linear polyamides of the nylon type have exhibited abnormally short axial spacings.[13] The authors have assumed a planar chain configuration and have attributed the shortening to a twisting of the polar groups from the molecular plane and a consequent alternate folding at the polar layer.

It is obvious that structural interpretation of homologous series of monomeric compounds or of fibrous polymers based chiefly on long crystal spacings or axial identity periods, although highly suggestive, are limited. A more detailed analysis is in order.

Experimental

I am indebted to Dr. A. W. Weitkamp and the Research Laboratories of the Standard Oil Company of Indiana for making available the samples of the branched chain fatty acids isolated from wool. The amides used in these studies were prepared from the acids in 50-mg. runs by way of the acid chlorides and ammonia. They were recrystallized from dilute methanol. In all cases the melting points were redetermined and found to agree closely with the values presented by Weitkamp.

The long crystal spacings were obtained from thin films of polycrystalline aggregates. The preparations were mounted on a goniometer head and oscillated in the X-ray beam at reflection angles of 0 to 20°. A copper target was employed and the radiation was filtered through nickel foil. Exposures ranged from 5 to 15 milliampere hours at about 40 kilovolts. The cylindrical camera had a specimen to film distance of 51.2 mm.

The films of the free acids were prepared by melting a few milligrams of the material between 1 cm. square glass microscope coverslips and allowing the melt to cool slowly from one end in a steep temperature gradient maintained by a hot resistance wire. This procedure accentuated the flat crystal habit and yielded a partially oriented polycrystalline film which remained coherent after removal of one of the cover slips. Identical spacings were obtained from lightly pressed aggregates of crystals obtained directly from solvents. However, diffraction photographs obtained from the latter preparations showed fewer orders and more diffuse scattering.

In contrast, preparations of the amides crystallized from the melt yielded poor diffraction diagrams whereas excellent ones were obtained from pressed crystals from solvents. The latter preparations were slightly solvated and showed small spacing differences from the melted preparations. Since the very small differences were uniform throughout the series, they did not affect the results and were not further investigated. Due to their small size, attempts to obtain rotation and Weissenberg projections of single amide crystals have so far been unsuccessful although it is hoped that such data will eventually be obtained.

Summary

The long crystal spacings of the iso series of fatty acids of wool fat increase linearly with carbon content. Both the spacings and diffraction patterns provide clear evidence of homology. The long crystal spacings of the iso amides show the same peculiar periodic sequence as the melting points. The results are discussed in terms of a spiral chain configuration.

ST. LOUIS, MISSOURI RECEIVED MAY 15, 1947

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[13] W. O. Baker and C. S. Fuller, THIS JOURNAL, **65**, 1120 (1943).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

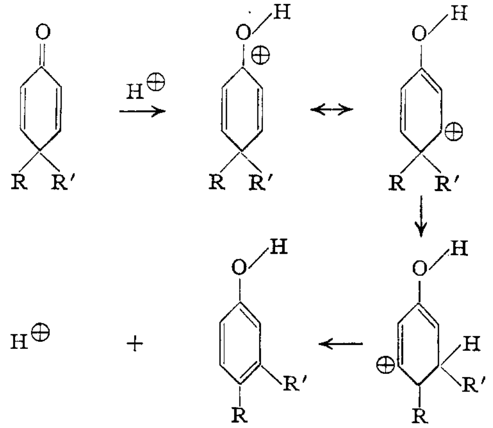
The Dienone–Phenol Rearrangement

BY RICHARD T. ARNOLD, JAY S. BUCKLEY, JR., AND JOHN RICHTER

Rearrangement of semibenzenes into alkylbenzenes has been studied in some detail by v. Auwers and co-workers.[1] These reactions are now regarded as typical examples of pinacol or neopentyl type rearrangements.

In our opinion the dienone–phenol rearrangement observed by Clemo in the conversion of santonin to desmotroposantonin[2] and more recently by Inhoffen[3] and co-workers in the cholestanone and androstenone series is mechanistically the same as the semibenzene–alkylbenzene rearrangement discussed above. These reactions are acid catalyzed and proceed under the same general experimental conditions.

