

tional to the first power of (G) and (K), so that the assumption of second-order kinetics in the rate constant calculations is reasonable.<sup>14</sup>

The coordination of magnesium to oxygen is an electrophilic attack, favored by electron-releasing groups in the ketone. The transfer of a negative alkyl group to the carbon in the second step is a nucleophilic attack, favored by electron-withdrawing groups such as the halogens. The experimental results show that a nucleophilic attack is the rate-determining step, as in any reaction where  $\rho$  is positive. If the electrophilic attack were not required, however, one would expect a  $\rho$  of about  $+2.498$ , which is the value for the alkaline hydrolysis of ethyl benzoates in ethanol, a reaction depending primarily on nucleophilic attack at the carbonyl group. It must be concluded that in the Grignard reaction the effects of a substituent in the two steps tend to cancel each other. A halogen, for instance, increases the reactivity of the addition complex, but reduces its rate of formation; thus the over-all effect is small. Other low reaction constants may similarly result from the second step being the rate-determining one.

(14) Second-order kinetics were assumed in order to avoid the difficulty of integrating a third-order expression. It seems unlikely that a large error in  $k/k^0$  would arise if the reaction were third order, as would be the case if  $k_{-1}$  were greater than  $k_2(G)$ . However, the ratio  $k/k_N$  would have no meaning, since the units of second- and third-order constants are different.

### Experimental

**Materials.**—Phenetole and the ketones were of reagent grade (Eastman Kodak Co. White Label). Methyl iodide was obtained from the General Chemical Company.

**Apparatus.**—A clear, colorless solution of methylmagnesium iodide in phenetole (0.8818 *M*, prepared in 67% yield), filtered through glass wool, was stored under nitrogen in a 500-cc. flask, from which it could be transferred to a 20-ml. buret by slight pressure. The buret delivered into a 100-cc. reaction-flask, which in turn was connected to a gas-buret, in which methane was collected by displacement of mercury. Pressure could be adjusted to atmospheric with a leveling bulb, final adjustment being made with the aid of a dibutyl phthalate manometer. Connections of "Tygon" tubing permitted shaking of the reaction flask.

**Procedure.**—The ketone (0.01110 mole) and  $\alpha$ -naphthol (0.4000 g., 0.002775 mole) were placed in the reaction-flask and dissolved in 20 cc. of phenetole. The system was flushed with nitrogen. Exactly 4 ml. (0.003527 mole) of the Grignard reagent was admitted from the buret (ratio of ketone to Grignard to naphthol, 4:1.27:1.) The mixture was shaken for 30 seconds, and as the gas was evolved the pressure was relieved by lowering the leveling bulb. The flask was shaken after five minutes and again after ten minutes. Although all visible reaction had ceased the mixture was allowed to stand another ten minutes; then the volume, temperature and atmospheric pressure were recorded. During the reaction a second flask was charged with ketone, naphthol and phenetole, so that a duplicate run could be made immediately. All runs were made within four days, in which time no deterioration of the Grignard reagent could have occurred.<sup>15</sup>

(15) E. P. Kohler, J. F. Stone, Jr., and R. C. Fuson, *THIS JOURNAL*, **49**, 3181 (1927).

NEWARK, DELAWARE

RECEIVED AUGUST 20, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

## The Rearrangement of Some Disubstituted Cyclic Ketones: An Unusual Dienone-Phenol Rearrangement<sup>1</sup>

BY ELLIOT N. MARVELL AND ADOLPH O. GEISZLER

The preparation and rearrangement of two 1-oxo-2,2-dialkyl-1,2-dihydronaphthalenes are described. Evidence for the structure of these compounds is given and the products of the rearrangements are identified as 3,4-dialkyl-1-naphthol derivatives. This rearrangement is most unusual since the same products are obtained upon rearrangement of 1-oxo-4,4-dialkyl-1,2-dihydronaphthalenes under identical conditions.

Six carbon cyclic ketones containing two double bonds, whether exo- or endocyclic, rearrange under acid catalysis into phenolic derivatives. This rearrangement, known as the dienone-phenol rearrangement, has incurred some interest recently because it is valuable in the synthesis of steroid materials.<sup>2</sup> A thorough knowledge of the course of the rearrangement, therefore, is desirable. If both the double bonds are endocyclic, the rearrangement to a phenol is spontaneous unless the process is blocked in some manner. Normally this blocking consists in the presence of two radicals or atoms directly attached to one carbon atom of the ring, thereby preventing aromatization. Under acid conditions one of these groups may be caused to migrate permitting the aromatization to proceed.

However, all of the known examples of this type of dienone-phenol rearrangement possess the blocking groups on the carbon atom gamma to the ketone.

