XVII was refluxed for four hours. Most of the excess phosphorus oxychloride was removed by distillation and the residue was poured onto 30 g. of ice. The resulting mixture was heated to boiling, treated with charcoal, filtered and cooled. It was made basic with aqueous sodium hydroxide (10%) yielding a white curdy precipitate. The product was crystallized from ethanol–water mixture from which it formed long silky needles, m. p. 118–119°; lit.[8] gives 119°; yield, 0.4 g. (74%).

Anal. Calcd. for $C_{14}H_{10}ONCl$: C, 69.00; H, 4.30. Found: C, 69.08, 69.23; H, 4.28, 4.41.

1-Morpholino-7-methoxybenzo(f)quinoline (XIX) was formed when 0.3 g. of XVIII and 2 ml. of morpholine was refluxed for eight hours. The mixture was poured into 25 ml. of water and a white precipitate formed. The product was treated with charcoal in dilute hydrochloric acid and regenerated by the addition of alkali. A small amount of gummy impurity was removed at *p*H of 6–7. Two crystallizations from ethanol–water, gave tiny white crystals, m. p. 136–137°.

This compound forms a water soluble yellow hydrochloride and is also soluble in the common organic solvents.

Anal. Calcd. for $C_{16}H_{16}O_2N_2$: C, 73.45; H, 6.16. Found: C, 73.54, 73.23; H, 6.16, 6.23.

1-Piperidino-7-methoxybenzo(f)quinoline (XX) was prepared from XVIII and piperidine, similar to the morpholine analog. The product crystallized from acetone–water mixture as white needles, m. p. 116–117°.

Anal. Calcd. for $C_{19}H_{20}ON_2$: C, 78.06; H, 6.90. Found: C, 78.24; H, 7.13.

(8) Carpmael, English Patent 481,874, *Chem. Zentr.*, **109**, II, 117 (1938).

Summary

1. The preparation of the hydrochlorides of 5-methoxy- and 8-methoxy-2-naphthylamine, respectively, from the corresponding aminonaphthols, has been described.

2. These methoxyamines have been converted to benzo(f)quinoline derivatives by condensation with oxalacetic ester and cyclization of the resulting products.

3. 1-Hydroxy-7-methoxybenzo(f)quinoline yielded 1-chloro-7-methoxybenzo(f)quinoline which gave the 1-substituted amino derivatives with morpholine and piperidine.

4. Apparently steric hindrance by the 10-methoxyl in 1-hydroxy-10-methoxybenzo(f)-quinoline prevented replacement of the hydroxyl group by halogen.

LINCOLN, NEBRASKA RECEIVED JANUARY 31, 1944

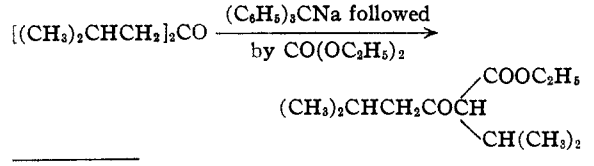
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

The Carbonation and Carbethoxylation of Certain Ketones Using Sodium Triphenylmethide Reagent: β-Keto Ester Synthesis[1,2,3]

BY ERWIN BAUMGARTEN, ROBERT LEVINE AND CHARLES R. HAUSER

Ketones may be converted to β-keto esters by carbethoxylation by means of an alkyl carbonate or by carbonation followed by esterification of the resulting β-keto-acid. Both reactions are brought about by bases. In the present paper, certain examples of these reactions brought about by sodium triphenylmethide are discussed.

Carbethoxylations.—The carbethoxylation of a number of ketones with diethyl carbonate has been effected by means of sodium ethoxide.[4] The reaction has failed, however, with certain ketones in the presence of this base.[4] One of these ketones, di-isobutyl ketone, has now been carbethoxylated with diethyl carbonate by means of the stronger base, sodium triphenylmethide, to form ethyl α-isovalerylisovalerate. Since certain ketones react



with diethyl carbonate in the presence of sodium ethoxide to give an ethyl vinyl carbonate (the "oxygen derivative" of the ketone),[4] instead of the β-keto ester (the "carbon derivative" of the ketone), the β-keto ester obtained in the present case has been characterized not only by the usual ketonic cleavage but also by acidic cleavage. While the regeneration of the original ketone on ketonic cleavage might result from either the β-keto ester or the "oxygen derivative," the formation of isovaleric acid on acidic cleavage could result only from the β-keto ester.