Wilds and Djersassi[4] recently published the first example of this rearrangement in which the structure of both the starting compound and product of the reaction were established by an independent synthesis.



In this paper is reported a new example which, because of the high yields involved, represents a convenient synthesis of 3,4-dialkyl-1-naphthols. Reaction between γ-methylvalerolactone (I, R = CH_3) and benzene to form 4,4-dimethyl-1-tetralone (II) proceeded smoothly in the presence of

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(1) v. Auwers and Ziegler, *Ann.*, **425**, 217 (1921).

(2) Clemo, *J. Chem. Soc.*, 1110 (1930).

(3) Inhoffen, Zuhlsdorf and Huang-Minlon, *Ber.*, **73**, 451 (1940).

(4) Wilds and Djerassi, THIS JOURNAL, **68**, 1712 (1946).

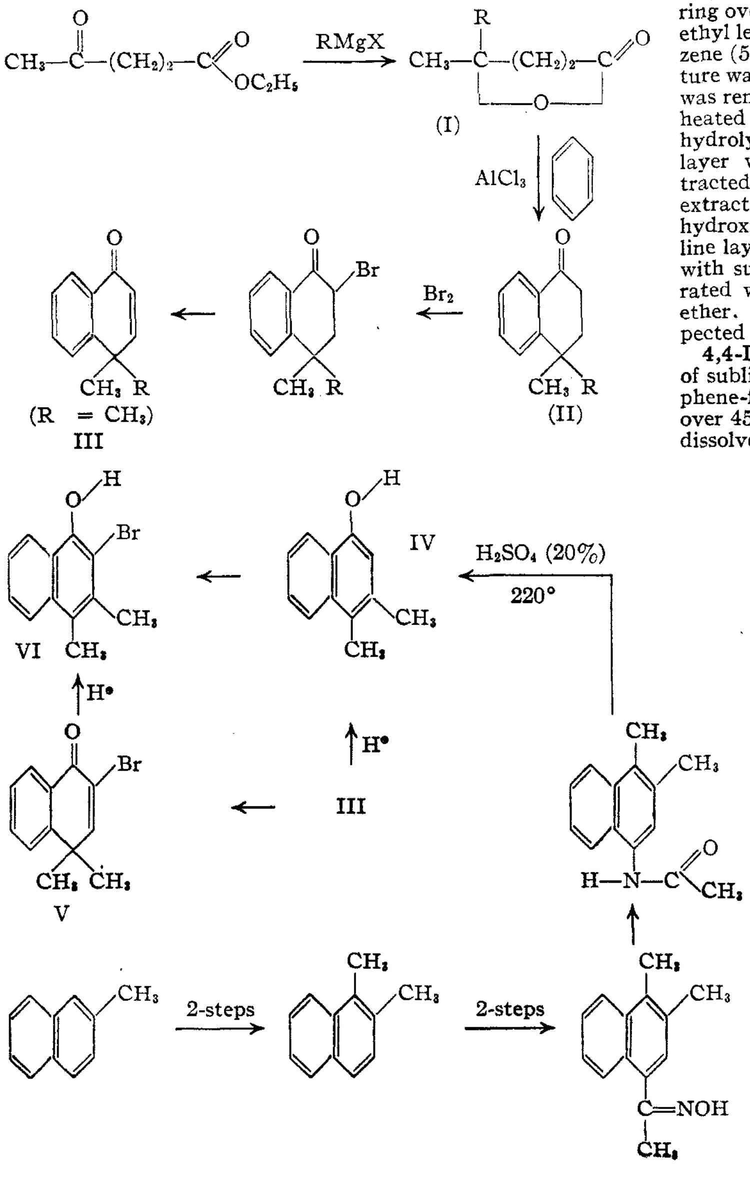
excess aluminum chloride. When only one mole of aluminum chloride was employed the substituted aryl butyric acid resulted.

4,4-Dimethyl-1-keto-1,4-dihydronaphthalene (III) was prepared from ethyl levulinate according to a procedure which permits wide variations. Treatment of an acetic anhydride solution of this dienone with a few drops of sulfuric acid gave the acetate of 3,4-dimethyl-1-naphthol (IV) whose identity was established by an independent route from 1,2-dimethylnaphthalene.

