tion at atmospheric pressure through a column, the residue was distilled under reduced pressure. After a small forerun, a fraction of 3.20 g. was collected, b.p. 91–94° (20 mm.), n^{25}D 1.4776. This fraction then was heated at 165° for 30 minutes with excess potassium and redistilled, yield 2.44 g. (26%), b.p. 90.0–91.0° (20 mm.), n^{25}D 1.4764, d^{25}_4 0.8855.

Anal. Found: C, 87.05; H, 12.61.

A higher boiling fraction and the distillation residue were combined and chromatographed on alumina. Elution with pentane yielded an additional 2.74 g. (29%) of *trans*-9-methyldecalin. Elution with ether and recrystallization from aqueous ethanol gave 0.70 g. (6.8%) of *trans*-9-decalylcarbinol, m.p. 83.8–84.5° (lit.[2,19] 84.2–84.6°).

Aluminum Chloride Isomerization of *trans*-9-Methyldecalin.—The pure hydrocarbon (0.75 g.) was allowed to stand over 0.25 g. of aluminum chloride for 6 days. The product was extracted with pentane, washed with sodium bicarbonate solution and the pentane removed by distillation. The residue was distilled through a short-path molecular type still at a pressure of 70 mm. and a block temperature of 90°. This afforded 0.61 g. (81%) of material, n^{25}D 1.4638.

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[CONTRIBUTION FROM THE ROLLIN H. STEVENS MEMORIAL LABORATORY OF THE DETROIT INSTITUTE OF CANCER RESEARCH]

The Reformatsky Reaction with 2-Hydroxymethylenecyclohexanone. 5,6,7,8-Tetrahydrocoumarin[1]

BY ANDRE S. DREIDING AND ARTHUR J. TOMASEWSKI

RECEIVED APRIL 26, 1954

The Reformatsky reaction of 2-hydroxymethylenecyclohexanone (II) with methyl bromoacetate produced a 25% yield of 5,6,7,8-tetrahydrocoumarin (I) and a 30% yield of a diene–diester fraction. The structure of I was proven by its conversion with alkali to β-(2-ketocyclohexylidene)-propionic acid (VII, R = H) under mild conditions and to cyclohexanone under stronger conditions. The pyrone (I) readily reacted with maleic anhydride. Saponification of the diene–diester fraction gave β-(2-carboxymethyl-1-cyclohexene)-acrylic acid (XII, R = H) (or possibly a double bond isomer). An examination of the Reformatsky product from the benzoate of 2-hydroxymethylenecyclohexanone (XVI) and ethyl bromoacetate verified the previously assigned structure as 2-benzoyloxymethylene-1-carbethoxymethylcyclohexanol (XVII, R = C_2H_5). It was converted to 2-carbethoxymethyl-1-cyclohexenecarboxaldehyde (X, R = C_2H_5) with acid and to 1-acetylcyclohexene (XXI) with alkali.

In continuation of our investigation of the use of hydroxymethylene ketones as starting materials for certain syntheses,[2] we have subjected 2-hydroxymethylenecyclohexanone (II) to a Reformatsky reaction with 3.1 moles of methyl bromoacetate in ether. The two major products were separated by fractional distillation.

The lower boiling product, $C_9H_{10}O_2$, m.p. 64.5–65°, 25% yield, was soluble in concentrated hydrochloric acid and in 10% sodium hydroxide, but not in water. It did not react with 2,4-dinitrophenylhydrazine in 50% sulfuric acid, but it did form a red 2,4-dinitrophenylhydrazone after being treated with alkali and then acidified. These reactions, as well as the absorption spectrum, $\lambda^{\text{alc}}_{\text{max}}$ 309 mμ (ϵ 7,000), are consistent with an α-pyrone structure.[3]

Two alternative structures can be proposed for an α-pyrone of this empirical formula, formed in this Reformatsky reaction. It is likely, as it was in the case of the reaction of II with Grignard reagents,[2] organolithium compounds[2] and lithium aluminum hydride,[4] that the Reformatsky reagent first reacted with the active hydrogen of II to give the enolate salt V. The latter could condense further with the reagent at position a or b, and thus form either IV or VI. By a loss of a molecule each of bromozinc methoxide and bromozinc hydroxide, IV could be converted to 5,6,7,8-tetrahydrocoumarin (I) directly in the Reformatsky medium, while VI could form 4,5-tetramethylene-α-pyrone (III) in the same manner.