Previous attempts to carbethoxylate methyl ethyl ketone with diethyl carbonate by means of sodium ethoxide[4] or sodium triphenylmethide[5] have failed, presumably because of the ease with which this ketone self-condenses. We have found that the carbethoxylation fails even in the presence of the more reactive carbethoxylating reagent, ethyl 4-phenyl phenyl carbonate, and sodium triphenylmethide.

Carbonations Followed by Esterification.—The carbonation of ketones to form β-keto acids has been carried out previously apparently only with camphor and a few cyclic ketones,[6] sodium amide being used to effect the reaction.

(1) Paper XXIV on "Condensations"; paper XXIII, THIS JOURNAL, **66**, 345 (1944).

(2) Presented at the Pittsburgh meeting of the A. C. S., Sept., 1943.

(3) Supported in part by a grant from the Duke University Research Council.

(4) Wallingford, Homeyer and Jones, THIS JOURNAL, **63**, 2252 (1941).

(5) Abramovitch and Hauser, *ibid.*, **64**, 2271 (1942).

(6) Bredt, *J. prakt. Chem.*, [2] **104**, 9 (1922); [2] **131**, 132 (1932); Gardner, Perkin and Watson, *J. Chem. Soc.*, **97**, 1756 (1910); Koetz and Grethe, *J. prakt. Chem.*, [2] **80**, 473 (1909).

In the present investigation methyl ethyl, methyl *t*-butyl, di-isopropyl and di-isobutyl ketones have been carbonated using sodim triphenylmethide and the resulting β-keto acids esterified with diazomethane to give, respectively, methyl propionylacetate (37%), methyl γ,γ,γ-trimethylacetylacetate (58%), methyl α-iso-butyrylisobutyrate (56%) and methyl α-isovalerylisovalerate (42%). None of these β-keto esters, or the corresponding ethyl esters, can be prepared satisfactorily by means of sodium alkoxides. The formation of methyl propionylacetate from methyl ethyl ketone, for example, may be represented as follows.

$$C_2H_5COCH_3 \xrightarrow[\text{by } CO_2 \text{ and acid}]{(C_6H_5)_3CNa \text{ followed}}$$
$$C_2H_5COCH_2COOH \xrightarrow{CH_2N_2} C_2H_5COCH_2COOCH_3$$

Desoxybenzoin appeared to form the corresponding β-keto acid in good yield but it decomposed before it could be esterified. The pronounced instability of this acid has been observed previously.[7]

Methyl propionylacetate has been characterized by several reactive hydrogen and carbonyl group reactions. With phenylhydrazine, methyl propionylacetate gave a pyrazolone, identical with that obtained from authentic ethyl propionylacetate, although the yield of the derivative from the methyl β-keto ester was low. That carbonation occurred at the methyl group of methyl ethyl ketone, rather than at the methylene group, was confirmed by the alkylation of the propionylacetate with *n*-butyl bromide and subsequent ketonic cleavage of the alkylated product to give ethyl *n*-amyl ketone in good yield.

$$C_2H_5COCH_2COOCH_3 \xrightarrow{n\text{-}C_4H_9Br}$$
$$C_2H_5COCH(C_4H_9)COOCH_3 \longrightarrow C_2H_5COC_5H_{11}$$

Methyl γ,γ,γ-trimethylacetylacetate has been characterized by the formation of a phenylpyrazolone and by ketonic cleavage. Methyl α-isobutylisobutyrate and methyl α-isovalerylisovalerate, which do not exhibit satisfactory reactive hydrogen and carbonyl group reactions, have been characterized by both acidic and ketonic cleavage.

