anol the product crystallized as long white needles; m. p. 75–76°.

Anal. Calcd. for $C_{12}H_{13}N$: C, 84.16; H, 7.65. Found: C, 83.8; H, 7.31.

Summary

1. 4,4-Dimethyl-1-keto-1,4-dihydronaphthalene and 2-bromo-4,4-dimethyl-1-keto-1,4-dihydronaphthalene have been prepared and rearranged in the presence of sulfuric acid to 3,4-dimethyl-1-naphthol and 2-bromo-3,4-dimethyl-1-naphthol, respectively.
2. These reactions are regarded as typical pinacol type rearrangements.
3. Further work to establish this point more conclusively is now in progress.

MINNEAPOLIS, MINNESOTA RECEIVED APRIL 29, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Metalations of Diphenylmethane and Related Compounds by Potassium Amide. Condensations with Carbonyl Compounds[1]

BY ROBERT S. YOST[2] AND CHARLES R. HAUSER

Diphenylmethane has been metalated by potassium amide in a mixture of liquid ammonia and ether according to the equation

$$(C_6H_5)_2CH_2 + KNH_2 \rightleftarrows (C_6H_5)_2CHK + NH_3$$

Although certain condensations have been effected fairly satisfactorily in this medium, the diphenylmethane is probably not completely metalated since this hydrocarbon appears to be only a slightly stronger acid than ammonia.[3] However, essentially complete metalation has been realized by driving off the ammonia leaving the diphenylmethylpotassium suspended in ether.[4] Carbonation of the ether suspension with excess Dry Ice has given a 90% yield of diphenylacetic acid.[5]

$$(C_6H_5)_2CHK \xrightarrow[+HCl]{CO_2} (C_6H_5)_2CHCO_2H$$

This method of preparation of diphenylacetic acid appears more convenient than those described previously.[6]

Diphenylmethylpotassium in ether suspension has been carbethoxylated with ethyl carbonate to form ethyl diphenylacetate; this reaction is accompanied by the metalation of the product by part of the diphenylmethylpotassium thereby regenerating the corresponding amount of diphenylmethane.

$$(C_6H_5)_2CHK \xrightarrow{(C_2H_5O)_2CO} (C_6H_5)_2CHCO_2C_2H_5 \xrightarrow{(C_6H_5)_2CHK} [(C_6H_5)_2CCO_2C_2H_5]K$$

With two molecular equivalents of diphenylmethylpotassium to one of ethyl carbonate the yield of ethyl diphenylacetate was 52%. Since half of the diphenylmethane was theoretically recoverable, this yield may be based on the hydrocarbon as well as on the ethyl carbonate. That ethyl diphenylacetate is metalated by part of the diphenylmethylpotassium is shown by the fact that if the reaction mixture is treated with benzoyl chloride, the corresponding β-keto ester is obtained.

$$[(C_6H_5)_2CCO_2C_2H_5]K \xrightarrow{C_6H_5COCl} C_6H_5COC(C_6H_5)_2CO_2C_2H_5$$

The 52% yield of ethyl diphenylacetate corresponds to only 26% conversion of diphenylmethane to the ester. A higher conversion (32%) of the hydrocarbon to the ester has been realized by carrying out the reaction in the presence of excess potassium amide which presumably then metalates the ester. Diphenylmethylpotassium may be carbethoxylated in a mixture of liquid ammonia and ether although the yields have been lower than when an ether suspension of the reagent is used. Diphenylmethylsodium also may be carbethoxylated in a mixture of liquid ammonia and ether.

Although the carbethoxylation of diphenylmethylpotassium is fairly satisfactory, a better over-all yield (77%) of ethyl diphenylacetate from diphenylmethane has been obtained by first carbonating the diphenylmethylpotassium and esterifying the resulting acid.

Diphenylmethylpotassium has been benzoylated with methyl benzoate to form α,α-diphenylacetophenone which presumably was metalated by part of the diphenylmethylpotassium.

