

*Anal.* Calcd. for  $C_{13}H_{12}NOI_3$ : I, 65.8; N, 2.42. Found: I, 63.0; N, 2.48.

This substance is very slightly soluble in water, benzene and ether, moderately soluble in absolute alcohol, and very soluble in acetone. A suspension of it in water slowly turns starch to a blue color.

**Method II.**—A solution of 0.05 mole of phenacylpyridinium iodide in 75 cc. of boiling glacial acetic acid was treated with 0.05 mole of iodine. On cooling, the triiodide (VI) separated; yield, 95%; m. p. 111–113°.

**Reaction of Phenacylpyridinium Triiodide (VI) with Acetophenone and Pyridine.**—A solution consisting of 2.57 g. (0.0044 mole) of VI in 5 g. of acetophenone and 5 g. of pyridine was heated for two hours on the steam-bath. At the end of this time most of the color had disappeared and a light brown crystalline solid was present in the reaction flask. This solid was separated and thoroughly washed with ether; yield 3.6 g. of crude solids. The material was then digested with 10 cc. of warm water, the suspension cooled in an ice-bath and filtered. The solid, weight 2.54 g. (0.0078 mole), was phenacylpyridin-

ium iodide (I). The water-soluble portion was concentrated and treated with perchloric acid. Pyridine perchlorate, 0.9 g. (0.0044 mole), m. p. 285°, separated. This was considered proof that pyridine hydroiodide was present in the reaction mixture as an ether insoluble salt and hence had been formed in the original reaction.

### Summary

1. The reaction of acetophenone with iodine, pyridine and water was studied and five products separated and identified. A reaction scheme to explain these products is given and independent experiments were carried out to establish each of the postulated reactions.

2. Phenacylpyridinium triiodide was prepared and it was demonstrated that it contains the triiodide ion.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, LABORATORIES OF THE MOUNT SINAI HOSPITAL]

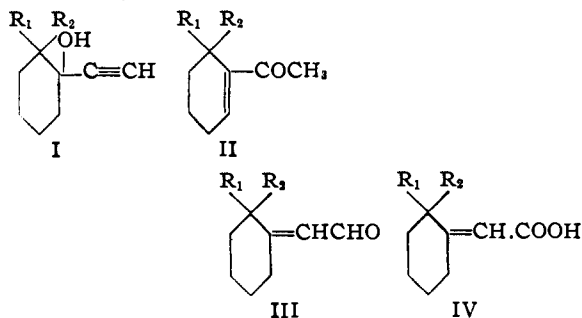
## The Action of Formic Acid on Ethynylcarbinols<sup>1</sup>

By J. D. CHANLEY

Ethynylcarbinols on treatment with formic acid yield isomeric unsaturated carbonyl compounds. Rupe,<sup>2</sup> in the years 1926–1929, studied this isomerization in a number of instances and originally concluded that the reaction products were unsaturated aldehydes. Fischer and Löwenberg,<sup>3</sup> however, showed that the interaction of 1-ethynyl-1-cyclohexanol (IA) and formic acid yielded the isomeric ketone, 1-acetyl-1-cyclohexene (IIA) and not cyclohexylideneacetaldehyde (IIIA), as postulated by Rupe; they suggested that ketones always were the main products of this type of reaction and that aldehydes, if formed, were present in small quantities. Rupe,<sup>4</sup> accepted their evidence and suggestion, but insisted that some aldehyde was present in each reaction product he had previously described.<sup>5</sup> Hurd and Christ<sup>6a</sup> also repeated Rupe's work on 1-ethynyl-1-cyclohexanol and phenylmethylethynylcarbinol and chose for further study the action of formic acid on ethynylbornyl alcohol. They reported that only the corresponding ketones 1-acetyl-1-cyclohexene, acetophenone and 2-acetyl-6-hydroxycamphane were formed and went beyond Rupe's

modified concept by doubting the presence of any aldehydes in Rupe's reaction products. However, their products must have contained some aldehydes, since their ketones, like Rupe's, gave a positive test for aldehydes with Schiff reagent. However, they discounted the significance of this test.<sup>6b</sup>

In the present paper evidence will be offered to show that 1-ethynyl-1-cyclohexanol (IA) on treatment with formic acid and after careful fractionation gives, in addition to the main product, 1-acetyl-1-cyclohexene (IIA) (50% yield), a small but significant quantity of cyclohexylideneacetaldehyde (0.8% yield). As a second example we prepared the new 1-ethynyl-2,2-dimethyl-1-cyclohexanol (IB) which on similar treatment gave the new ketone 2,2-dimethyl-1-acetyl-1-cyclohexene (IIB) (56% yield) and the new aldehyde 2,2-dimethylcyclohexylideneacetaldehyde (IIIB) (6% yield). Neither of the above mentioned pure ketones gave a positive test for aldehydes with Schiff reagent.