Carbonations *versus* Carbethoxylations Using Sodium Triphenylmethide.—The mechanism of the carbonation of ketones is represented by the ionic[8] equations (1) and (2), while that for the carbethoxylation of ketones (which is similar to that for the acetoacetic ester reaction[9]) is represented in somewhat simplified form by the equations (1), (3) and (4).

$$(1)\quad RCOCH_2R' + (C_6H_5)_3C^- \longrightarrow [RCOCHR']^- + (C_6H_5)_3CH$$
$$(2)\quad [RCOCHR']^- + CO_2 \longrightarrow RCOCHR'COO^-$$
$$(3)\quad [RCOCHR']^- + CO(OC_2H_5)_2 \longrightarrow RCOCHR'COOC_2H_5 + C_2H_5O^-$$
$$(4)\quad RCOCHR'COOC_2H_5 + [RCOCHR']^- \longrightarrow [RCOCR'COOC_2H_5]^- + RCOCH_2R'$$

One mole of sodium triphenylmethide ion converts one mole of the ketone essentially completely into its anion (1). In the carbonation, the ketone anion condenses with carbon dioxide to form the carboxylate anion (2) which does not appear to react further[10] under the conditions employed; in the carbethoxylation, however, the ketone anion condenses with diethyl carbonate to form a β-keto ester (3) which generally undergoes a rapid proton exchange with unchanged ketone anion regenerating one-half of the original ketone (4). Thus, on the basis of these mechanisms, one mole of sodium triphenylmethide reagent may effect the carbonation of one mole of the ketone, but the carbethoxylation of only one-half mole of ketone.

Actually, per mole of sodium triphenylmethide the yield of α-isovalerylisovaleric ester obtained by the carbonation of di-isobutyl ketone followed by esterification has been much better than that obtained by the carbethoxylation of the same ketone. Similarly, the carbonation of methyl ethyl ketone followed by esterification gave a higher yield of propionylacetic ester per mole of sodium triphenylmethide used than the acylation of ethyl acetate with 4-phenylphenyl propionate,[5] the mechanism of which is similar to a carbethoxylation.

In general, for the synthesis of β-keto esters using sodium triphenylmethide, the method of carbonation of ketones followed by esterification is probably to be preferred to that of the carbethoxylation of ketones or that of the acylation of esters with esters.

Experimental[11]

Preparation of Ketone Anions (Sodium Derivatives).—Sodium triphenylmethide reagent was prepared from one mole of triphenylchloromethane and analyzed.[12,13] By means of the apparatus described elsewhere,[14] approximately two-tenths mole aliquots of the reagent were transferred to one-liter Pyrex bottles. In most cases, the reagent was chilled, air being excluded by an atmosphere of nitrogen. A molecular equivalent of the ketone was added to the reagent with shaking; the ketone anion was formed instantaneously as shown by the discharge of the characteristic color of the reagent. The solution of the ketone anion thus formed was used immediately for the carbonation and carbethoxylation reactions described below.

Ethyl α-Isovalerylisovalerate.—Di-isobutyl ketone (28.4 g., 0.2 mole) was converted to its anion at 0° and the

(7) Beckmann and Paul, *Ann.*, **266**, 1 (1891).

(8) The representation of the reactions of only the anions is simpler and, we believe, adequate for the present purpose, although the positive sodium ion also might play an important role in the detailed mechanism in the ether medium. In this connection, see Morton, Little and Strong, THIS JOURNAL, **65**, 1339 (1943).

(9) See Hauser and Hudson, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1942, Chapter 9.

(10) In certain cases, however, the further carbonation of the carboxylate ion has been observed; see Gilman and Pacewitz, THIS JOURNAL, **62**, 1301 (1940).

(11) Microanalyses by Dr. T. S. Ma, University of Chicago, Chicago, Ill.

(12) Hudson and Hauser, THIS JOURNAL, **63**, 3156 (1941).

(13) Hauser and Hudson, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1943, 2nd Coll. Vol., p. 609 (Note 3).

(14) Baumgarten and Hauser, THIS JOURNAL, **66**, 1037 (1944).

resulting solution was carbethoxylated with 23.7 g. (0.2 mole) of diethyl carbonate. After seven days at room temperature glacial acetic acid and water were added to the reaction mixture. The ether phase (after extraction with saturated bicarbonate solution) was dried (sodium sulfate followed by "Drierite") and the solvent removed at atmospheric pressure. The residue was distilled *in vacuo* (up to 170° 15 mm.); the distillate gave on redistillation 11 g. (50%) of ethyl α-isovalerylisovalerate, b. p. 118–119.5° (15 mm.).[12]