Addition of bromine to the dienone (III) gave an unstable dibromide which lost hydrogen bromide readily to form 2-bromo-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (V). This substance rearranged in the presence of sulfuric acid to yield 2-bromo-3,4-dimethyl-1-naphthol (VI) which was obtained directly from the bromination of 3,4-dimethyl-1-naphthol (IV). These results are similar to the bromination of santonin[5] and the subsequent rearrangement into the acetate of bromodesmotroposantonin.[6,7]

A summary of the transformations described in the Experimental is given below.

Molecules of type III in which the alkyl groups are different (*i. e.*, $R \neq CH_3$) should rearrange in such a way that the relative ease of migration is the same as in the pinacol–pinacolone rearrangement. This more extensive problem is now under investigation in our laboratory.



Experimental

γ,γ-Dimethylbutyrolactone.—By employing benzene as a solvent for the Grignard reaction[8] good yields were obtained.

The Grignard reagent was prepared from methyl iodide (142 g.), magnesium turnings (24.3 g.) and dry ether (400 cc.). This solution was added with vigorous stirring over forty-five minutes to a solution containing ethyl levulinate (130.2 g.), ether (500 cc.) and benzene (500 cc.). During the addition, the temperature was held at 0°. By slow distillation the ether was removed and the resulting benzene solution was heated at the boiling point for three hours. After hydrolysis with dilute sulfuric acid the benzene layer was separated and the aqueous phase extracted with ether. Treatment of the combined extracts at 0° with a solution containing sodium hydroxide (40 g.) and water (200 g.) gave an alkaline layer from which the lactone could be generated with sulfuric acid (50%). This solution was saturated with ammonium sulfate and extracted with ether. Distillation gave 63.7 g. (62%) of the expected lactone; b. p. 201–206° (760 mm.).

4,4-Dimethyl-1-tetralone.—To a stirred mixture of sublimed aluminum chloride (220 g.), and thiophene-free benzene (350 cc.) held at 5° was added, over 45 minutes, γ,γ-dimethylbutyrolactone (63 g.) dissolved in benzene (100 cc.). The mixture was warmed slowly to 90–100° and held at that temperature for three hours. Decomposition with ice and hydrochloric gave a benzene layer which was washed successively with dilute hydrochloric acid, water and sodium carbonate solution. Distillation through an 18-inch Vigreux column gave 66.7 g. (70%) of colorless ketone; b. p. 119–120° (6 mm.). The 2,4-dinitrophenylhydrazone melted at 217–218°.

Anal. Calcd. for $C_{18}H_{18}N_4O_4$: C, 61.01; H, 5.12. Found: C, 61.07; H, 5.23.

2-Bromo-4,4-dimethyl-1-tetralone.—The above ketone (17.4 g.) was allowed to react with bromine (16 g.) in dry ether as a solvent. Upon evaporation of the ether, the residue slowly crystallized. Two recrystallizations from aqueous methanol gave 17 g. of pure bromo ketone; m. p. 87.5–88.5°.

Anal. Calcd. for $C_{12}H_{13}BrO$: C, 56.93; H, 5.18. Found: C, 56.90; H, 5.23.

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[5] Wedekind, *Ber.*, **41**, 359 (1908).

[6] Huang-Minlon, Lo and Chu, THIS JOURNAL, **65**, 1780 (1943).

[7] Huang-Minlon, Lo and Chu, *ibid.*, **66**, 1954 (1944).

[8] Cason, Adams, Bennett and Register, *ibid.*, **66**, 1764 (1944).

4,4-Dimethyl-1-keto-1,4-dihydronaphthalene (III).—Thirty-four grams of the above bromo ketone was dehydrobrominated by refluxing in γ-collidine (100 cc.) for seventy minutes.[9] After cooling to 0°, ether (300 cc.) was added and γ-collidine hydrobromide (21.2 g.) precipitated. This was collected on a filter and the ethereal filtrate was washed with dilute hydrochloric acid, water and sodium hydroxide (5%). After removing the ether, the product was distilled at 112–118° (3 mm.) as a viscous oil which solidified on standing. Two recrystallizations from petroleum ether (30–60°) gave the pure, light sensitive dienone; yield 18 g.; m. p. 69.5–70.5°.

