.90	...	6.8	32.92
5[b]	Isobutyrate	None[c]	32.80	...	6.5	32.96
6[a]	Isobutyrate	None[c]	32.80	...	5.2	33.10
7[a]	Isobutyrate	None[c]	32.80	...	6.6	32.84

[a] Allowed to react twenty-four hours at 100°. [b] Allowed to react forty-eight hours at 100°. [c] Excess of ester used in these runs.

Discussion of Results

The failure to obtain ketene acetal from the reaction of sodium ethoxide and ethyl acetate in this work must be due to one of the following causes: (a) the present authors do not possess the manipulative skill necessary for the isolation of such a compound, (b) the directions of the original investigators[3] are not sufficiently precise, or (c) the compound in question is not formed in the reaction. Further work along this line by other investigators should show which of these alternatives is responsible for the present disagreement of results. In this connection it should be noted that Arbusow[8] has recently reported his failure to duplicate Scheibler's preparation of carbon monoxide acetal.

It is seen from the data in the above table that in the case of ethyl acetate the values for the sodium content of the reaction product calculated on the assumption that it contains only sodio-acetoacetic ester and sodium ethoxide are only slightly higher than those actually found. This difference is due, in all probability, to small amounts of sodium acetate which were not determined because of the complication introduced by the presence of the acetoacetic ester. With ethyl isobutyrate, however, the absence of the β-keto ester makes possible the accurate determination of

(8) Arbusow, *Ber.*, **64**, 698 (1931).

the isobutyric acid in the reaction product. The very close agreement between the calculated values of column 7 and the found values in column 4 definitely shows that these reaction products are simply sodium ethoxide mixed with a small amount of sodium isobutyrate.[9]

These data also confirm the contention made by Adickes[10] in a recent publication that such esters as ethyl acetate and isobutyrate form no stable, isolable compounds with sodium ethoxide. That there is no ester, either combined or adsorbed, in the reaction product from ethyl isobutyrate is shown not only by the above analyses but also by the fact that careful fractionation of the ester which was removed from the reaction product during its preparation gave small amounts of lower boiling fractions consisting of a mixture of ester and alcohol and which contained quantities of alcohol (estimated from the saponification value) approximately equivalent to the sodium isobutyrate present in the reaction product. No product other than alcohol and the ester could be found in these lower boiling fractions.

On the basis of these results it seems safe to conclude that the "primary reaction product" (which contains 11.6% Na when derived from ethyl acetate) postulated by Scheibler and co-workers[11] as an intermediate for both the acetoacetic condensation and ketene acetal formation, does not exist. Earlier evidence has been submitted[12] that the precursor, an ester enolate ($RCH{=}C(ONa)OC_2H_5$), of this intermediate is not formed by the action of sodium ethoxide on such esters. The data for ethyl acetate do not absolutely preclude the presence of a small amount of such an intermediate in the reaction product, but in the case of ethyl isobutyrate the data definitely do indicate the absence of such a compound. Consequently, the claim that ethyl isobutyrate undergoes a reaction with sodium ethoxide to form such a reaction product and that this product is converted by hydrolysis into the corresponding ketene acetal[13] cannot be reconciled with the data presented in the present paper.

Summary

All attempts to prepare a ketene acetal by the directions given by Scheibler and co-workers have been uniformly unsuccessful.

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(9) The manner in which the sodium salt of the acid was formed is unknown. It may have resulted from traces of moisture present in the ester or entering the reaction mixture during the course of the reaction, although this hardly seems likely in view of the precautions which were taken to exclude moisture. Scheibler [*Ber.*, **65**, 998 (1932)] has reported the formation of sodium benzoate from the reaction of ethyl benzoate and sodium ethoxide, thus $C_6H_5COOC_2H_5 + C_2H_5ONa \longrightarrow C_6H_5COONa + C_2H_5OH + C_2H_4$. It is possible that a similar reaction is responsible for the sodium isobutyrate obtained in the present work. However, for the purpose of the present discussion the origin of this product is immaterial.

(10) Adickes, *Ber.*, **65**, 522 (1932).

(11) Scheibler and Marhenkel, *Ann*, **458**, 5 (1927).

(12) McElvain, THIS JOURNAL, **51**, 3124 (1929).

(13) Scheibler and Friese, *Ann.*, **445**, 149 (1925); Scheibler and Marhenkel, *Ann.*, **458**, 14 (1927). However, these authors do not describe the properties of this particular ketene acetal.

An examination of the dry, solid residues remaining after the reaction of ethyl acetate and ethyl isobutyrate with sodium ethoxide has been made and from the results obtained the conclusion is drawn that the so-called "primary reaction product" postulated by Scheibler as the intermediate in the acetoacetic ester condensation and ketene acetal formation does not exist.

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Notes

Aryl *p*-Bromobenzenesulfonates as Derivatives for the Identification of Phenols

BY VLADIMIR C. SEKERA

In connection with the work on the higher alkyl sulfonates[1] one or two aryl esters were prepared. These beautifully crystalline compounds were so readily prepared and so easily purified that further examples were characterized in order to show their value as derivatives for identification of phenols.

The general method of preparation consisted of mixing equimolecular quantities of the phenol and *p*-bromobenzenesulfonyl chloride with about four equivalents of pyridine and stirring the mixture for about three hours at 15° or lower. With small quantities, less time was needed for the reaction. The reaction mixture was decomposed with ice water containing enough dilute hydrochloric acid to combine with the pyridine. The aryl sulfonate was collected on a Buchner funnel and air dried. One recrystal-

TABLE I

SOME ARYL *p*-BROMOBENZENESULFONATES

Phenol	Yield, %	M. p., °C.	Anal., % Br Calcd.	Found
Phenol	86	115.5	25.5	25.5
α-Naphthol	81	104	22.0	21.9
β-Naphthol	69	151–152	22.0	22.4
o-Cresol	75	78–79	24.4	24.6
m-Cresol	74	69–70	24.4	24.3
p-Cresol	76	100	24.4	24.5
o-Nitrophenol	70	97–98	22.3	22.6
m-Nitrophenol	70	108–109	22.3	22.4
p-Nitrophenol	69	112	22.3	22.6
o-Bromophenol	57	125	40.8	41.0
Thymol	71	103.5	21.6	21.5
Gualacol	61	103–104	23.3	23.6
2,4,6-Tribromophenol	85	139–140	58.1	58.4

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[1] Sekera and Marvel, THIS JOURNAL, 55, 345 (1933).