An α-pyrone with structure I has not been previously described while structure III has been assigned by Plattner, Treadwell and Scholz[5] to an unstable oil, b.p. 120–130° at high vacuum, which solidified on cooling and liquefied at about 28°. This incomplete characterization as well as some uncertainty as to the structure (see below) did not allow a conclusion on the structure of the Reformatsky product and it was thus necessary to adduce independent evidence: A treatment of the pyrone with 5% alkali produced an 81% yield of cyclohexanone. This can best be rationalized on the basis of structure I for the pyrone, which must have suffered a hydrolysis, ring opening followed by hydration and retroaldolization.[6] Confirmation of structure I was obtained from the mild alkaline hydrolysis which yielded β-(2-ketocyclohexylidene)-propionic acid (VII, R = H) as the 2,4-dinitrophenylhydrazone, whose ultraviolet absorption spectrum was almost identical with that of the derivative of 2-ethylidenecyclohexanone,[2] but differed from that of 2-methyl-1-cyclohexenecarboxaldehyde (XVIII)[2] (see below).

On this basis, it can be concluded that the lower boiling fraction of the Reformatsky product is 5,6,7,8-tetrahydrocoumarin (I). It is of interest that the palladium-catalyzed dehydrogenation did not yield coumarin. I readily underwent a Diels–Alder reaction with maleic anhydride in boiling xylene to give a high melting product (possibly XIII), which may have resulted from the introduc-

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[1] This work was supported by institutional grants to the Detroit Institute of Cancer Research from the American Cancer Society, Inc., the American Cancer Society, Southeastern Michigan Division and The Kresge Foundation.

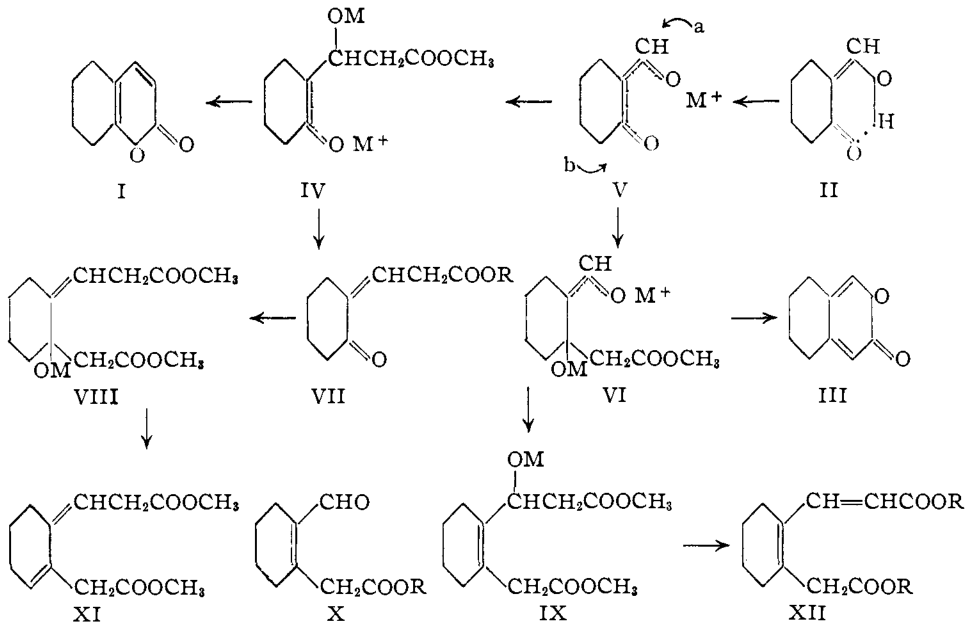
[2] A. S. Dreiding and S. N. Nickel, THIS JOURNAL, **76**, 3965 (1954).