Anal. Calcd. for $C_{12}H_{12}O$: C, 83.68; H, 7.03. Found: C, 84.10; H, 6.96.

The 2,4-dinitrophenylhydrazone crystallized in bright red needles from alcohol–ethyl acetate; m. p. 236–237°.

Anal. Calcd. for $C_{18}H_{16}N_4O_4$: C, 61.36; H, 4.58. Found: C, 61.33; H, 4.65.

Acetate of 3,4-Dimethyl-1-naphthol.—When the above dienone (1.72 g.) was allowed to stand for five hours at room temperature in a solution containing acetic anhydride (35 cc.) and sulfuric acid (0.5 g.) rearrangement occurred. This mixture was poured slowly into cold water (250 cc.) with vigorous stirring. Filtration yielded colorless crystals (2.01 g.) of the naphthol acetate, m. p. 88–90°. Recrystallization from aqueous ethanol raised the melting point to 89.5–91°.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.39; H, 6.79.

3,4-Dimethyl-1-naphthol.—(a) Alkaline hydrolysis of the acetate (1.5 g.) obtained by the above rearrangement gave 3,4-dimethyl-1-naphthol; yield 0.95 g.; m. p. 121.5–123°.

(b) This same dimethylnaphthol was obtained in excellent yield from the acid hydrolysis of 3,4-dimethyl-1-acetamidonaphthalene.

In a sealed Carius tube, 1-acetamido-3,4-dimethylnaphthalene (4.0 g.) was treated with sulfuric acid (20 cc., 15%) at 220–240° for four hours. Ether extraction of the crude product followed by distillation in a sausage flask gave 2.5–2.8 g. of colorless product. Several recrystallizations from carbon tetrachloride gave stout, snow-white needles; m. p. and mixed m. p. with the above sample 121–122°. 3,4-Dimethyl-1-naphthol is obtained in poor yield from 1,2-dimethylnaphthalene by sulfonation followed by fusion with alkali.[10]

Anal. Calcd. for $C_{12}H_{12}O$: C, 83.7; H, 6.9. Found: C, 83.9; H, 7.05.

2-Bromo-4,4-dimethyl-1-keto-1,4-dihydronaphthalene.—To a solution of the dienone III composed of ketone (0.85 g.) and carbon tetrachloride (10 cc.) was added with stirring bromine (0.8 g.) dissolved in carbon tetrachloride (10 cc.). Evolution of hydrogen bromide was brisk during the evaporation of the solvent at atmospheric pressure. The oily residue solidified on standing and was recrystallized from aqueous ethanol; yield 0.90 g.; m. p. 88–89°. This compound was insoluble in sodium hydroxide (10%) and rapidly decolorized permanganate.

Anal. Calcd. for $C_{12}H_{11}OBr$: C, 57.39; H, 4.42. Found: C, 57.52; H, 4.62.

Acetate of 2-Bromo-3,4-dimethyl-1-naphthol.—To a solution of 2-bromo-3,4-dimethyl-1-keto-1,4-dihydronaphthalene (500 mg. in 5 cc. acetic anhydride) was added sulfuric acid (100 mg.) dissolved in acetic anhydride (3 cc.) and the mixture was allowed to stand at 30° for five hours. Decomposition in ice water gave 0.54 g. (92%) of product; m. p. 137–138°. Recrystallization from aqueous ethanol gave white needles, m. p. 137.5–138.5°.

Anal. Calcd. for $C_{14}H_{13}O_2Br$: C, 57.35; H, 4.47. Found: C, 57.45; H, 4.51.

2-Bromo-3,4-dimethyl-1-naphthol.—(a) Hydrolysis of the corresponding acetate with methanolic potassium hydroxide gave the free bromonaphthol which was readily soluble in alkali; m. p. 101–102°.

(b) The same product was obtained in the following manner. 3,4-Dimethyl-1-naphthol (0.85 g.) was allowed to react with bromine (0.8 g.) in acetic acid (15 cc.). The product (0.83 g.) separated as a crystalline solid when the reaction mixture was poured into ice water (60 cc.). After recrystallization the melting point was 101.5–102.5°.