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[1] Paper XXXIX on "Condensations"; paper XXXVIII, THIS JOURNAL, **69**, 295 (1947).

[2] Eli Lilly Fellow, 1946–1947.

[3] See Morton, *Chem. Rev.*, **35**, 14 (1944).

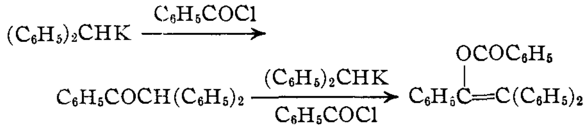
[4] Like potassium amide, sodium amide metalates diphenylmethane in a mixture of liquid ammonia and ether but the diphenylmethylsodium is destroyed when the ammonia is driven off; this is indicated by the disappearance of the characteristic orange-red color of the diphenylmethyl ion and by the fact that carbonation of the resulting ether suspension gives no diphenylacetic acid. A similar difference in stability between the potassium and sodium derivatives of triphenylmethane has been observed; Kraus and Rosen, THIS JOURNAL, **47**, 2739 (1925); Levine, Baumgarten and Hauser, *ibid.*, **66**, 1230 (1944).

[5] Lower yields of diphenylacetic acid have been obtained on carbonation of toluene suspensions of diphenylmethylpotassium; the yield was 42% when the suspension was first stirred for four hours at room temperature and only 26% when it was heated on the steam-bath.

[6] A 70% yield of diphenylacetic acid has been reported (I. G. Farbenind, A.-G., German Patent 671,098; *C. A.*, **33**, 3391 (1939)) from the metalation of diphenylmethane by phenylsodium followed by carbonation. The preparation of diphenylacetic acid described in "Organic Syntheses," Coll. Vol. I, 224 (1941), involves the reduction of benzilic acid.

$$(C_6H_5)_2CHK \xrightarrow{C_6H_5CO_2CH_3} C_6H_5COCH(C_6H_5)_2 \xrightarrow{(C_6H_5)_2CHK} [C_6H_5COC(C_6H_5)_2]K$$

Similar to the carbethoxylation, the use of two equivalents of diphenylmethylpotassium to one of methyl benzoate has given the best yield (55%) of the ketone while the use of excess potassium amide has given the highest conversion (39%) of hydrocarbon to ketone. However, in contrast to the carbethoxylation, these results were obtained in the presence of liquid ammonia (see experimental). Diphenylmethylpotassium also has been benzoylated with benzoyl chloride but the yield was only 26% when equivalents of the reactants were used; with an extra equivalent of the acid chloride dibenzoylation occurred.



$$(C_6H_5)_2CHK \xrightarrow{C_6H_5COCl} C_6H_5COCH(C_6H_5)_2 \xrightarrow[C_6H_5COCl]{(C_6H_5)_2CHK} C_6H_5\overset{OCOC_6H_5}{\overset{|}{C}}{=}C(C_6H_5)_2$$

The benzoylation of diphenylmethylsodium, prepared from benzohydryl methyl ether and sodium, with benzoyl chloride,[7] benzyl benzoate[8] and benzonitrile[8] has been reported to form the ketone in yields of 57, 38 and 68%, respectively.

The potassium salt of ethyl diphenylacetate, prepared by means of potassium amide, has been benzoylated with benzoyl chloride to form ethyl α,α-diphenylbenzoylacetate in 42% yield[9]; the reaction is represented above. This β-keto ester was remarkably stable toward ketonic cleavage; it was recovered after refluxing with hydriodic acid[10] in acetic acid or with 5% sodium hydroxide. However, the corresponding β-keto ester, obtained by benzoylating the potassium salt of *t*-butyl diphenylacetate, was cleaved readily by acid to form α,α-diphenylacetophenone in an over-all yield of 40%.[11]

$$(C_6H_5)_2CHCO_2C(CH_3)_3 \xrightarrow{KNH_2} [(C_6H_5)_2CCO_2C(CH_3)_3]K \xrightarrow{C_6H_5COCl} C_6H_5CO(C_6H_5)_2CO_2C(CH_3)_3 \xrightarrow[HOAc]{HI} C_6H_5COCH(C_6H_5)_2$$