[3] J. Fried and R. C. Elderfield, *J. Org. Chem.*, **6**, 266 (1941).

[4] A. S. Dreiding and J. A. Hartman, THIS JOURNAL, **75**, 939 (1953).

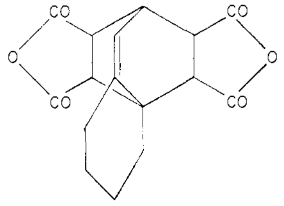
[5] Pl. A. Plattner, P. Treadwell and C. Scholz, *Helv. Chim. Acta*, **28**, 771 (1945).

[6] This term is used to designate the reverse process of an aldolization or aldol condensation.



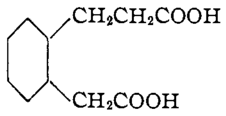
M = ZnBr

tion of two molecules of maleic anhydride and the elimination of carbon dioxide.[7] 5,6,7,8-Tetrahydrocoumarin (I) has been found to be a potent blastokolin.[8]



XIII

The higher boiling fraction of the Reformatsky product consisted of a 30% yield of a mixture of unsaturated diesters, which, after treatment with sodium ethoxide, followed by saponification, afforded a single diene–diacid, m.p. 217–218.5°, in 93% yield. The carbon skeleton was established by catalytic hydrogenation of the acid to the known *cis*-β-(2-carboxymethylcyclohexane)-propionic acid (XIV).[10] Evidently two acetic ester moieties had been introduced into 2-hydroxymethylenecyclohexanone. This might have occurred either by path II → V → IV → VII → VIII → XI or by scheme II → V → VI → X → IX → XII, which are similar to the reaction courses proposed for the lithium aluminum hydride reduction of II.[4] The assumption that the Reformatsky diester fraction contains XI and XII ($R = CH_3$) is in agreement with the two maxima in its ultraviolet absorption spectrum. The peak at 238 mμ could be due to XI, which is the expected absorption of a tetra-substituted diene with an exocyclic double bond,[11] while the peak at 275 mμ is similar to that of several α,β,γ,δ-unsaturated acids[12] and thus may be due to XII ($R = CH_3$). The diene–diacid, m.p. 218°, showed a single absorption maximum at 276 mμ, which indicates that it possibly has structure XII ($R = H$).[13] Since the absorption of the ester at 238 mμ was removed by the saponification, it must be concluded that the alkaline treatment caused a shift of one or both of the the double bonds in XI to a more stable position.



XIV

If the first step in the Reformatsky reaction of II is indeed the formation of the enolate salt V then the introduction of two acetic ester residues can be rationalized as being due to the ability of the intermediates (IV and VI) to lose an oxygen as a zinc salt and thus free another carbonyl group (as in VII and X) for a further Reformatsky reaction. As in the lithium aluminum hydride reductions,[2,4] such a loss of an oxygen did not occur when an enolic derivative of II was used: Plattner, Treadwell and Scholz[5] showed that the Reformatsky reaction with the benzoate of 2-hydroxymethylenecyclohexanone (XVI) and ethyl bromoacetate in benzene resulted in the introduction of only one acetic ester residue.

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[7] M. Kloetzel in R. Adams, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 37.

[8] Miss Gloria Bellinger of this Laboratory has found that 5,6,7,8-tetrahydrocoumarin inhibited the germination of melon seeds in dilutions of 1:1,000 and 1:10,000 at 37° to a slightly greater extent than coumarin.[9]

[9] R. Kuhn, D. Jerchel, F. Moewus and E. F. Moeller, *Naturwiss.*, **31**, 468 (1943); A. Kroeckemann, *Ber.*, **52**, 523 (1934).