Anal. Calcd. for $C_{12}H_{11}OBr$: C, 57.39; H, 4.42. Found: C, 57.56; H, 4.59.

1-Chloromethyl-2-methylnaphthalene.—β-Methylnaphthalene (142 g.), paraformaldehyde (35 g.), glacial acetic acid (125 g.), concentrated hydrochloric acid (126 cc.) and sirupy phosphoric acid (60 cc., 85%) were heated with stirring for five hours at 70–80°. The reaction mixture was poured into cold water (1000 cc.) and the aqueous layer was decanted from a heavy viscous oil. This oil (which sometimes crystallized at this stage) was taken up in benzene and the product carefully fractionated. The chloromethyl compound solidified in the receiver; b. p. 140–144° (4 mm.); m. p. 62–64°. This is a much shorter procedure than that described by Darzens and Levy[11] and gives the same yield (55%) of pure product.

1,2-Dimethylnaphthalene.—This compound was prepared by the reduction of 1-chloromethyl-2-methylnaphthalene with zinc dust and aqueous ethanol.[12]

1-Acetyl-3,4-dimethylnaphthalene.—A solution of 1,2-dimethylnaphthalene (20 g.) in benzene (70 cc.) was cooled and treated with aluminum chloride (18 g.) at 5° with efficient stirring. To this was added over a period of two hours acetyl chloride (10 g.) dissolved in benzene (20 cc.). After an additional two hours the mixture was decomposed with ice and hydrochloric acid. The benzene layer was washed with hydrochloric acid, water, sodium carbonate solution and then dried over "Drierite." Distillation gave the ketone; yield 19.3 g.; b. p. 165–168° (2 mm.). With the aid of a Dry Ice–acetone bath, the sample was finally crystallized from alcohol; m. p. 51.5–53°.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.8; H, 7.1. Found: C, 84.8; H, 6.9.

Plattner and Ronco[13] reported this substance as an oil and proved its structure. Their melting points for the semicarbazone (225°) and picrate (134–135°) agree with our values.

Oxime of 1-Acetyl-3,4-dimethylnaphthalene.—When the ketone (15 g.), ethanol (67 cc.), water (30 cc.), sodium acetate (25 g.) and hydroxylamine hydrochloride (11 g.) were heated under reflux for four hours there was obtained the oxime (12.8 g.); m. p. 185–187°.

Anal. Calcd. for $C_{14}H_{15}NO$: C, 78.9; H, 7.1; N, 6.56. Found: C, 79.1; H, 7.0; N, 6.56.

1-Acetamido-3,4-dimethylnaphthalene.—A solution containing the above oxime (13 g.), acetic acid (105 g.), and acetic anhydride (41 g.) was held at its boiling point for thirty minutes, cooled to 0°, saturated with dry hydrogen chloride and allowed to stand at room temperature for three days. The solvent was evaporated under vacuum (20 mm.) and the solid residue recrystallized from ethanol; yield 11 g.; m. p. 191–191.5°.

Anal. Calcd. for $C_{14}H_{15}ON$: C, 78.85; H, 7.1; N 6.56. Found: C, 78.61; H, 7.0; N, 6.51.

Hydrolysis of the acetamido derivative with concentrated hydrochloric acid gave 1-amino-3,4-dimethylnaphthalene hydrochloride; yield 91%; m. p. 276–278°.

Anal. Calcd. for $C_{12}H_{14}NCl$: N, 6.74; Cl, 12.26. Found: N, 6.95; Cl, 12.16.

Neutralization of the amine hydrochloride with 2 *N* potassium hydroxide at 50° gave 1-amino-3,4-dimethylnaphthalene. After recrystallization from aqueous eth-

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[9] Wilds and Djerassi, THIS JOURNAL, **68**, 2125 (1946).

[10] Kruber and Schade, *Ber.*, **68**, 11 (1935).

[11] Darzens and Levy, *Compt. rend.*, **202**, 73 (1936).

[12] Hewett, *J. Chem. Soc.*, 293 (1940).

[13] Plattner and Ronco, *Helv. Chim. Acta*, **27**, 400 (1944).

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.