Similarly, the potassium salt of *t*-butyl diphenylacetate has been acetylated with acetyl chloride and the resulting β-keto ester cleaved to form α,α-diphenylacetone.[12]

The potassium salt of ethyl diphenylacetate has been carbethoxylated with ethyl chlorocarbonate to form ethyl diphenylmalonate but the yield was very poor.

Finally, fluorene has been metalated by potassium amide and the potassium derivative carbonated to form fluorene-9-carboxylic acid in 89% yield.[13] The potassium derivative of fluorene could probably also be carbethoxylated or benzoylated.

Experimental

Diphenylmethylpotassium and Diphenylacetic Acid.—In a two-liter three-necked round-bottomed flask equipped with a dropping funnel, a Dry Ice reflux condenser and a mercury sealed Hershberg stirrer (to the bottom of which was attached a piece of rusty iron gauze) was placed 800 ml. of commercial anhydrous liquid ammonia. To the stirred ammonia was added in small pieces 21.5 g. (0.55 mole) of potassium which was converted within two hours to potassium amide; this conversion was indicated by the discharge of the deep blue color of the solution. The Dry Ice condenser was then replaced by a water condenser and to the stirred, practically colorless, solution of potassium amide was added 84.0 g. (0.5 mole) of diphenylmethane (b. p. 129° at 11 mm.) in 800 ml. of anhydrous ether. The resulting orange colored mixture was heated on the steam-bath until the liquid ammonia had evaporated (ether being added, if necessary, to maintain the volume at 800 ml.) and then for two hours longer. To the stirred ether suspension of diphenylmethylpotassium was added slowly and carefully approximately 400 g. of powdered Dry Ice and the stirring continued until the solid carbon dioxide had disappeared. The mixture was poured into 400 ml. of water and, after shaking, the aqueous layer was separated and acidified to litmus with concentrated hydrochloric acid. The white precipitate of diphenylacetic acid was filtered off and dried; yield 95 g. (90%), white crystals, m. p. 147–148° (reported m. p. 148°).[14]

Fluorene-9-carboxylic Acid.—Fluorene (83 g., 0.5 mole, m. p. 113–114°) was metalated by potassium amide and the potassium derivative carbonated as described for diphenylmethane to form 93 g. (89%) of fluorene-9-carboxylic acid, m. p. 225–227°.

Ethyl Diphenylacetate. (A) From Diphenylmethylpotassium. Procedure (1).—To an ether suspension of diphenylmethylpotassium, prepared on the 0.5 mole scale as described above, was added 29.5 g. (0.25 mole) of ethyl carbonate (b. p. 125–126°) in 250 ml. of ether. The color changed to light yellow. After refluxing for two hours, the mixture was poured, with stirring, onto a mixture of 500 g. of crushed ice and 40 ml. of glacial acetic acid. The ether layer was washed with water, 5% sodium bicarbonate, and again with water. After drying over Drierite, the solvent was removed and the residue was distilled through a 25-cm. Vigreux column until the boiling temperature reached 111° at 2 mm. The fraction (42.7 g., 0.25 mole) boiling at 100–111° at 2 mm. was chiefly diphenylmethane. The residue in the distilling flask, which solidified on cooling, was recrystallized from alcohol and water yielding 31 g. (52%) of white

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(7) Bergmann and Weiss, *Ber.*, **64**, 1489 (1931).

(8) Bergmann, *J. Chem. Soc.*, 412 (1936).