[10] L. Helfer, *Helv. Chim. Acta*, **6**, 785 (1923); A. Skita, *Ber.*, **57B**, 1977 (1924); J. W. Barrett, A. H. Cook and R. P. Linstead, *J. Chem. Soc.*, 1065 (1935).

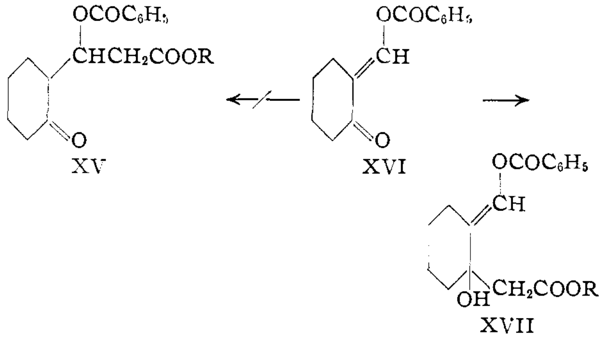
[11] R. B. Woodward, THIS JOURNAL, **64**, 72 (1942).

[12] K. Dimroth, *Angew. Chem.*, **52**, 551 (1948); W. E. Bachmann and A. S. Dreiding, *J. Org. Chem.*, **13**, 317 (1948); A. S. Dreiding and R. J. Pratt, THIS JOURNAL, **75**, 3717 (1953).

[13] The possibility that the diene–diacid and its ester may be double bond isomers of XII cannot be excluded with certainty on the basis of the ultraviolet absorption characteristics alone. The carbon skeleton of the acid could accommodate three more α,β,γ,δ-unsaturated acid structures, two with a *transoid* and one with a *cisoid* arrangement of the double bonds. Another possible structure would be that of a homoannular conjugated diene, not conjugated with a carboxyl group, the absorption of which can be calculated to be near 273 mμ.[14]

[14] L. Dorfman, *Chem. Rev.*, **53**, 122 (1953).

These authors assigned structure XVII (R = C_2H_5) to the product and consequently considered the α-pyrone derived from it as III.

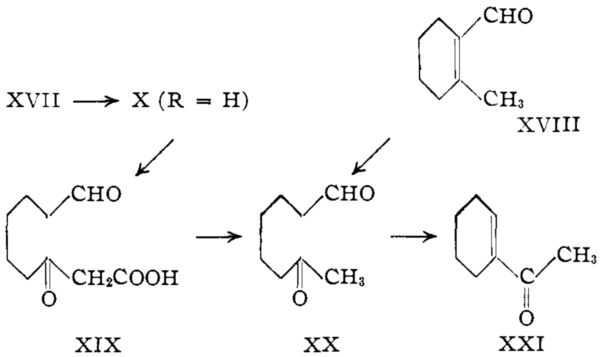


Since the isopropyl ether of II showed a considerable tendency toward 1,4-addition even with organolithium compounds,[2] it was considered advisable to examine the possible consequences if 1,4-addition had occurred in Plattner's Reformatsky reaction with XVI. This possibility, which would have resulted in XV and then in I, was not excluded by the properties described by Plattner, Treadwell and Scholz[5] for their Reformatsky product or pyrone.

It has now been found that this Reformatsky ester has an absorption peak at 2.89 μ, indicating the presence of a hydroxyl group, which is consistent with structure XVII but not XV. Further confirmation of structure XVII was obtained from the mild acid hydrolysis in the presence of 2,4-dinitrophenylhydrazine, which yielded the 2,4-dinitrophenylhydrazone of 2-carbethoxymethyl-1-cyclohexenecarboxaldehyde (X, R = C_2H_5) with an ultraviolet absorption spectrum almost identical with that of the derivative of 2-methyl-1-cyclohexenecarboxaldehyde (XVIII).[2]

A better yield (65%) of a more easily isolated product was obtained when Reformatsky reaction of XVI was conducted with methyl bromoacetate in ether. The ester (XVII, R = CH_3) also exhibited an absorption peak at 2.89 μ and yielded the 2,4-dinitrophenylhydrazone of X (R = CH_3).