For formulas IA-IVA,  $R_1 = R_2 = H$ ; for IB-IVB,  $R_1 = R_2 = CH_3$

(1) This investigation was supported in part by a grant in aid from the United Hospital Fund, New York City, to Dr. Harry Sobotka. It grew out of a project, conducted by Dr. Harry Sobotka and co-workers, dealing with syntheses in the carotenoid group.

(2) Rupe and co workers, *Helv. Chim. Acta*, **9**, 672 (1926); **11**, 449, 656, 965 (1928).

(3) Fischer and Löwenberg, *Ann.*, **475**, 203 (1929).

(4) Rupe and Hirschmann, *Helv. Chim. Acta*, **14**, 688 footnote (1931).

(5) Subsequently Rupe claimed that 1-ethynyl-2-isopropyl-5-methyl-1-cyclohexanol, 1-ethynyl-3-isopropyl-6-methyl-1-cyclohexanol and ethynylphenyl alcohol were rearranged exclusively to unsaturated aldehydes of type III (see Rupe and Kuenzy, *Helv. Chim. Acta*, **14**, 708 (1931); **17**, 283 (1934)).

(6a) Hurd and Christ, *THIS JOURNAL*, **69**, 118 (1937).

(6b) Cf. also Price and Meisel, *ibid.*, **69**, 1497 (1947).

It is further shown that the unsaturated ketones IIA and IIB may be oxidized to the corresponding unsaturated glyoxals which are rearranged under the influence of hydroxyl-ion to the glycolic acids.

The empirical formulas of both aldehydes (IIIA and IIIB) were established by analysis of the liquids or their semicarbazones. Their structures were ascertained by air oxidation to their respective acids, cyclohexylideneacetic acid (IVA) and 2,2-dimethylcyclohexylideneacetic acid (IVB), which showed no depression in melting point on admixture with the corresponding authentic samples.<sup>7a,b</sup> The semicarbazone of cyclohexylideneacetaldehyde melted at 188–192°. Although this is not in agreement with the values reported in the literature,<sup>8a</sup> its ultraviolet spectrum,  $\lambda_{\max} = 269 \text{ m}\mu$ ,  $\epsilon_{\max} = 33,800$ , is in fair agreement and the spectrum of the liquid aldehyde,  $\lambda_{\max} = 237 \text{ m}\mu$ ,  $\epsilon_{\max} = 14,400$ , confirms the findings of Aldersley and Burckhardt<sup>8b</sup>. This corroborative evidence shows that our sample of cyclohexylideneacetaldehyde was reasonably pure. The ultraviolet spectrum of the new aldehyde (IIIB) and that of its semicarbazone was very similar to that of aldehyde (IIIA) and its semicarbazone (Fig. 1); both aldehydes gave positive tests with Schiff reagent.

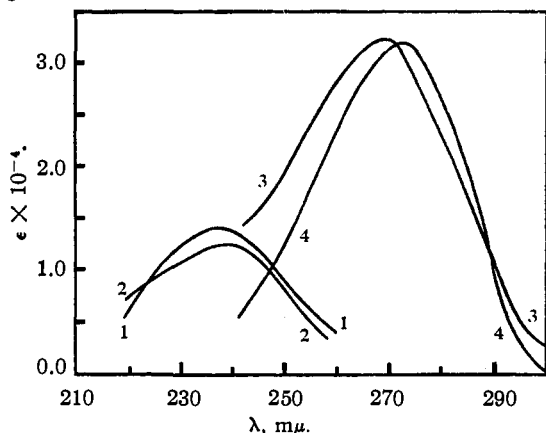


Fig. 1.—Molecular extinction curves of: (1) cyclohexylideneacetaldehyde; (2) 2,2-dimethylcyclohexylideneacetaldehyde; (3) semicarbazone of cyclohexylideneacetaldehyde; (4) semicarbazone of 2,2-dimethylcyclohexylideneacetaldehyde.