(9) A 34% yield has been reported for the corresponding benzoylation of the sodium salt of methyl diphenylacetate, prepared by means of triphenylmethylsodium; Schlenk, Hilleman and Rodloff, *Ann.*, **487**, 147 (1931).

(10) This acid has been found especially effective for the ketonic cleavage of the somewhat related β-keto esters obtained by the benzoylation of the sodium salts of ethyl methylethylacetate and ethyl diethylacetate; Hudson and Hauser, THIS JOURNAL, **63**, 3163 (1941).

(11) This is an adaptation of the method developed in this laboratory for effecting the elimination reaction with *t*-butyl esters; Breslow, Baumgarten and Hauser, THIS JOURNAL, **66**, 1286 (1944).

(12) An unsuccessful attempt was made to prepare this ketone by acetylating diphenylmethylpotassium with purified acetyl chloride; Bergmann (ref. 8) also reported failure for the analogous acetylation of diphenylmethylsodium.

(13) Burtner and Cusic (THIS JOURNAL, **65**, 264 (1943)) effected the metalation of fluorene with phenylsodium and butyllithium, followed by carbonation, to form this acid in yields of 59 and 75%, respectively.

(14) Huntress, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 154.

crystals of ethyl diphenylacetate, m. p. 58–59° (reported m. p. 58°[15]). The result was the same with one-fifth quantities of reactants. The yield was 32% when an ether suspension of a mixture of diphenylmethylpotassium and potassium amide, prepared from 0.05 mole of diphenylmethane and 0.1 mole of potassium amide, was treated with 0.1 mole of ethyl carbonate.

Procedure (2).—To 0.1 mole of potassium amide in 100 ml. of liquid ammonia was added with stirring 0.1 mole of diphenylmethane followed, after five minutes, by 0.05 mole of ethyl carbonate in 40 ml. of anhydrous ether. After stirring two hours the ammonia was removed on the steam-bath; 100 ml. of ether being added. There was isolated from the mixture ethyl diphenylacetate (m. p. 58–59°) in 45% yield. The yield was 38% when the experiment was repeated using sodium amide instead of potassium amide, and 16% with 0.1 mole each of sodium amide and ethyl carbonate to 0.05 mole of diphenylmethane.

(B) **From Diphenylacetic Acid.**—A mixture of 40.0 g. (0.19 mole) of diphenylacetic acid, 170 ml. of commercial absolute ethanol and 8 ml. of 95% sulfuric acid was refluxed on the steam-bath for six hours, chilled in an ice-bath, and the precipitated ethyl diphenylacetate filtered off. Additional ester was recovered from the filtrate; total yield of the ester 38.8 g. (86%) (m. p. 58–59°).

***t*-Butyl Diphenylacetate.**—This ester (m. p. 80–81°) was prepared in 52% yield from diphenylacetic acid by the general method[16] involving the conversion of the acid to its acid chloride, followed by reaction of the latter with *t*-butyl alcohol in the presence of dimethylaniline.

Anal.[17] Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 81.06; H, 7.69.

α,α-Diphenylacetophenone. (A) **From Diphenylmethylpotassium. Procedure** (1).—To 0.1 mole of potassium amide in 150 ml. of liquid ammonia was added, with stirring, 16.8 g. (0.1 mole) of diphenylmethane in 200 ml. of ether followed, after ten minutes, by 6.8 g. (0.05 mole) of methyl benzoate (b. p. 91° at 20 mm.) in 50 ml. of ether. The liquid ammonia was evaporated on the steam-bath and the yellow ether suspension was refluxed for two hours. The mixture was poured into water with stirring. The ether phase was dried over drierite and the solvent distilled. The residue was distilled through a 10-cm. Vigreux column until the boiling temperature reached 131° at 10 mm. The residue in the distilling flask, which solidified on cooling, was recrystallized from alcohol yielding 7.4 g. (55%) of α,α-diphenylacetophenone, m. p. 135.5–136.5° (reported m. p. 136°).[18] The benzoyl derivative of the ketone melted at 152–153° (reported m. p. 153°).[19] By employing 0.1 mole of potassium amide, 0.05 mole of diphenylmethane and 0.0625 mole of methyl benzoate instead of the quantities used above, a 39% yield (based on diphenylmethane) of the ketone was obtained.