When the Reformatsky ester (XVII, R = C_2H_5) was subjected to a steam distillation from 7% sodium hydroxide, a 73% yield of 1-acetylcyclohexene (XXI) was isolated as the 2,4-dinitrophenylhydrazone. The conversion was probably brought about by successive saponification, hydration, retroaldolization,[6] decarboxylation, aldolization and dehydration (XVII → X(R = H) → XIX → XX → XXI). This was confirmed by the observation that the 2-methyl-1-cyclohexenecarboxaldehyde (XVIII)[2] under the same conditions also afforded 1-acetylcyclohexene (XXI).



We are grateful to Dr. J. M. Vandenbelt and Mr. Bruce Scott of Parke, Davis and Company for the measurements and discussions of the ultraviolet and infrared absorption spectra mentioned in this paper.

Experimental[15]

Reformatsky Reaction with 2-Hydroxymethylenecyclohexanone (II) and Methyl Bromoacetate.—A mixture of 32 g. (0.25 mole) of II[5] (b.p. 39–40° at 0.1 mm.), 40 g. (0.26 mole) of methyl bromoacetate, 40 g. of granular zinc and 500 cc. of dry ether was brought to the boiling point when an exothermic reaction started spontaneously. In 10-minute intervals, two further portions of 40 g. of bromoester and 40 g. of zinc each were added and the mixture, which had become turbid, was heated for 30 minutes. After the addition of cold dilute acetic acid, the ethereal layer was separated, the aqueous layer was saturated with sodium chloride and extracted with ether, and the combined ethereal solution washed with dilute hydrochloric acid and saturated sodium chloride solution. The dried solution was concentrated and the residue distilled through a 6 inch Vigreux column to give, after a forerun of 10 g., b.p. 20–80° at 10 mm., 31 g. of Reformatsky products, b.p. 120–146° (1 mm.). After two redistillations, the product separated into two fractions: (a) b.p. 115–123° (1 mm.), yield 9.5 g.; and (b) b.p. 120–142° (0.75 mm.), yield 18 g.

Fraction (a) solidified and remained solid at room temperature. It represented a 25% yield of crude **5,6,7,8-tetrahydrocoumarin** (I) which, after two recrystallizations from ether–petroleum ether, melted at 64.5–65°; $\lambda_{\max}^{\text{alc}}$ 309 mμ (ε 7,000), $\lambda_{\min}^{\text{alc}}$ 245 mμ (ε 600), $\lambda_{\text{infl}}^{\text{alc}}$ 222 mμ (ε 2,900); $\lambda_{\max}^{\text{mineral oil}}$ 5.82(s), 6.08(s), 6.42(s), 6.85(m), 7.26 (w), 7.35(m), 7.79(w), 8.09(m), 8.31(m), 8.52(w), 8.72(w), 8.89(m), 9.17(m), 9.25(m), 9.39(w), 10.27(m-w), 10.61 (m-w), 11.04(w), 11.35(m), 11.71(m), 11.83(m), 12.17(w), 13.22(w), 14.05(m) μ.

Anal. Calcd. for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 72.06; H, 7.05.

5,6,7,8-Tetrahydrocoumarin (I) does not form an insoluble picrate and did not give a color with alcoholic ferric chloride. It is insoluble in aqueous sodium bicarbonate, but it dissolves readily in cold concentrated hydrochloric acid and in warm dilute sodium hydroxide to give a yellow solution. It does not form a 2,4-dinitrophenylhydrazone in 25% sulfuric acid. Unless very pure, it slowly decomposes on standing at room temperature.

Fraction (b) consisted of a 30% yield of a mixture containing **methyl β-(2-carbomethoxymethyl-2-cyclohexenylidene)-propionate** (XI) and **methyl β-(2-carbomethoxymethyl-1-cyclohexene)-acrylate** (**XII, R = CH_3**) (consider also double bond isomers of XII); $\lambda_{\max}^{\text{alc}}$ 238 and 275 mμ (ε 7,030 and 5,950), $\lambda_{\min}^{\text{alc}}$ 257 mμ (ε 4,560).