The assignment of structure IIB to the new ketone, prepared from the corresponding ethynylcarbinol (IB), is based on its synthesis, analysis and ultraviolet absorption spectrum. Its spectrum and that of its semicarbazone closely resem-

(7) (a) Wallach, *Ann.*, **365**, 261 (1909); (b) Elliot and Linstead, *J. Chem. Soc.*, 776 (1933).

(8) (a) Dimroth, *Ber.*, **71**, 1333 (1938), gives a m. p. of 210°; Aldersley and Burckhardt, *J. Chem. Soc.*, 545 (1938), report m. p. of 205°.

(8) (b) Aldersley, Burckhardt, Gillam and Hindley, *J. Chem. Soc.*, 10 (1940), report  $\lambda_{\max} = 240 \text{ m}\mu$ ,  $\epsilon_{\max} = 15,900$  for the aldehyde and  $\lambda_{\max} = 272 \text{ m}\mu$ ,  $\epsilon_{\max} = 28,000$  for the semicarbazone, whereas Dimroth (ref. 8a) gives  $\lambda_{\max} = 232 \text{ m}\mu$ ,  $\epsilon_{\max} = 17,400$  and  $\lambda_{\max} = 274 \text{ m}\mu$ ,  $\epsilon_{\max} = 32,300$  for the two compounds, respectively.

ble those of compound IIA and its semicarbazone<sup>9</sup> (Fig. 2). The possibility that a methyl group may have migrated or that a five-membered ring might have been formed and thus lead to an isomeric unsaturated ketone may be discounted, since no plausible rearrangement could give an  $\alpha,\beta$ -unsaturated ketone.

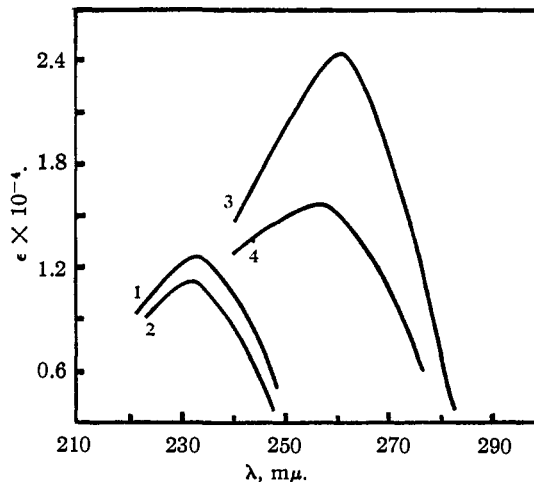
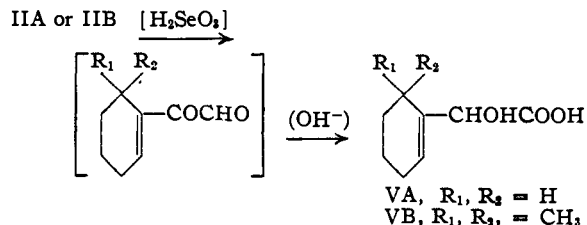


Fig. 2.—Molecular extinction curves of: (1) 1-acetyl-1-cyclohexene; (2) 2,2-dimethyl-1-acetyl-1-cyclohexene; (3) semicarbazone of 1-acetyl-1-cyclohexene; (4) semicarbazone of 2,2-dimethyl-1-acetyl-1-cyclohexene.

1-Acetyl-1-cyclohexene (IIA), on oxidation with selenous acid, yielded a red oil which was extracted with sodium carbonate solution and then with sodium hydroxide solution. Acidification of the sodium hydroxide extract gave a solid acid,  $\text{C}_8\text{H}_{12}\text{O}_3$ , which was now soluble in sodium bicarbonate solution with evolution of carbon dioxide. This acid on hydrogenation yielded D,L-hexahydromandelic acid. Assuming that the double bond has remained in the same position during oxidation and extraction with base, we have assigned to this acid the structure VA. Analogously, the oxidation of compound IIB gave the corresponding glycolic acid  $\text{C}_{10}\text{H}_{16}\text{O}_3$  (VB). The course of this reaction may be explained by the initial oxidation of the ketones to the glyoxals which undergo, in the presence of hydroxyl ions, a facile "benzic acid type" rearrangement to the corresponding glycolic acids.