Procedure (2).—To an ether suspension of diphenylmethylpotassium, prepared on a 0.1 mole scale, was added 0.05 mole of methyl benzoate in 50 ml. of ether. The mixture was refluxed for two hours and worked up giving a 41% yield of the ketone. The yield was 35% (based on diphenylmethane) with 0.1 mole of potassium amide, 0.05 mole of diphenylmethane and 0.0625 mole of methyl benzoate.

Procedure (3).—An ether suspension of diphenylmethylpotassium was prepared on a 0.1 mole scale with nitrogen passing through it during the two hours of refluxing. To the mixture, cooled to about −30° by means of a Dry Ice–ether-bath, was added all at once 0.1 mole of benzoyl chloride in 40 ml. of ether. The bath was removed and, after stirring for thirty minutes, the mixture was poured into water. The precipitate was filtered off and recrystallized from alcohol yielding 7.0 g. (26%) of α,α-diphenylacetophenone, m. p. 134–135°. Additional ketone (m. p. 120–125°) was obtained from the filtrate but it could not be purified readily. When the same size run was carried out using an additional 0.1 mole of benzoyl chloride, there was obtained a 30% yield of the benzoyl derivative of the ketone, m. p. 152–153°.[19]

(B) **From *t*-Butyl Diphenylacetate.**—To 0.1 mole of potassium amide in 150 ml. of liquid ammonia was added with stirring 26.8 g. (0.1 mole) of *t*-butyl diphenylacetate dissolved in 175 ml. of toluene. The ammonia was evaporated and the mixture was refluxed two hours while passing nitrogen through it. After cooling to room temperature, 28.0 g. (0.2 mole, 23 ml.) of benzoyl chloride in 25 ml. of toluene was added with stirring. The mixture was stirred and refluxed for fifteen minutes, then cooled and poured into water. The toluene phase was washed with 10% sodium bicarbonate, dried over sodium sulfate and the solvent distilled. The crude *t*-butyl α,α-diphenylbenzoylacetate, which failed to crystallize, was refluxed with 60 ml. of 47% hydriodic acid and 30 ml. of glacial acetic acid for two hours or until no more gas was evolved. The mixture was cooled (the oil solidifying) and neutralized with 20% sodium hydroxide. The solid was filtered off and recrystallized from alcohol yielding 10.8 g. (40%) of α,α-diphenylacetophenone, m. p. 134–135°.

α,α-Diphenylacetone.—*t*-Butyl diphenylacetate (0.065 mole) was converted to its potassium derivative which was acetylated with acetyl chloride (0.13 mole) as described above for the benzoylation After the solvent was distilled the residue was refluxed with 25 ml. of benzene containing 0.25 g. of *p*-toluenesulfonic acid monohydrate until the evolution of gas ceased (three hours). After cooling, the solution was poured into water. The benzene phase was distilled and the residue fractionated. The fraction boiling at 146–148° at 3 mm. solidified on standing overnight. Recrystallization from petroleum ether yielded 2.0 g. (15%) of α,α-diphenylacetone, m. p. 45–46° (reported m. p. 46°).[20] The semicarbazone melted at 168–169° (reported m. p. 170°).[20]

Ethyl α,α-Diphenylbenzoylacetate.—Ethyl diphenylacetate (24.0 g., 0.1 mole) was converted to its potassium derivative which was benzoylated as described for the *t*-butyl ester. After the solvent was removed, an unsuccessful attempt was made to effect ketonic cleavage by refluxing the residue with 60 ml. of 47% hydriodic acid and 30 ml. of glacial acetic acid. After cooling, the mixture was neutralized with 20% sodium hydroxide. The solid was filtered off and recrystallized from alcohol yielding 14.4 g. (42%) of ethyl α,α-diphenylbenzoylacetate, m. p. 148–149°.