Ethyl α-isovalerylisovalerate was characterized by ketonic cleavage[15] to di-isobutyl ketone, identified by its semicarbazone, m. p. 121–122°.[16] Acidic cleavage was carried out by refluxing for two hours a solution of 2 g. of ethyl α-isovalerylisovalerate and 0.03 mole of sodium ethoxide in 25 ml. of absolute ethanol, diluting with 5 ml. of water and refluxing for two hours longer. The solvent was evaporated and the solid residue was heated with an excess of thionyl chloride for thirty minutes. The crude acid chloride was converted[17] to isovaleryl anilide, m. p. 109–111°.[18]

Methyl Ethyl Ketone with Ethyl 4-Phenylphenylcarbonate.—The carbethoxylation of the anion of methyl ethyl ketone (0.2 mole, prepared at 0°) with 48.4 g. (0.2 mole) of ethyl 4-phenylphenyl carbonate[19] gave after four and one-half hours at room temperature 9.2 g. of material, b. p. 60–80° (20 mm.) (mainly at 64–69° 20 mm.), consisting presumably of 3-methylheptene-3-one-5 (reported, 66–68°).[5]

Carbonation Followed by Esterification: General Procedure.—The ether solution of the ketone anion, prepared as described above, was transferred onto an approximately ten-fold excess of Dry-Ice by means of a siphon under nitrogen pressure. After the excess of Dry-Ice had evaporated, water and ether were added to the mixture with shaking. The aqueous phase was combined with an ice-cold alkaline extract of the ether phase and acidified with iced mineral acid. The liberated β-keto acid was taken up in ether and the ether solution was dried with sodium sulfate at 0°. Esterification of the β-keto acid was effected with a 10–20% excess of diazomethane[20] (prepared from nitrosomethyl urea), and the excess diazomethane destroyed with glacial acetic acid, which in turn was removed by saturated sodium bicarbonate solution. The ether solution of the β-keto ester was dried over sodium sulfate followed by "Drierite" and the product was isolated by distillation.

Methyl Propionylacetate.—Methyl ethyl ketone (22.4 g., 0.312 mole) was converted at −15° to its anion which was carbonated immediately. Ether and the minimum of water (200 ml.) were added and the ether solution was extracted with 100 ml. of 5% sodium hydroxide solution. The combined aqueous solutions (washed with ether) were acidified with 75 ml. of 12 *N* hydrochloric acid in 100 g. of crushed ice, saturated with sodium chloride and extracted with successive 200-ml. portions of ether until the extract was substantially free from titratable acidity. The combined ether extracts, containing 0.22 equivalent of acid, were dried and esterified as indicated above. Material boiling up to 77° (15 mm.) was redistilled, giving 4.2 g. of a combined fore-run, b. p. 71–73° (16 mm.), and after-run, b. p. 76–78° (16 mm.), and 15.1 g. (37%) of methyl propionylacetate, b. p. 73–76° (16 mm.). A mid-fraction was analyzed.

Anal. Calcd. for $C_6H_{10}O_3$: C, 55.37; H, 7.74. Found: C, 55.04; H, 7.57.

With ammoniacal copper acetate solution, methyl propionylacetate formed a copper salt, m. p. 154–156°, and m. p. 160.3–160.9° after recrystallization from benzene–petroleum ether. With phenylhydrazine in glacial acetic acid solution, the β-keto ester gave, after recrystallization from very dilute ethanol, a low yield of 3-ethyl-1-phenylpyrazolone-5, m. p. and mixed m. p. 97–98° (reported,[21] 100°).

Methyl propionylacetate (26 g., 0.2 mole) was alkylated with an equivalent of sodium methoxide and an excess of *n*-butyl bromide in methanolic solution at 60° for seventy-two hours. Sodium bromide was removed by filtration and the solution concentrated. The reaction mixture was diluted with iced dilute hydrochloric acid and extracted with ether. The ether solution (neutralized with sodium bicarbonate and dried) was distilled, yielding 17.5 g. (47%) of methyl α-butylpropionylacetate, b. p. 108–120° (16 mm.). Redistillation gave 11 g., b. p. 108–112° (16 mm.).

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 65.24; H, 9.54.

Ketonic cleavage of 9.3 g. (0.05 mole) of methyl α-butylpropionylacetate in glacial acetatic acid-sulfuric acid mixture[15] gave 4.3 g. (67%) of ethyl *n*-amyl ketone, b. p. 160–166° (mainly 163–165°) (reported, 167–168°).[22] The crude semicarbazone melted at 92–98° and after seven recrystallizations from ether–petroleum ether the pure derivative melted at 116–117°.[23] The 2,4-dinitrophenylhydrazone formed in methanolic hydrochloric acid solution melted at 55–59° (crude) and after two recrystallizations from methanol at 64–65.5°.