A mechanism for the dienone-phenol rearrangement, similar to the mechanism postulated for the retrograde pinacolinic rearrangement, has been suggested by Arnold.<sup>3</sup> According to this conception of the rearrangement the presence of the blocking groups on the carbon alpha to the ketone should not alter the course of the reaction. An investigation of some cases of the rearrangement involving such blocking, therefore, was undertaken and the results are described here.

Since the simple dienones of the cyclohexane series are relatively difficult to synthesize, the dihydronaphthalene system was chosen. Two examples were picked because the analogous  $\gamma$ -blocked systems had been studied previously<sup>3,4</sup> and because the expected products are known.

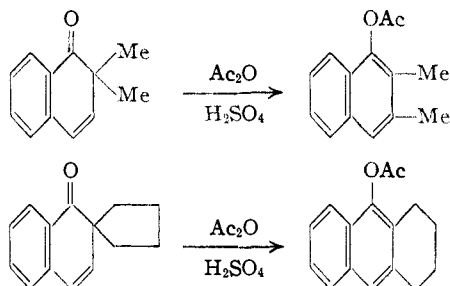
(3) R. T. Arnold, J. Buckley and J. Richter, *ibid.*, **69**, 2322 (1947).

(4) R. T. Arnold, J. S. Buckley and R. M. Dodson, *ibid.*, **72**, 3153 (1950).

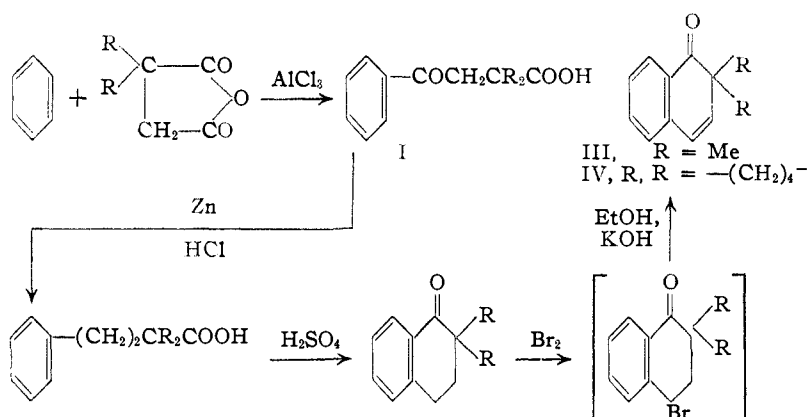
(1) Published with the approval of the Monographs Publications Committee, Oregon State College, as Research Paper No. 188, School of Science, Department of Chemistry. This article is based on a thesis submitted by A. O. Geiszler in partial fulfillment of the requirements for the Ph.D. degree at Oregon State College, June, 1951.

(2) A list of references to work in the steroid series is given in footnote 3 of an article by R. B. Woodward and T. Singh, *THIS JOURNAL*, **72**, 404 (1950).

The two compounds prepared for rearrangement were 1-oxo-2,2-dimethyl-1,2-dihydronaphthalene and 1-oxo-2,2-tetramethylene-1,2-dihydronaphthalene. In strictest analogy to the postulated mechanism the reactions might be expected to proceed according to the equations shown.

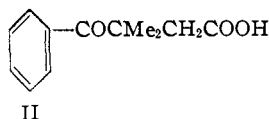


The synthesis of the naphthalenones was accomplished readily according to standard procedures. The method is illustrated by the flow diagram.



The necessary disubstituted succinic anhydrides were prepared conveniently by the procedure of Smith and Horwitz.<sup>5</sup> However, since neither of the two 1-oxo-2,2-dialkyl-1,2-dihydronaphthalenes had been prepared previously, it seemed desirable to provide confirmatory evidence for the structure of the products.

The most important key to the structure of the final product is the structure of the substance obtained from the initial Friedel-Crafts reaction. The reaction between benzene and *asym*-dimethylsuccinic anhydride has been investigated previously.<sup>6-8</sup> Barring any rearrangement two compounds, I and II, could be formed by that reaction. The



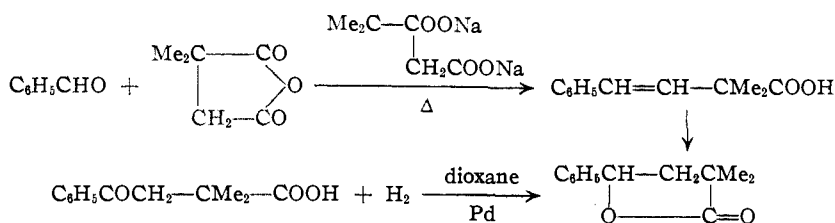
only product isolated from the reaction has been