(9) The low value,  $\lambda_{\max} = 255 \text{ m}\mu$ , for the semicarbazone of compound IIB is not unique. A more extreme case is  $\beta$ -ionone,  $\lambda_{\max} = 293.5 \text{ m}\mu$ , the semicarbazone of which has a maximum at  $\lambda = 276.5 \text{ m}\mu$ . See Burawoy, *J. Chem. Soc.*, 20 (1941).

Experimental<sup>10,11</sup>

**2,2-Dimethyl-1-cyclohexanone.**—Crude dimethylcyclohexanone was prepared in 2-mole batches from 2-methyl-1-cyclohexanone<sup>12</sup> essentially according to Haller and Cornubert.<sup>13</sup> Sodamide was freshly prepared,<sup>14</sup> and methyl iodide was used rather than methyl sulfate. The crude reaction product was fractionated through a packed column of 13–15 theoretical plates and the impure ketone fraction boiling at 168–173° was collected and purified by regeneration from its pure semicarbazone.<sup>15</sup> Pure ketone, boiling at 170–170.5° (cor.) (761 mm.),  $n_D^{20}$  1.4482 was obtained in an over-all yield of 30%; reported<sup>15</sup> b. p. 169–170°, (cor.) (768 mm.),  $n_D^{25}$  1.4460. The semicarbazone melted at 199–201°; reported m. p. 197–198°,<sup>15</sup> 201–202°<sup>7b</sup>; oxime m. p. 93–94°; reported 93–93.5°.<sup>16</sup>

*Anal.* Calcd. for C<sub>8</sub>H<sub>14</sub>O: C, 76.13; H, 11.18. Found: C, 75.56; H, 11.14. Calcd. for C<sub>9</sub>H<sub>17</sub>N<sub>3</sub>O: C, 58.98; H, 9.35; N, 22.92. Found: C, 59.00; H, 9.12; N, 23.30.

**1-Ethynyl-1-cyclohexanol (IA)**, b. p. 72.5–73° (11 mm.),  $n_D^{25}$  1.4810, m. p. 28–30°, was prepared in 1-mole batches in 50% yield according to the directions of Campbell and co-workers.<sup>17</sup>

**1-Ethynyl-2,2-dimethyl-1-cyclohexanol (IB)**, b. p. 113–113.5° (49 mm.),  $n_D^{20}$  1.4790 was prepared analogously<sup>17</sup> in 0.5-mole batches in 68% yield from the pure ketone (IIB) and sodium acetylde. It gave a white precipitate with alcoholic silver nitrate solution.

*Anal.* Calcd. for C<sub>10</sub>H<sub>16</sub>O: C, 78.89; H, 10.59. Found: C, 78.82; H, 10.63.

**1-Acetyl-1-cyclohexene (IIA) and Cyclohexylideneacetaldehyde (IIIA).**—The conditions of the reaction described below are those of Rupe with minor modifications. A mixture of 65 g. (0.5 mole) of 1-ethynyl-1-cyclohexanol and 400 ml. of formic acid (90%) was gently heated under reflux until a vigorous reaction ensued. After heating under reflux for forty-fifty minutes the mixture was poured into 2 liters of ice water. The petroleum ether extract was washed with sodium hydroxide solution (10%) and the residue from the petroleum ether was steam-distilled. The organic layer in the steam distillate was separated, dried and gave a positive test with Schiff reagent. It was carefully fractionated under reduced pressure through a column of 8–10 theoretical plates which was fitted with a total condensation still head and an electrically heated outer jacket. This column had an internal diameter of 12.5 mm. and was packed for 30 cm. with 1.5 mm. diameter single helices made from 25 gauge stainless steel. Table I gives the properties of the five fractions collected.