Methyl γ,γ,γ-Trimethylacetylacetate.—The anion of pinacolone, prepared at 0° from 19.0 g. (0.19 mole) of pinacolone, was carbonated immediately. γ,γ,γ-Trimethylacetylacetic acid was liberated and esterified as described above. There were obtained 1.6 g. of a fore-run, b. p. 80–82° (17 mm.), and 17 g. (57%) of methyl γ,γ,γ-trimethylacetylacetate, b. p. 82–84° (17 mm.).

Anal. Calcd. for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.94; H, 8.93.

Ketonic cleavage[16] of methyl γ,γ,γ-trimethylacetylacetate gave a 50% yield of pinacolone, b. p. 104–106°. Semicarbazone, m. p. 154.5–156° (reported, 157–158°).[24] Reaction of the β-keto ester with an equivalent of phenylhydrazine gave a 40% yield of 3-*t*-butyl-1-phenylpyrazolone-5, m. p. 110.5–111°.[25]

Methyl α-Isobutyrylisobutyrate.—The anion of di-isopropyl ketone, prepared from 22.8 g. (0.2 mole) of di-isopropyl ketone at 0°, was carbonated. α-Isobutyrylisobutyric acid was liberated and esterified as described. Distillation gave 1.1 g. of fore-run, b. p. 92–94° (26 mm.), 19 g. (55%) of methyl isobutyrylisobutyrate, b. p. 94–96° (26 mm.), and 10 g. of after-run, b. p. 96–98° (26 mm.).

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.76; H, 9.37. Found: C, 62.75; H, 8.96.

Ketonic cleavage[16] of methyl α-isobutyrylisobutyrate gave a 54% yield of di-isopropyl ketone, b. p. 123–124.5°; m. p. of semicarbazone 157–157.5° (reported, 160°).[26] Acidic cleavage gave isobutyric acid, identified by its anilide, m. p. 104–106°.[27]

Methyl α-Isovalerylisovalerate.—The anion of di-isobutyl ketone, prepared at 0° from 28.4 g. (0.2 mole) of di-isobutyl ketone, was carbonated. Isovalerylisovaleric acid was liberated and esterified as described. There were obtained 0.6 g. of fore-run, b. p. 111–114° (19 mm.), 17 g. (42%) of methyl α-isovalerylisovalerate, b. p. 114–116.5° (19 mm.), and 0.4 g. of after-run, b. p. 116.5–118° (19 mm.).[28]

Anal. Calcd. for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.58; H, 9.47.

(15) Hudson and Hauser, THIS JOURNAL, 63, 3163 (1941).

(16) Spielman and Schmidt, *ibid.*, 59, 2010 (1937).

(17) Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1935, p. 144.

(18) Underwood and Gale, THIS JOURNAL, 56, 2119 (1934).

(19) Baumgarten, Walker and Hauser, *ibid.*, 66, 303 (1944).

(20) Arndt, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1943, 2nd Coll. Vol. p. 166 (Note 3), p. 461.

(21) Blaise, *Compt. rend.*, 132, 978 (1901).

(22) Bouveault and Locquin, *Bull. soc. chim.*, [3] 31, 1158 (1904).

(23) Whitmore and Williams, THIS JOURNAL, 55, 410 (1933).

(24) Gilman and Nelson, *Rec. trav. chim.*, 55, 529 (1936).

(25) Wahlberg, *Ber.*, 44, 2072 (1911).

(26) Hauser and Renfrow, THIS JOURNAL, 59, 1823 (1937).

(27) Fieser and Campbell, *ibid.*, 60, 168 (1938).

(28) This experiment yielded a relatively large amount of high boiling material. Distillation through a 5" "Vigreux" column gave 6.1 g. of distillate, b. p. 60–130° (5 mm.), without separation.