- (5) P. A. S. Smith and J. Horwitz, *THIS JOURNAL*, **71**, 3418 (1949).  
 (6) G. Clemo and H. G. Dickenson, *J. Chem. Soc.*, 255 (1937).  
 (7) G. Clemo, R. Haworth and E. Walton, *ibid.*, 1110 (1930).  
 (8) S. C. Bhargava, *J. prakt. Chem.*, **101**, 98 (1929).

assigned the structure I, mainly because the ethyl ester of its Clemmensen reduction product does not react with ethyl oxalate in the presence of sodium ethoxide.<sup>8</sup> During the course of this work confirmatory evidence for this structure has been provided. The *asym*-dimethylsuccinic anhydride has been condensed with benzaldehyde by the Perkin method. The condensation must occur on the unsubstituted carbon atom, hence only one structure needs to be considered for the product. This product added hydrogen bromide to give an unstable bromine-containing material which was hydrolyzed easily to  $\alpha,\alpha$ -dimethyl- $\gamma$ -phenyl- $\gamma$ -butyrolactone. This lactone was compared with the lactone formed by direct reduction of the Friedel-Crafts product and the two compounds were found to be identical.

The desired  $\gamma$ -phenyl- $\alpha,\alpha$ -dimethylbutyric acid was obtained by a Clemmensen reduction of the Friedel-Crafts product and by catalytic reduction of  $\gamma$ -phenyl- $\alpha,\alpha$ -dimethylisocrotonic acid prepared by the Perkin method. Both samples of the substituted butyric acid were identical. Therefore the structure of the Friedel-Crafts product would seem to be firmly established as I.

Treatment of  $\gamma$ -phenyl- $\alpha,\alpha$ -dimethylbutyric acid with sulfuric acid gave a ketone which formed an oxime but not a phenylhydrazone or semicarbazone. This compound reacted slowly with bromine to liberate hydrogen bromide and produce an unstable bromine-containing substance. No attempt was made to isolate this bromide, but it was heated with alcoholic potash and a stable bromine-free ketone isolated. This compound, which has been assigned the structure III, is a liquid ketone which



forms an oxime but not a phenylhydrazone or semicarbazone. It is not soluble in aqueous base, and adds bromine readily. On the basis of its mode of preparation and that it is an unsaturated, hindered ketone, the compound synthesized can logically be assigned the structure III.

A series of attempts to cyclize  $\gamma$ -phenyl- $\alpha,\alpha$ -dimethylisocrotonic acid directly to III led in all cases to tarry products. The inability to cyclize either the acid or its chloride may perhaps be attributed to the failure of the isocrotonic acid to form a *cis* modification.

The 1-oxo-2,2-tetramethylene-1,2-dihydronaphthalene (IV) was prepared in a manner analogous to that used to prepare III. The structure was

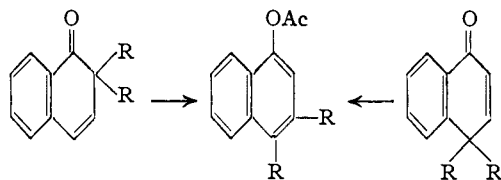
assigned by analogy. Both III and IV rearrange readily when allowed to stand in acetic anhydride solution containing a few drops of sulfuric acid. The products obtained are acetates of aromatic hydroxy compounds. The product obtained from III was studied first and the melting point of the free naphthol indicated that it was not 2,3-dimethyl-1-naphthol. Table I lists the properties of the product along with those of a number of isomeric dimethyl-1-naphthols. The data indicate that the product is 3,4-dimethyl-1-naphthyl acetate, and the melting point of a mixture of the product with an authentic sample of that acetate (kindly provided by Dr. R. T. Arnold) confirmed those indications.

TABLE I

## PROPERTIES OF THE ISOMERIC DIMETHYL-1-NAPHTHOLS

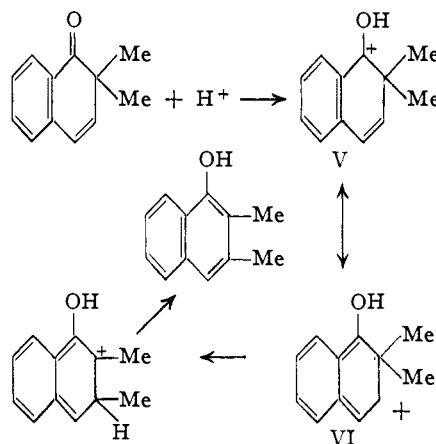
Position of Me groups	M.p. of acetate, °C.	M.p. of naphthol, °C.	M.p. of brominated naphthol, °C.	M.p. of <i>p</i> -nitrobenzeneazo derivative, °C.
2,3	.....	84 <sup>b</sup>	.....	225-226 <sup>c</sup>
2,4	.....	84-85 <sup>10,11</sup>	.....	.....
3,4	88.5-90 <sup>a</sup>	121.5-123 <sup>a</sup>	101.5-102.5 <sup>a</sup>	.....
2,6	.....	133 <sup>12</sup> (113) <sup>13</sup>	.....	.....
Product	88.5-89.5	120-122	99-101	243-244