A solution of 550 mg. of this mixture of diene–diesters in alcoholic sodium ethoxide (made from 220 mg. of sodium and 20 cc. of absolute alcohol) was refluxed for 30 minutes. Some water was added and some of the alcohol was distilled out. Cooling and acidification precipitated 450 mg. (93% yield) of **β-(2-carboxymethyl-1-cyclohexene)-acrylic acid** (**XII, R = H**) (consider also double bond isomers of XII), m.p. 200–207°. Recrystallization as colorless needles from methanol and then acetone raised the m.p. to 217–218.5° (slightly above the m.p. a gas was evolved); $\lambda_{\max}^{\text{alc}}$ 276 mμ (ε 20,600); $\lambda_{\max}^{\text{mineral oil}}$ 3.66(m), 3.79(m), 5.90(s), 6.21(s), 7.05(s), 7.56(s), 7.79(s), 7.99(m), 8.09(m), 8.20(s), 8.49(w), 8.68(w), 10.20(m), 10.60(s), 11.14(w), 11.52(w), 11.67(w), 12.14(w), 13.01(w), 13.77(w) μ.

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 62.92; H, 6.82.

The hydrogenation of this diene–diacid with Adams catalyst in acetic acid produced an almost quantitative yield

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(15) The analyses are by Micro-Tech Laboratories, Skokie, Ill. The melting points were measured on a Fisher-Johns block and are not corrected.

of *cis*-β-(2-carboxymethylcyclohexane)-propionic acid (XIV), m.p. 108–109° (reported[10] 109–110°).

2,4-Dinitrophenylhydrazone of β-(2-Ketocyclohexylidene)-propionic Acid (VII, R = H).—A suspension of 200 mg. of 5,6,7,8-tetrahydrocoumarin (I) in 3 cc. of 5% aqueous sodium hydroxide and a few drops of methanol was warmed until a clear solution resulted. After cooling and acidification with concentrated hydrochloric acid, a solution of 5% 2,4-dinitrophenylhydrazine in 50% aqueous sulfuric acid was added quickly to give 430 mg. (93% yield) of the orange-red **2,4-dinitrophenylhydrazone of VII (R = H)**, m.p. 160–165°. Recrystallization as crimson needles from ethyl acetate raised the m.p. to 174–175°; $\lambda_{\max}^{\text{alc}}$ 212, 254 and 383 mμ (ε 20,700, 13,600 and 23,200) (reported[2] for the 2,4-dinitrophenylhydrazone of 2-ethylidenecyclohexanone, $\lambda_{\max}^{\text{alc}}$ 216, 255 and 381 mμ, ε 17,900, 12,200 and 22,000).

Anal. Calcd. for $C_{15}H_{16}N_4O_6$: C, 51.72; H, 4.63; N, 16.09. Found: C, 51.81; H, 4.61; N, 15.87.

Diels–Alder Reaction with 5,6,7,8-Tetrahydrocoumarin and Maleic Anhydride.—A solution of 500 mg. of 5,6,7,8-tetrahydrocoumarin (I) and 550 mg. of maleic anhydride in 3 cc. of xylene was refluxed for 30 minutes when the precipitation of a white solid appeared complete, yield 695 mg. (69%) of what is probably the bis-adduct (XIII),[7] m.p. 303–305°. An analytical sample was obtained by recrystallizing as colorless prisms from xylene, m.p. 310–311°.

Anal. Calcd. for $C_{16}H_{14}O_6$: C, 63.57; H, 4.67. Found: C, 63.54; H, 5.11.

Cleavage of 5,6,7,8-Tetrahydrocoumarin with Alkali.—A solution of 350 mg. of I in 20 cc. of 10% aqueous sodium hydroxide and 10 cc. of ethanol was subjected to a distillation at atmospheric pressure. The distillate was collected in a solution of excess 2,4-dinitrophenylhydrazine in 50% aqueous sulfuric acid, where 525 mg. (81%) of the yellow 2,4-dinitrophenylhydrazone of cyclohexanone precipitated, m.p. 151–154°. After recrystallization from ethyl acetate, the m.p. was 163–164°, undepressed on admixture with an authentic sample.