The semicarbazone prepared from fraction B, 1-acetyl-1-cyclohexene melted at 220–221°,  $\lambda_{max.}$  = 260.5  $\mu$ ,  $\epsilon_{max.}$  = 24,200. Reported m. p. 220–221°<sup>8a</sup> and  $\lambda_{max.}$  = 260.5  $\mu$ ,  $\epsilon_{max.}$  = 20,150.<sup>18</sup>

The semicarbazone prepared from fraction E, cyclohexylideneacetaldehyde, melted at 188–192° and further

(10) The ultraviolet absorption spectra measurements were made on a Beckman Quartz Spectrophotometer Model D. U. and absolute alcohol was used as solvent. All melting points are corrected.

(11) Microanalyses by Dr. Gertrude Oppenheimer, Microchemical Laboratory, The California Institute of Technology, Pasadena, California.

(12) We are indebted to Drs. Luthy and Fiori of Givaudan-Delawanna, Inc., Delawanna, New Jersey, for supplying this compound.

(13) Haller and Cornubert, *Bull. soc. chim.*, [4] **41**, 367 (1927).

(14) Vaughn, Vogt and Nieuwland, *THIS JOURNAL*, **56**, 2120 (1934).

(15) Adamson, Marlow and Simonsen, *J. Chem. Soc.*, 774 (1938).

(16) Johnson and Posvic, *THIS JOURNAL*, **67**, 505 (1945).

(17) K. Campbell, B. Campbell and Eby, *ibid.*, **60**, 2282 (1938).

(18) Evans and Gillam, *J. Chem. Soc.*, 815 (1941); 565 (1943), also report  $\lambda_{max.}$  = 233.5  $\mu$ ,  $\epsilon_{max.}$  = 9,660 for this ketone.

TABLE I

Fraction	Yield, g.	B. p., °C., 49 mm.	$n_D^{20}$	$\lambda_{max.}$ , $\mu$	$\epsilon_{max.}$	Schiff reaction <sup>b</sup>
A	3.5	76–111	1.4435–1.4893	...	....	Neg.
B	32.0	111	1.4900	232 <sup>18</sup>	12,500	Neg.
C	3.0	111–115 <sup>a</sup>	1.4920	...	....	Slightly pos. in one min.
D	0.5	115–117	1.4958	...	....	Pos. in 30 sec.
E <sup>c</sup>	0.5	.....	1.5020	237	14,400	Pos. instantly

<sup>a</sup> At this point, temperature of the outer heating jacket was raised to 150°. <sup>b</sup> Freshly prepared reagent, according to Shriner and Fuson, "The Systematic Identification of Organic Compounds," New York, N. Y., 1940, p. 62, was used without solvent. <sup>c</sup> This fraction was obtained from the "holdup" of the column by reducing the pressure to 5 mm.

recrystallizations from ethanol and methanol did not alter the melting point.

*Anal.* Calcd. for C<sub>8</sub>H<sub>12</sub>N<sub>2</sub>O: C, 59.68; H, 8.35; N, 23.20. Found: C, 59.63; H, 8.55; N, 23.31.

**2,2-Dimethyl-1-acetyl-1-cyclohexene (IIB), 2,2-Dimethylcyclohexylideneacetaldehyde (IIIB) and Compound C<sub>10</sub>H<sub>14</sub>.**—The reaction mixture of 65 g. (0.42 mole) of 1-ethynyl-2,2-dimethyl-1-cyclohexanol (IB) and 350 ml. formic acid (90%) was worked up in the same manner as described above. Table II gives the properties of the five fractions obtained by distillation.

TABLE II

Fraction	Yield, g.	B. p., °C., 49 mm.	$n_D^{20}$	$\lambda_{max.}$ , $\mu$	$\epsilon_{max.}$	Schiff reaction
A	3.0	80–85	1.4682	...	....	Neg.
B	3.0	114–118	1.4772–1.4800	...	....	Neg.
C	36.5	118–118.5	1.4810	232	10,100	Neg.
D	0.5	118.5–141	1.4840	...	....	Pos. <sup>a</sup>
E	4.0	141–143	1.5010	239	12,000	Pos. <sup>a</sup>

<sup>a</sup> The color development was not instantaneous because of the insolubility of the aldehyde in the reagent. A purple color developed after a minute of shaking and was concentrated in the insoluble aldehyde layer.