Anal.[17] Calcd. for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85. Found: C, 80.40, 80.37; H, 6.02, 5.86.

An ether suspension of the potassium salt of ethyl diphenylacetate obtained in the reaction mixture from diphenylmethylpotassium (prepared on the 0.1 mole scale) and 0.05 mole of ethyl carbonate was benzoylated in a similar manner, yielding 2.9 g. of the β-keto ester (m. p. 148–149°). This corresponds to a 17% over-all yield from ethyl carbonate. This over-all yield is only a little lower than that (22%) obtained when the ethyl diphenylacetate was isolated and then benzoylated.

Summary

1. Diphenylmethylpotassium, prepared from diphenylmethane and potassium amide, has been carbonated, carbethoxylated and benzoylated to form diphenylacetic acid, ethyl diphenylacetate and α,α-diphenylacetophenone, respectively. Conditions effecting the carbethoxylation and benzoylation have been studied. Diphenylacetic acid has been converted to its ethyl and *t*-butyl esters.

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[15] Ref. 14, p. 288.

[16] Hauser, Hudson, Abramovitch and Shivers, "Organic Syntheses," Vol. 24, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 19.

[17] Microanalyses by Arlington Laboratories, Fairfax, Virginia.

[18] Biltz, *Ber.*, **26**, 1957 (1893).

[19] Biltz, *ibid.*, **32**, 655 (1899).

[20] Stoermer, *ibid.*, **39**, 2303 (1906).

2. Fluorene has similarly been converted to fluorene-9-carboxylic acid.

3. The potassium salt of *t*-butyl diphenylacetate, prepared by means of potassium amide, has been benzoylated and acetylated and the resulting β-keto esters cleaved to α,α-diphenylacetophenone and α,α-diphenylacetone, respectively.

4. Ethyl α,α-diphenylbenzoylacetate, prepared by benzoylating the potassium salt of ethyl diphenylacetate, is stable toward ketonic cleavage.

DURHAM, N. C. RECEIVED JANUARY 29, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Reactions of Mercaptans with Acrylic and Methacrylic Derivatives

BY CHARLES D. HURD AND LEON L. GERSHBEIN

That hydrogen sulfide adds to methyl acrylate, acrylonitrile or crotonaldehyde when a basic catalyst is present, but not to methyl methacrylate, was established recently.[1] The present paper reports an extension of this type of reaction to mercaptans and thiophenols. Both acrylic and methacrylic esters give high yields of β-substituted propionates and isobutyrates: $RSH + CH_2{=}CHCOOCH_3 \rightarrow RSCH_2CH_2COOCH_3$; but unless a basic condensing agent is present, the reaction is very slow and the yield small.

A few instances are on record involving the addition of methanethiol, ethanethiol, or thiophenol to acrylic acid, cinnamic acid, methyl methacrylate, or acrolein, but the specified reaction conditions often involve relatively long periods of reaction,[2] the presence of mercuric salts,[3] or irradiation.[4] It should be pointed out that β-mercaptopropionic or β-mercaptoisobutyric acids or esters frequently have been made by the metathetic approach. New interest in methyl β-methylmercaptopropionate stems from the fact that it has been isolated[5] from pineapple fruit pulp.

The presence of two functional groups (SH and OH) in 2-mercaptoethanol makes this substance one of particular interest, since alcohols are known to undergo addition[6] to acrylic ester in the presence of a basic catalyst. We found that only the mercapto group of 2-mercaptoethanol participates in the reaction with methyl acrylate. Methyl β-(2-hydroxyethylmercapto)-propionate, $HOCH_2CH_2SCH_2CH_2COOCH_3$, (I), was isolated in a yield of 97% when benzyltrimethylammonium hydroxide was the catalyst, but only 52% when sodium methoxide was employed.