Attempted Dehydrogenation of 5,6,7,8-Tetrahydrocoumarin (I).—A mixture of 250 mg. of I and 250 mg. of 5% palladium-on-charcoal catalyst was heated at 250° in a nitrogen atmosphere for 6 minutes. Extraction yielded a colorless oil with a cresolic odor and with an absorption spectrum which showed that no coumarin was present, $\lambda_{\max}^{\text{alc}}$ 274 mμ ($E_{1\,\text{cm}}^{1\%}$ 94.7), $\lambda_{\max}^{\text{liqu. film}}$ 2.88(m), 5.61(s), 5.67(s, unsharp) μ.

Reformatsky Reaction with the Benzoate of 2-Hydroxymethylenecyclohexanone (XVI) and Methyl Bromoacetate in Ether.—A solution of 9.5 g. (0.041 mole) of XVI (m.p. 84–84.5°)[5] and 15 g. (0.1 mole) of methyl bromoacetate in 250 cc. of dry ether was stirred and heated in the presence of 13 g. of granular zinc. The reaction was started by the addition of a crystal of iodine and proceeded smoothly for 15 minutes. After the addition of another 10 g. each of methyl bromoacetate and zinc, heating and stirring was continued for 50 minutes. The complex was decomposed with cold dilute acetic acid and the ethereal layer was washed with water, sodium bicarbonate and sodium chloride solution. The colorless residue from the concentration of the dried solution was crystallized from ether–petroleum ether to give 8.2 g. (65%) of a colorless solid, m.p. 98–100°. Recrystallization from ether afforded a pure sample of **2-benzoyloxymethylene-1-carbomethoxymethylcyclohexanol (XVII, R = CH₃)** as colorless needles, m.p. 100–101°; $\lambda_{\max}^{\text{mineral oil}}$ 2.89(m), 5.76(s), 6.0(m, infl), 6.24(w), 7.42(m), 7.59(m), 7.67(w), 7.84(s), 7.93(s), 8.19(m), 8.35(w), 8.52(s), 8.79(s), 8.97(w), 9.17(m), 9.30(s), 9.49(m), 9.77(m), 10.07(m), 10.31(m), 10.45(w), 10.96(w), 11.12(w), 11.41(w), 11.62(s), 12.23(w), 12.48(w), 13.20(m), 14.13(s) μ.

Anal. Calcd. for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 67.39; H, 6.83.

When an alcoholic solution of this Reformatsky ester was treated with an excess of 5% 2,4-dinitrophenylhydrazine in 50% sulfuric acid, the red **2,4-dinitrophenylhydrazone of 2-carbomethoxymethyl-1-cyclohexenecarboxaldehyde** (X, R = CH_3) precipitated which, upon recrystallization from ethyl acetate as orange-red needles, melted at 189–190°; $\lambda_{\max}^{\text{alc}}$ 257, 291 and 381 mμ (ε 15,350, 8,900, 2,200) (reported[2] for the 2,4-dinitrophenylhydrazone of 2-methyl-1-cyclohexenecarboxaldehyde, $\lambda_{\max}^{\text{alc}}$ 258, 292 and 385 mμ (ε 20,000, 11,850 and 35,400).

Anal. Calcd. for $C_{16}H_{18}N_4O_6$: C, 53.03; H, 5.01; N, 15.46. Found: C, 53.30, H, 5.13, N, 15.57.