The semicarbazone prepared from fraction C (Table II), 2,2-dimethyl-1-acetyl-1-cyclohexene, and recrystallized from ethanol melted at 200–201.5°,  $\lambda_{max.}$  = 255  $\mu$ ,  $\epsilon_{max.}$  = 15,600. Ten recrystallizations from ethanol and methanol did not alter its physical properties.

*Anal.* Calcd. for C<sub>11</sub>H<sub>19</sub>N<sub>3</sub>O: C, 63.13; H, 9.15; N, 20.08. Found: C, 63.24; H, 9.21; N, 20.37.

**2,2-Dimethyl-1-acetyl-1-cyclohexene** obtained by steam distilling an equimolecular mixture of the pure semicarbazone and phthalic anhydride, boiled at 115.8–116° (47 mm.),  $n_D^{25}$  1.4815,  $\lambda_{max.}$  = 232  $\mu$ ,  $\epsilon_{max.}$  = 12,000. It gave no coloration with Schiff reagent.

*Anal.* Calcd. for C<sub>10</sub>H<sub>16</sub>O: C, 78.89; H, 10.59. Found: C, 79.02; H, 10.48.

**Fraction E**, 2,2-dimethylcyclohexylideneacetaldehyde, on redistillation, boiled at 130–130.5° (32 mm.),  $n_D^{20}$  1.5022,  $\lambda_{max.}$  = 239  $\mu$ ,  $\epsilon_{max.}$  = 12,300 and gave a purple color with Schiff reagent.

*Anal.* Calcd. for C<sub>10</sub>H<sub>16</sub>O: C, 78.89; H, 10.59. Found: C, 79.05; H, 10.56.

The semicarbazone prepared from fraction E, Table II, and recrystallized from methanol, melted at 220°;  $\lambda_{max.}$  = 273  $\mu$ ,  $\epsilon_{max.}$  = 32,300.

*Anal.* Calcd. for C<sub>11</sub>H<sub>19</sub>N<sub>3</sub>O: C, 63.13; H, 9.15; N, 20.08. Found: C, 63.28; H, 9.31; N, 19.93.

**Fraction A** (Table II) on redistillation boiled at 81.8° (54 mm.),  $n_D^{20}$  1.4700, showed no absorption in the range

from 216 to 300  $\mu$  and gave a white precipitate with alcoholic silver nitrate solution.

*Anal.* Calcd. for  $C_{10}H_{14}$ : C, 89.49; H, 10.51. Found: C, 89.47; H, 10.30.

**Oxidation of Cyclohexylideneacetaldehyde (IIIA) to Cyclohexylideneacetic Acid (IVA).**—One-tenth of a ml. of Fraction E (Table I) was allowed to stand exposed to the air for three days. The resulting semisolid crystalline mass was dissolved in ether and extracted several times with 10% sodium carbonate solution. The combined alkaline extracts, on acidification, yielded 40 mg. of the acid, m. p. 89–90°, which after recrystallization from petroleum ether (b. p. 40–60°), melted at 90–92° and showed no depression of melting point on admixture with authentic cyclohexylideneacetic acid, m. p. 90–92°, prepared by the dehydration of (1-hydroxycyclohexyl)-acetic acid<sup>19</sup> according to the direction of Wallach<sup>20</sup> who reports m. p. 91°.

**Oxidation of 2,2-Dimethylcyclohexylideneacetaldehyde (IIIB) to 2,2-Dimethylcyclohexylideneacetic acid (IVB).**—In a similar manner 1 ml. of 2,2-dimethylcyclohexylideneacetaldehyde, after standing two weeks, exposed to the air, gave 300 mg. of 2,2-dimethylcyclohexylideneacetic acid, m. p. 89–90°. The acid after recrystallization from acetic acid, melted at 90–91° and showed no depression of melting point on admixture with an authentic sample<sup>20</sup>; m. p. 90–91°; reported<sup>7b</sup> m. p. 91–92°.