The product of the rearrangement of IV was found to be the known 9-phenanthryl acetate. Comparison of the melting points of the product acetate, the free phenanthrol and its 3,5-dinitrobenzoate with the melting points of the same derivatives of 9-phenanthrol provided evidence for this assignment. Finally the melting point of a mixture of the product and an authentic sample of 9-phenanthryl acetate was not different from the melting point of either sample. It seems evident therefore, that both 1-oxo-2,2-dialkyl-1,2-dihydro-naphthalenes and 1-oxo-4,4-dialkyl-1,2-dihydro-naphthalenes rearrange to give identical products.



One possible interpretation of the Arnold mechanism for the Dienone-Phenol rearrangement, would indicate that the dienone III could rearrange as follows to give 2,3-dimethylnaphthyl acetate. Acetylation might occur at any step in the process. However, the resonance form VI should be so much less stable than is V that VI would not make a significant contribution to the hybrid state of the molecule.<sup>14</sup>

It is probable, therefore, that the rearrangement prefers an alternate course on this account. However, the Arnold mechanism in a somewhat modi-



fied form may be used to explain the experimental results. Experiments designed to test that modified mechanism are underway in these laboratories. Studies in the cyclohexadienone system, in which the forms analogous to V and VI above are of equivalent stability, are being contemplated.

**Acknowledgment.**—The authors are indebted to Dr. Richard Arnold for supplying the samples of 3,4-dimethyl-1-naphthyl acetate and 9-phenanthryl acetate used for melting point tests. We should also like to note our appreciation of his helpful comments and suggestions received during the course of this work.

## Experimental

**Ethyl  $\alpha$ -Cyano- $\alpha$ -(1-cyanocyclopentyl)-acetate.**—This compound was prepared in one molar batches from cyclohexanone and ethyl cyanoacetate according to the procedure of Smith and Horwitz.<sup>5</sup> The product was purified by distillation; b.p. 176-180° (14 mm.);  $n_D^{20}$  1.4658; yield 70%.

**Anal.** Calcd. for  $C_{11}H_{14}O_2N_2$ : C, 64.06; H, 6.84. Found: C, 63.78; H, 7.14.

**1-Carboxycyclopentane-1-acetic Acid.**—The above compound was hydrolyzed and decarboxylated by boiling with concentrated hydrochloric acid. It was then isolated essentially by the method of Smith and Horwitz.<sup>5</sup> The acid was recrystallized from hot water, m.p. 164-165°; yield 82%. A melting point of 160-161° has been reported previously<sup>15</sup> for this acid.

**1-Carboxycyclopentane-1-acetic Anhydride.**—A mixture of 100 g. (0.58 mole) of the above acid, 100 ml. of acetic anhydride and 20 ml. of acetyl chloride was boiled under reflux for four hours. The excess acetic anhydride and the acetic acid were removed by distillation, and the product was distilled under reduced pressure, b.p. 142-145° (18 mm.); yield 74 g. (83%). This anhydride has been reported<sup>16</sup> to boil at 135-137° (13 mm.).

**$\beta$ -Benzoyl- $\alpha,\alpha$ -dimethylpropionic Acid.**—A suspension of 130 g. of anhydrous aluminum chloride in 300 ml. of dry benzene was placed in a 1-l. flask, and 62 g. (0.50 mole) of  $\alpha,\alpha$ -dimethylsuccinic anhydride<sup>5,16</sup> was added over a period of about 30 minutes. During the first hour the rate of the reaction was controlled by periodic cooling with an ice-bath. The reaction was completed by heating the mixture for two hours on a steam-bath. This mixture was poured into 1200 ml. of 5% hydrochloric acid, the benzene evaporated under reduced pressure, and the product isolated by suction filtration. After being recrystallized from 95% ethanol the keto acid melted at 173-174°; yield 82 g. (80%). This keto acid has been prepared previously, m.p. 170-172°<sup>6</sup> and 173°.<sup>4</sup>

**$\beta$ -Benzoyl- $\alpha,\alpha$ -tetramethylenepropionic Acid.**—This acid was prepared in 0.15-molar batches according to the procedure given for the preparation of  $\beta$ -benzoyl- $\alpha,\alpha$ -dimethyl-

(9) W. Cocker, *J. Chem. Soc.*, 36 (1946).