A Reformatsky reaction with XVI and ethyl bromoacetate in benzene, exactly as described by Plattner, Treadwell and Scholz,[5] yielded a dark brown sticky crude product from which a 39% yield of 2-benzoyloxymethylene-1-carbethoxymethylcyclohexanol (XVII, R = C_2H_5) could be isolated as a colorless solid, m.p. 86–88° (reported[5] m.p. 86°, 45% yield); $\lambda_{\max}^{\text{mineral oil}}$ 2.89(m), 5.78(s), 5.86(s), 6.24(w), 7.52(s), 7.60(m), 7.86(s), 8.09(s), 8.46(s), 8.60(m), 8.79(s), 9.14(m), 9.29(m), 9.47(w), 9.73(m), 10.09(w), 10.40(m), 10.69(w), 11.05(w), 11.24(m), 11.70(s), 11.82(m), 12.22(w), 14.07(s), 14.55(w) μ.

When an alcoholic solution of 300 mg. of this Reformatsky ester (XVII, R = C_2H_5) was treated with an excess of 5% 2,4-dinitrophenylhydrazine in 50% sulfuric acid in the cold, a slow precipitation of the **2,4-dinitrophenylhydrazone of 2-carbethoxymethyl-1-cyclohexenecarboxaldehyde (X, R = C_2H_5)** took place, yield 330 mg. (93%), m.p. 185–189°. Two recrystallizations from ethyl acetate yielded an analytical sample as orange-red needles, m.p. 196–197°, $\lambda_{\max}^{\text{alc}}$ 257.5, 291 and 381 mμ (ε 16,920, 9,900 and 30,400).

Anal. Calcd. for $C_{17}H_{20}N_4O_6$: C, 54.25; H, 5.36; N, 14.89. Found: C, 54.26; H, 5.43; N, 14.96.

Conversion of 2-Benzoyloxymethylene-1-carbethoxymethylcyclohexanol (XVII, R = C_2H_5) to 1-Acetylcyclohexene (XXI).—A solution of 500 mg. of XVII (R = C_2H_5), m.p. 86–88°, in 25 cc. of 10% aqueous sodium hydroxide and 10 cc. of ethanol was subjected to a distillation at atmospheric pressure. The distillate was collected in a 5% solution of 2,4-dinitrophenylhydrazine in 50% sulfuric acid, where 350 mg. (73%) of the orange-red 2,4-dinitrophenylhydrazone of 1-acetylcyclohexene (XXI) precipitated. After recrystallization from ethyl acetate as orange-red needles, it melted at 205–206° (reported 204°[16] and 199–201°[17]).

An authentic sample of 1-acetylcyclohexene (XXI) was prepared by the action of methyllithium on 1-cyclohexenecarboxylic acid.[4] Its 2,4-dinitrophenylhydrazone melted at 206–207° and did not depress the m.p. of the above sample. Another authentic sample of XXI was obtained through the courtesy of Professor M. S. Newman,[17] and the 2,4-dinitrophenylhydrazone derived from it was identical in m.p. and mixed m.p. with the above two samples.

In another experiment, performed in the same manner, the distillate was treated with semicarbazide hydrochloride and sodium acetate to give the semicarbazone of 1-acetylcyclohexene (XXI), m.p. 222–223° (reported[18] 219–221°). This m.p. was undepressed on admixture with an authentic sample.

Conversion of 2-Methyl-1-cyclohexenecarboxaldehyde (XVIII) to 1-Acetylcyclohexene (XXI).—A solution of 700 mg. of the sodium bisulfite adduct of 2-methyl-1-cyclohexenecarboxaldehyde[2] in 20 cc. of 10% aqueous sodium hydroxide and 15 cc. of ethanol was distilled and the distillate converted to the 2,4-dinitrophenylhydrazone of 1-acetylcyclohexene (XXI) as described in the preceding experiment, yield 640 mg. (68%, m.p. 191–195°; after recrystallization from ethyl acetate, m.p. 202–204°.

DETROIT, MICHIGAN

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(16) J. L. Everett and G. A. R. Kon, *J. Chem. Soc.*, 3131 (1950).

(17) M. S. Newman, THIS JOURNAL, **75**, 4740 (1953).

(18) C. D. Hurd and R. E. Christ, *ibid.*, **59**, 118 (1937).