**(1-Cyclohexenyl)-glycolic Acid (VA).**—A solution of 6.2 g. (0.05 mole) of 1-acetyl-1-cyclohexene and 6.5 g. (0.05 mole) of selenous acid in 40 ml. of dioxane was heated under reflux for three and one-half hours, decanted from the precipitated selenium and evaporated to dryness *in vacuo* under nitrogen. The ethereal solution of the residue was thoroughly extracted with sodium carbonate solution (10%). (At this point, much red selenium precipitates and is allowed to sink into the carbonate solution.) The carbonate extract gave only intractable tars upon acidification. The ether layer was then extracted six times with dilute sodium hydroxide solution (10%). The combined sodium hydroxide extracts were filtered, warmed on the steam-bath, acidified with a slight excess of warm dilute hydrochloric acid and filtered from precipitated tarry material. The filtrate was saturated with salt and precipitation induced by scratching the sides of the container; 1.5 g. of a yellow colored solid, m. p. 122–124° was collected. After recrystallization from Skellysolve L (b. p. 97–129°), with Norite, a colorless solid acid, m. p. 126–126.5° was obtained. It was now soluble in sodium bicarbonate solution with evolution of carbon dioxide; yield 1.4 g.

(19) We are indebted to Dr. Erwin Schwenk of Schering Corp., Bloomfield, New Jersey, for a sample of this acid.

(20) The authentic sample was prepared in the following manner: ethyl (2,2-dimethyl-1-hydroxycyclohexyl)-acetate (prepared according to Simonsen, *et al.*<sup>16</sup>) was hydrolyzed with alcoholic potassium hydroxide and dehydrated with acetic anhydride according to the directions of Elliott and Linstead.<sup>7b</sup>

*Anal.* Calcd. for  $C_8H_{10}O_3$ : C, 61.52; H, 7.75; neut. equiv., 156.2. Found: C, 61.61; H, 8.04; neut. equiv., 159.0.

**Hydrogenation of Compound VA to D,L-Hexahydro-mandelic Acid.**—Two hundred and forty-seven mg. (0.00157 mole) of compound VA, in glacial acetic acid, was hydrogenated at atmospheric pressure with platinum oxide; 98% of the theoretical amount of hydrogen was absorbed. The resulting acid recrystallized from chloroform melted at 134–135° and showed no depression of m. p. in admixture with D,L-hexahydro-mandelic acid of m. p. 135–136°, prepared from D,L-mandelic acid by hydrogenation. Reported m. p. 134–135°.<sup>21</sup>

**(2,2-Dimethyl-1-cyclohexenyl)-glycolic Acid (VB).**—Similarly, 4.2 g. ( $1/30$  mole) of 2,2-dimethyl-1-acetyl-1-cyclohexene (IIB) was treated with 3.6 g. ( $1/30$  mole) of selenous acid in 20 ml. of dioxane with the following modifications. The sodium hydroxide extract after acidification was not filtered, since the acid separates in a semi-solid state at this point. The precipitated orange-colored crude acid was purified by dissolving in a small amount of hot sodium carbonate solution (10%) treated with norite, filtered and reprecipitated by the addition of dilute hydrochloric acid solution. Yield was 0.9 g., m. p. 118–120°. Two recrystallizations from ethanol-water mixture gave the pure colorless acid, m. p. 121°.

*Anal.* Calcd. for  $C_{10}H_{16}O_3$ : C, 65.19; H, 8.76; neut. equiv., 184.2. Found: C, 65.08; H, 8.71; neut. equiv., 186.5.

**Acknowledgment.**—The author wishes to thank Dr. Harry Sobotka for his interest and suggestions, and Mrs. Edith Rosen Kaplan and Miss Bernice Hamerman for their very able assistance.

### Summary

1. 1-Ethynyl-1-cyclohexanol is isomerized under the influence of formic acid to 1-acetyl-1-cyclohexene (50% yield) and cyclohexylideneacetaldehyde (0.8% yield). Similarly 2,2-dimethyl-1-ethynyl-1-cyclohexanol gave 2,2-dimethyl-1-acetyl-1-cyclohexene (56% yield) and 2,2-dimethylcyclohexylideneacetaldehyde (6% yield).

2. The selenous acid oxidation product of 1-acetyl-1-cyclohexene on treatment with a dilute solution of sodium hydroxide yielded (1-cyclohexenyl)-glycolic acid. Similarly 2,2-dimethyl-1-acetyl-1-cyclohexene yielded (2,2-dimethyl-1-cyclohexenyl)-glycolic acid. An interpretation of the course of this reaction is given.

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(21) Freudenberg, Brauns and Siegel, *Ber.* **56**, 197 (1923).