(10) W. Cocker and C. Lipman, *ibid.*, 583 (1947).

(11) J. Conforth, R. Conforth and R. Robinson, *ibid.*, 168 (1943).

(12) V. Vesely and F. Stursa, *Collection Czechoslov. Chem. Commun.*, 4, 21 (1932); *cf. C. A.*, 29, 2190 (1932).

(13) French Patent 807,830, January 22, 1947; *cf. C. A.*, 31, 6023 (1937).

(14) G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 15.

(15) I. Vogel, *J. Chem. Soc.*, 2010 (1928).

(16) P. B. Verkrade and H. Hartman, *Rec. trav. chim.*, 69, 946 (1933).

propionic acid. The product, after one crystallization from 95% ethanol, weighed 27 g. (78%); m.p. 170–171°.

*Anal.* Calcd. for  $C_{14}H_{16}O_2$ : C, 72.39; H, 6.94. Found: C, 72.55; H, 7.16.

The semicarbazone of the above acid was prepared according to the directions of Shriner and Fuson.<sup>17</sup> This semicarbazone was recrystallized from 50% aqueous ethanol until the melting point remained constant at 164–165°.

*Anal.* Calcd. for  $C_{14}H_{16}O_2N_2$ : C, 62.26; H, 6.62. Found: C, 62.08; H, 6.92.

**$\gamma$ -Phenyl- $\alpha,\alpha$ -dimethylbutyric Acid.**—A mixture of 22.0 g. (0.106 mole) of  $\beta$ -benzoyl- $\alpha,\alpha$ -dimethylpropionic acid, 105 g. of amalgamated zinc and 115 ml. of concentrated hydrochloric acid was heated under reflux for 52 hours. Every 12 hours 20 ml. of concd. hydrochloric acid was added to the mixture. At the end of that time the mixture was allowed to cool, and the reduction product isolated on a buchner funnel. The acid was distilled under reduced pressure, b.p. 140–143° (0.2–0.3 mm.); m.p. 97–98°. Sengupta<sup>8</sup> has reported that this acid melts at 98°.

This acid has also been prepared from  $\gamma$ -phenyl- $\alpha,\alpha$ -dimethylisocrotonic acid as follows. Two grams (0.01 mole) of  $\gamma$ -phenyl- $\alpha,\alpha$ -dimethylisocrotonic acid was dissolved in 30 ml. of glacial acetic acid and 100 mg. of palladium-on-carbon catalyst was added. Hydrogenation was accomplished at room temperature and 20 p.s.i. initial hydrogen pressure. Shaking was continued until no further reduction of pressure was observed. The acetic acid solution was diluted with distilled water and the product isolated by suction filtration. After being recrystallized from petroleum ether the product, 1.8 g. (90%), melted at 96–97°. A mixture of this acid and the acid obtained by Clemmensen reduction of  $\beta$ -benzoyl- $\alpha,\alpha$ -dimethylpropionic acid melted at 96–97° also.

**$\gamma$ -Phenyl- $\alpha,\alpha$ -tetramethylenebutyric Acid.**—This acid was obtained by Clemmensen reduction of  $\beta$ -benzoyl- $\alpha,\alpha$ -tetramethylenepropionic acid according to the procedure given for the preparation of  $\gamma$ -phenyl- $\alpha,\alpha$ -dimethylbutyric acid. The reduction was accomplished in 22 hours, and the product was recrystallized from Skellysolve B. It melted at 96.5–97.5° and was obtained in 80% yield.

*Anal.* Calcd. for  $C_{14}H_{18}O_2$ : C, 77.03; H, 8.31. Found: C, 77.50; H, 8.37.

The *p*-bromophenacyl ester of the above acid was prepared according to the method of Shriner and Fuson.<sup>18</sup> The ester melts at 83–84°.

*Anal.* Calcd. for  $C_{22}H_{22}BrO_2$ : C, 63.72; H, 5.61. Found: C, 63.94; H, 5.47.

**1-Oxo-2,2-dimethyl-1,2,3,4-tetrahydronaphthalene.**—This ketone was prepared by cyclization of  $\gamma$ -phenyl- $\alpha,\alpha$ -dimethylbutyric acid by the procedure of Clemo and Dickens.<sup>5</sup> The ketone was obtained in 81% yield; b.p. 124–126° (11 mm.);  $n_D^{20}$  1.5388. Boiling points of 137° (15 mm.)<sup>6</sup> and 150° (27 mm.)<sup>7</sup> have been reported for this ketone.