Ketonic cleavage[15] of methyl α-isovalerylisovalerate gave a 63% yield of di-isobutyl ketone, b. p. 164–166°. The semicarbazone melted at 121.2–121.8°.[16] Acidic cleavage gave isovaleric acid, identified by its anilide, m. p. 109–111°.[18]

Summary

1. The carbethoxylation of di-isobutyl ketone with diethyl carbonate, which fails in the presence of sodium ethoxide, has been effected by means of sodium triphenylmethide to form ethyl α-isovalerylisovalerate. An attempt to carbethoxylate methyl ethyl ketone using this base in conjunction with ethyl 4-phenylphenyl carbonate has failed.

2. Four ketones, which are not carbethoxylated in the presence of sodium ethoxide, have been carbonated using sodium triphenylmethide and the resulting β-keto acids esterified with diazomethane to form the corresponding methyl β-keto esters.

3. The β-keto esters have been characterized by suitable reactions. The methyl group of methyl ethyl ketone was shown to undergo carbonation.

4. The relative amounts of carbonation and carbethoxylation of ketones that sodium triphenylmethide is capable of effecting is considered in connection with the mechanism of these reactions.

DURHAM, N. C. RECEIVED FEBRUARY 29, 1944

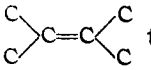
[CONTRIBUTION FROM THE HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

Resin Acids. The Structure of the Lactone of Hydroxytetrahydroabietic Acid[1]

BY RICHARD F. B. COX

The lactonization of dihydroabietic acids derived from abietic and levo-pimaric acids has always led to a single individual lactone melting at 131–132°. No stereoisomeric lactones have yet been produced from these dihydroabietic acids even though acids of rotations −30° to +108° have been investigated. This lactone appears, therefore, to be characteristic of the abietic family of dihydro acids.

Although the lactone has been known for many years[2a] there is very little known about its structure. Hasselstrom[2b] at one time suggested that on the basis of a γ-lactone structure the point of lactonization is probably C-10. Fleck and Palkin[3] then attempted to prove this structure by oxidizing the hydroxytetrahydroabietic acid obtained on saponification of the lactone. Under no conditions were they able to effect an oxidation to a keto acid which would be expected on the basis of Hasselstrom's formula. Moreover, they were unable to esterify the hydroxyl group of the free acid or its methyl ester. They concluded, therefore, that the hydroxyl group must be in a tertiary position which, to fit the molecular models, must be at C-4b.[2a]

It was expected that more concrete evidence in favor of formula I for the lactone might be given by an investigation of the reactions of the dihydroabietic acids produced by dehydration of the hydroxytetrahydroabietic acid. For example, only the Fleck and Palkin formula would be expected to lead to a dihydroabietic acid (4b, 8a) having the  type of double bond which will give a blue nitrosyl chloride derivative.

The stability of the lactone and the ease of lactonization of the hydroxytetrahydroabietic acid under dehydration conditions appeared at first to oppose this method of approach. It was then discovered in the course of our work on resin acids that the lactone underwent a reaction with methylmagnesium iodide which resembled a dehydration in that the product was a mixture of dihydroabietic acids.

The reaction appeared to be an abnormal Grignard reaction as a result of the highly hindered position of the carbonyl group of the lactone. One mechanism to explain the results is shown below.

According to this mechanism, the methylmagnesium iodide first forms a coördination complex (II) with the lactone, as a result of which the carbonyl carbon becomes deficient in electrons. The resulting increased attraction for the oxygen in the bridge then causes the formation of a carbonyl from this oxygen and a shift in the electron deficiency to C-4b. Simultaneously the methyl radical is freed to combine with the activated protons at positions 8a and 5 (III). The end-result of this rearrangement is thus the formation of the dihydroabietic acids as their magnesium salts (IV and V).

Since the gases produced in the reaction included hydrogen, it appears as though the protons at C-5 and C-8a have been displaced completely to combine either with another proton or the methyl radical. Thus the presence of hydrogen leads to the assumption that part of the

(1) Presented before the Division of Organic Chemistry at the 106th meeting of the American Chemical Society, Pittsburgh, Pennsylvania, September 7, 1943.

(2a) Ruzicka and Meyer, *Helv. Chim. Acta*, **5**, 333 (1922); Ruzicka, Waldmann, Meier and Hösli, *ibid.*, **16**, 178 (1933).

(2b) Hasselstrom and McPherson, THIS JOURNAL, **60**, 2340 (1938).

(3) Fleck and Palkin, THIS JOURNAL, **61**, 3197 (1939).