Seven β-mercapto esters were prepared from methyl acrylate and five from methyl methacrylate in the present work: R in $RSCH_2CH_2COOCH_3$ representing methyl, isopropyl, carbethoxymethyl, benzyl, phenyl, *t*-butyl and 2-hydroxyethyl; and R′ in $R'SCH_2CH(CH_3)COOCH_3$ being the same as the first five R groups listed above. All were distillable liquids with a density of 1.0–1.1. Some of them were oxidized by hydrogen peroxide to the corresponding sulfone esters.

Extension of the addition reaction to sodium acrylate revealed that the alkalinity of a hot aqueous solution of the latter was sufficient to produce an excellent yield of 3-benzylmercaptopropionic acid from phenylmethanethiol without using any added base.

Acrolein and crotonaldehyde were converted into 3-methylmercaptopropanal and 3-benzylmercaptobutanal, respectively, by reaction with methanethiol and phenylmethanethiol. Synthesis of the former has been reported by reaction of methanethiol with acrolein in the presence of a mercury salt.[3]

The reaction between acrylonitrile[7] and alkanethiols or thiophenols also proceeds practically quantitatively if a small amount of alkaline condensing agent is present: $RSH + CH_2{=}CHCN \rightarrow RSCH_2CH_2CN$, R representing methyl, ethyl, butyl, isobutyl, *t*-butyl, isopropyl, carbethoxymethyl, benzyl, 2-hydroxyethyl, phenyl, *o*-, *m*-, and *p*-tolyl, 2-benzoxazolyl, 2-benzothiazolyl. Although in most of the runs where alkaline agents were employed, the product was allowed to stand overnight, the reaction yielding $RSCH_2CH_2CN$[8] was virtually complete within the first hour.

Of the simple mercaptans tested some (2-propanethiol, 2-methyl-1-propanethiol, ethyl mercaptoacetate) were almost non-reactive[9] at 25°

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[1] Gershbein and Hurd, THIS JOURNAL, **69**, 241 (1947).

[2] Holmberg and Schjånberg, *Arkiv Kemi, Mineral Geol.*, **A15**, No. 20, 14 (1942); *C. A.*, **38**, 2943 (1944); *Chem. Zentr.*, **114**, I, 388 (1943); Posner, *Ber.*, **40**, 4791 (1907).

[3] Kaneko and Mii, *J. Chem. Soc. Japan*, **59**, 1383 (1938).

[4] Jacobson, U. S. Patent 2,199,799 (1940).

[5] Haagen-Smit, Kirchner, Deasy and Prater, THIS JOURNAL, **67**, 1651 (1945).

[6] (a) Koelsch, *ibid.*, **65**, 437 (1943); (b) Rehberg, Dixon and Fisher, *ibid.*, **68**, 544 (1946); (c) Purdie and Marshall, *J. Chem. Soc.*, **59**, 468 (1891).

[7] Since completion of this work, Gribbins, Miller and O'Leary, U. S. Patent 2,397,960 (1946), list examples of ethyl-, benzyl-, β-hydroxyethyl- and β-mercaptoethyl-mercaptopropionic acids. These were produced by hydrolyzing the corresponding nitriles which, in turn, were made by adding mercaptans to acrylonitrile in the presence of piperidine; but the nitriles were not characterized by analysis.

[8] β-Methylmercaptopropionitrile is the only simple compound of this type to have been previously prepared and analyzed. It was made by metathesis of sodium cyanide and 2-methylmercaptoethyl bromide: Akahori, Kaneko and Matizuki, *J. Chem. Soc. Japan*, **59**, 1136 (1938).

[9] We found 2-propanol also to be completely indifferent toward acrylonitrile at 25° (eleven days) when no basic agent was present.