The oxime of 1-oxo-2,2-dimethyl-1,2,3,4-tetrahydronaphthalene was made by the method of Sengupta.<sup>8</sup> After being recrystallized three times from Skellysolve B the oxime melted at 128–129°. Further crystallization lowered the melting point. Sengupta's oxime melted at 131–132°.

**1-Oxo-2,2-tetramethylene-1,2,3,4-tetrahydronaphthalene.**—A procedure identical with the one used for the preparation of 1-oxo-2,2-dimethyl-1,2,3,4-tetrahydronaphthalene was employed for the production of this compound. Generally about 80% of a product boiling at 166–167° (25 mm.),  $n_D^{20}$  1.5609, was obtained.

*Anal.* Calcd. for  $C_{14}H_{16}O$ : C, 83.95; H, 8.05. Found: C, 83.45; H, 8.01.

The oxime of 1-oxo-2,2-tetramethylene-1,2,3,4-tetrahydronaphthalene was prepared according to the procedure described for the oxime of 1-oxo-2,2-dimethyl-1,2,3,4-tetrahydronaphthalene. This oxime was recrystallized from dilute ethanol and melts at 101–102°.

*Anal.* Calcd. for  $C_{14}H_{17}NO$ : C, 78.10; H, 7.96. Found: C, 77.74; H, 8.05.

(17) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1940, p. 142.

(18) Cf. reference 14, p. 132.

**1-Oxo-2,2-dimethyl-1,2-dihydronaphthalene.**—In a three-necked flask fitted with reflux condenser, liquid-sealed stirrer and dropping funnel was placed a solution containing 10.0 g. (0.05 mole) of 1-oxo-2,2-dimethyl-1,2,3,4-tetrahydronaphthalene in 20 ml. of carbon tetrachloride. This solution was heated by means of a 60-watt frosted bulb placed four inches below the flask. A solution of 10 g. (0.062 mole) of bromine in 20 ml. of carbon tetrachloride was added in 2-ml. portions over a period of one hour. The solvent was removed by distillation and the oily residue heated with 100 ml. of 10% ethanolic potassium hydroxide for one-half hour. After distillation of most of the ethanol, 200 ml. of water was added and the product extracted with ether. The ether solution was dried over anhydrous sodium sulfate, the ether allowed to evaporate and the residue distilled under reduced pressure. The desired ketone distilled at 123–125° (12 mm.); 7.6 g. (77%);  $n_D^{20}$  1.5705.

*Anal.* Calcd. for  $C_{12}H_{12}O$ : C, 83.68; H, 7.03. Found: C, 83.36; H, 7.26.

The oxime of the above ketone was prepared by a process identical with that used for the oxime of 1-oxo-2,2-dimethyl-1,2,3,4-tetrahydronaphthalene. The product tended to form an oil and only after standing for three weeks did the oil form crystals. The semi-solid was recrystallized once from Skellysolve B and twice from dilute ethanol. The final product was a white crystalline solid, m.p. 91–92.5°.

*Anal.* Calcd. for  $C_{12}H_{13}NO$ : C, 76.97; H, 7.00. Found: C, 76.65; H, 7.07.

**1-Oxo-2,2-tetramethylene-1,2-dihydronaphthalene.**—This dienone was prepared in 82% yield by the method used for the preparation of 1-oxo-2,2-dimethyl-1,2-dihydronaphthalene. The product boils at 170–173° (13 mm.);  $n_D^{20}$  1.5932.

*Anal.* Calcd. for  $C_{14}H_{16}O$ : C, 84.81; H, 7.12. Found: C, 84.82; H, 7.35.

The oxime of the above ketone was prepared by the same process as the oxime of 1-oxo-2,2-dimethyl-1,2,3,4-tetrahydronaphthalene. It acted much like the oxime of 1-oxo-2,2-dimethyl-1,2-dihydronaphthalene and was purified in the same way. The compound melts at 109.5–111°.

*Anal.* Calcd. for  $C_{14}H_{15}NO$ : C, 78.84; H, 7.09. Found: C, 78.31; H, 6.87.

**3,4-Dimethyl-1-naphthyl Acetate.**—This compound was obtained by the rearrangement of 1-oxo-2,2-dimethyl-1,2-dihydronaphthalene according to the procedure of Arnold, Buckley and Richter.<sup>3</sup> The reaction gave the acetate, m.p. 84–86°, in 96% yield. After purification the acetate melted at 89.5–91°, and the melting point of a mixture of our acetate and a sample of acetate supplied by Dr. Arnold was 89.5–91°.

**1,2,3,4-Tetrahydro-9-phenanthryl Acetate.**—Rearrangement of 1-oxo-2,2-tetramethylene-1,2-dihydronaphthalene by the Arnold<sup>3</sup> procedure gave this acetate, m.p. 80–81.5°, in 91% yield. The melting point of a mixture of our acetate and a sample of acetate prepared by Arnold, Buckley and Dodson<sup>4</sup> was 80–81.5°.

**3,4-Dimethyl-1-naphthol.**—One gram of 3,4-dimethyl-1-naphthyl acetate was hydrolyzed by heating for five minutes with 20 ml. of 5% methanolic potassium hydroxide. The naphthol was recrystallized from dilute ethanol and melts at 120–122°. Arnold<sup>4</sup> has reported that this naphthol melts at 121.5–123°.

**2-(*p*-Nitrobenzeneazo)-3,4-dimethyl-1-naphthol** was prepared by coupling the above naphthol with *p*-nitrobenzene-diazonium chloride. The deep red coupling product was recrystallized from dilute acetic acid and melts at 243–245°. No attempt was made to purify the dye for analysis although it is apparently a new compound.

**2-Bromo-3,4-dimethyl-1-naphthol.**—The above naphthol was treated with an equimolar amount of bromine in acetic acid solution and allowed to stand until the color had disappeared. The solution was poured into ice-water and the product isolated by suction filtration. The product melts at 99–101°. This compound has been reported<sup>3</sup> to melt at 101–102°.

**1,2,3,4-Tetrahydro-9-phenanthrol.**—The corresponding acetate was hydrolyzed by heating with 5% methanolic potassium hydroxide for ten minutes. After isolation and recrystallization the phenanthrol melted at 103.5–105°. This compound is reported<sup>4</sup> to melt at 105.5–106.5°.

The 3,5-dinitrobenzoate ester of the above phenanthrol was prepared and found to melt at 219–220°. It has been reported<sup>4</sup> to melt at 222°.

**$\gamma$ -Phenyl- $\alpha,\alpha$ -dimethylisocrotonic Acid.**—A mixture of 23.0 g. (0.18 mole) of  $\alpha,\alpha$ -dimethylsuccinic anhydride, 12 g. (0.07 mole) of sodium  $\alpha,\alpha$ -dimethylsuccinate and 26.0 g. (0.24 mole) of freshly distilled benzaldehyde was heated at 190–200° for 60 hours. The reaction mixture was poured into 100 ml. of water and the whole made alkaline to litmus and submitted to steam distillation. The aqueous residue was heated with Norite, filtered and the filtrate acidified with concentrated hydrochloric acid. A light brown precipitate formed and was isolated by suction filtration. After being recrystallized from 50% aqueous ethanol the acid melted at 113–114°; yield 26 g. (75%); neut. equiv., calcd., 190; found, 194.

*Anal.* Calcd. for  $C_{12}H_{14}O_2$ : C, 75.76; H, 7.42. Found: C, 75.64; H, 7.26.

The acid chloride, prepared in 92% yield by reaction with thionyl chloride, boils at 140–142° (11 mm.). When the acid chloride was added to an ether solution of aniline the anilide was produced. After being recrystallized from aqueous ethanol this derivative melted at 113–114°. A mixture of the acid and the anilide melts at 94–99°.

*Anal.* Calcd. for  $C_{18}H_{19}ON$ : C, 81.48; H, 7.22. Found: C, 81.23; H, 7.42.

**$\gamma$ -Phenyl- $\gamma$ -bromo- $\alpha,\alpha$ -dimethylbutyric Acid.**—One gram of the above acid was dissolved in 10 ml. of glacial acetic acid. This solution was cooled in an ice-bath while dry hydrogen bromide was passed into the solution for one-half hour. The solid product was isolated by suction filtration and recrystallized from chloroform, m.p. 110–111°. A mix-

ture of this product and the original acid melted at 94–97°. This material is not stable and loses hydrogen bromide during storage. It is readily hydrolyzed to  $\gamma$ -phenyl- $\alpha,\alpha$ -dimethyl- $\gamma$ -butyrolactone and the structure was assigned on that evidence. The acid could not be purified so as to give a satisfactory analysis.

The same acid was obtained when  $\gamma$ -phenyl- $\alpha,\alpha$ -dimethyl- $\gamma$ -butyrolactone (from  $\beta$ -benzoyl- $\alpha,\alpha$ -dimethylpropionic acid) was treated with dry hydrogen bromide. Prepared by that method the acid melts at 107–109°.

**$\gamma$ -Phenyl- $\alpha,\alpha$ -dimethyl- $\gamma$ -butyrolactone.**—A mixture of 500 mg. of palladium-on-charcoal and 10.3 g. (0.05 mole) of  $\beta$ -benzoyl- $\alpha,\alpha$ -dimethylpropionic acid dissolved in 175 ml. of dioxane was shaken for 19 hours using 30.5 p.s.i. initial hydrogen pressure. Approximately 0.05 mole of hydrogen was taken up. The catalyst was removed by filtration, the solvent by distillation under reduced pressure and the oil residue shaken with 100 ml. of cold saturated sodium bicarbonate solution. The insoluble solid was recovered by filtration and recrystallized from petroleum ether; m.p. 49–50°; yield 7.9 g. (80%).

*Anal.* Calcd. for  $C_{12}H_{14}O$ : C, 75.76; H, 7.42. Found: C, 75.54; H, 7.60.

A sample of the unstable, bromine-containing acid was heated with water for five minutes. When the mixture was cooled a white solid separated which was recrystallized from petroleum ether; m.p. 49–50°. A mixture of this product with the above lactone melted at 49–50°.

CORVALLIS, OREGON

RECEIVED AUGUST 13, 1951

[FROM THE WEIZMANN INSTITUTE OF SCIENCE]

## Infrared Spectra of (Trichloromethyl)-carbinols

BY ERNST D. BERGMANN AND S. PINCHAS

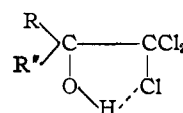
The infrared spectra of acetonechloroform and four aryltrichloromethylcarbinols have been measured in the O–H and the C–Cl regions and compared with the spectrum of phenylmethylcarbinol. An assignment for the bands observed is suggested. The hydroxyl group in the chlorinated alcohols shows only a very slight tendency to participation in hydrogen bonds. This fact is related to the extreme resistance of acetonechloroform to, e.g., esterification reactions.

Gerrard and Wyvill<sup>1</sup> have commented upon the unusual inertness of the hydroxyl group of acetonechloroform (dimethyltrichloromethylcarbinol)  $(CH_3)_2C(OH)CCl_3$ , e.g., in esterification reactions.<sup>2</sup> It seemed interesting to investigate whether this peculiarity is reflected in the infrared absorption of the hydroxyl group in this compound and related substances which have become easily available.<sup>3,4</sup>

Table I summarizes the results obtained; for comparison, the spectrum of phenylmethylcarbinol is included. The apparatus was a Perkin-Elmer Infrared Spectrometer, Model 12 C, with a rock salt prism.

Whilst in phenylmethylcarbinol the band (3330  $cm^{-1}$ ) characteristic for the hydrogen-bonded hydroxyl is strong and that of the free hydroxyl group (3640  $cm^{-1}$ ) weak, the situation is reversed in the chlorinated alcohols, in which also the location of the hydrogen-bonded hydroxyl frequency is shifted, to shorter wave lengths. It follows that in the chlorinated compounds the hydroxyl hydrogen atom participates only to a slight extent

in a hydrogen bond, probably of the intramolecular type



This formula recalls the investigations on the hydrogen bonding in *o*-chlorophenol<sup>5</sup> and in ethylenechlorohydrin.<sup>6</sup> Also in certain substituted 2-aminoethanols, the presence of five-membered hydrogen-bonded rings has been demonstrated by infrared absorption measurements.<sup>7</sup> In the main the hydroxyl group in the trichloroalcohols is free. This may be attributed to the strongly negative inductive effect of the chlorine atoms which causes a firmer bonding of the lone electron pair of the oxygen atom, and thus prevents it from participating in hydrogen bonding. As esterification, in the first stage, also involves this lone electron pair, the difficulty of the esterification of acetonechloroform becomes understandable.

In Table I infrared measurements are also re-

(1) W. Gerrard and P. L. Wyvill, *C. A.*, **44**, 2440 (1950).

(2) Similar inertness has been observed by C. Willgerodt and F. Duerr (*Ber.*, **30**, 539 (1887)) in the corresponding chloride  $(CH_3)_2CClCCl_3$ .

(3) Ch. Weizmann, E. Bergmann and M. Sulzbacher, *THIS JOURNAL*, **70**, 1189 (1948).

(4) E. Bergmann, D. Ginsburg and D. Lavie, *ibid.*, **78**, 5012 (1950).

(5) O. R. Wulf and U. Liddel, *ibid.*, **57**, 1464 (1935); O. R. Wulf, U. Liddel and S. B. Hendricks, *ibid.*, **58**, 2287 (1936).

(6) L. R. Zumwalt and R. M. Badger, *ibid.*, **63**, 305 (1940); compare O. Bastiansen, *Acta Chem. Scand.*, **3**, 415 (1949); J. Glaser and E. E. Turner, *J. Chem. Soc.*, 197 (1951).

(7) E. D. Bergmann, E. Gil-Av and S. Pinchas, unpublished results.