## A New Route to 1-Substituted 3-Cyclopentenes

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Received January 19, 1962

The condensation of cis-1,4-dichloro-2-butene with malonic ester followed by saponification gave a mixture of 3-cyclopentene-1,1-dicarboxylic acid (VI) and 2-vinylcyclopropane-1,1-dicarboxylic acid (VII). The cyclopentene diacid was readily isolated, then converted in several steps *via* a Curtius rearrangement to the hydrochloride of 3-cyclopentene-1-ylamine (XVI). In a proof of structure the oxidative cleavage of 3-cyclopentene-1-carboxylic acid gave the expected tricarballylic acid (VIII).

Intended syntheses of cyclopentane counterparts of deoxyribonucleosides<sup>1,2</sup> as possible anticancer agents required the availability of 3-cyclopenten-1-ylamine (XVI). A likely precursor for this amine is diethyl 3-cyclopentene-1,1-dicarboxylate (III). Skinner, *et al.*, have reported that this pyrolytic decarboxylation gave not the expected 3cyclopentene-1-carboxylic acid (IX), but an isomeric, neutral substance. Infrared data suggested the presence of vinyl- and  $\gamma$ -lactone functions. A closer examination of the literature revealed that the 1,4-dibromo-2-butene used by Skinner, *et al.*,<sup>3</sup>



cyclopentene diester is formed in good yield by the condensation of 1,4-dibromo-2-butene with malonic ester. They also described an improved synthesis of the dibromobutene, obtained from bromine and 1,3-butadiene.<sup>3</sup> We repeated the preparation of their diester, then saponified it to give a diacid with the expected composition. However, subsequent was the *trans* isomer I.<sup>4</sup> Moreover, Kierstead, *et al.*, had studied the condensation of I with malonic ester without mentioning the formation of any cyclopentene derivatives.<sup>5</sup> They showed that the major product from this condensation was diethyl 2-vinylcyclopropane-1,1-dicarboxylate (IV), saponifiable to a diacid VII with the same melting point

 $<sup>(1)\,</sup>$  K. C. Murdock and R. B. Angier, papers in process of publication.

<sup>(2)</sup> A different approach leading to some 9-(2-hydroxycyclopentyl)purines was reported by H. J. Schaeffer and R. D. Weimar, Jr., J. Am. Chem. Soc., 81, 197 (1959); J. Org. Chem., 25, 774 (1960).

<sup>(3)</sup> G. S. Skinner, G. Limperos, and R. H. Pettebone, J. Am. Chem. Soc., 72, 1648 (1950).

<sup>(4)</sup> K. Mislow, *ibid.*, **75**, 2512 (1953).

 $<sup>(5)\,</sup>$  R. W. Kierstead, R. P. Linstead, and B. C. L. Weedon, J. Chem. Soc., 3610 (1952).

as our diacid. Our neutral pyrolysis product was observed to have a composition and physical constants in agreement with those of  $\gamma$ -vinyl- $\gamma$ -butyrolactone (X), prepared by Russel and VanderWerf from malonic ester and the monoepoxide of butadiene.<sup>6</sup> Very shortly thereafter there appeared a paper by Birch, Dean, and Hunter<sup>7</sup> in which it was established that the pyrolysis product from 2vinylcyclopropane-1,1-dicarboxylic acid (VII) was indeed this lactone.

Logically, the intended synthesis of the cyclopentene diester III should begin with a *cis* olefin, so *cis*-1,4-dichloro-2-butene (II) was prepared<sup>8,9</sup> and then condensed with malonic ester. The desired cyclopentene diester III was formed along with a roughly equal amount of the cyclopropane isomer IV and 2.6% of a third isomer or dimer which is still under investigation.<sup>10</sup> Saponification of the mixed diesters III and IV gave a mixture of crystalline diacids VI and VII from which the higher melting cyclopentene diacid VI was isolated readily in 31% yield. Decarboxylation gave the monoacid IX.

Tiffeneau and Tchoubar reported that 4,5-oxidoclohexene rearranges during pyrolysis or in contact with ethyl magnesium bromide to give a mixture of 3-cyclopentene-1-carboxaldehyde and 3-cyclohexen-1-one.<sup>11</sup> Oxidation of the aldehyde gave the acid IX.<sup>11,12</sup> The yields in these reactions were not stated. Both this route and our own might be considered to give a product of equivocal structure. Accordingly, the cyclopentenecarboxylic acid IX was subjected to oxidative degradation with alkaline permanganate. The product was the expected tricarballylic acid (VIII).<sup>13</sup> Data in agreement with the required symmetry in the disposition of the olefinic and carboxyl functions in IX was provided by the isolation of a single, relatively high-melting dibromo derivative in 74% yield. This dibromide is presumably the racemate of V. The indicated trans configuration of the bromine atoms would be in accord with the usual stereochemistry resulting from the addition of bromine to olefins.<sup>14</sup>

The acid IX was converted to an acid chloride XII which gave an anilide XI with the same melting point as an anilide prepared by Tiffeneau and Tchoubar. This acid chloride XII did not react

(14) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, Inc., New York, N. Y., 1940, p. 147. with activated<sup>15</sup> sodium azide in dry benzene, but a cold, aqueous reaction system<sup>16</sup> was found to be very satisfactory. The resulting acyl azide (XIV) and the corresponding isocyanate (XV) obtained by the Curtius rearrangement were not isolated, although the isocyanate was characterized as a phenylurea, XIII. Brief hydrolysis of the isocyanate with concentrated hydrochloric acid gave the hydrochloride of the required amine XVI.

The over-all yield in the sequence from the diacid VI to the amine XVI was 72%. Utilization of this symmetrical olefinic amine for the sterically controlled synthesis of a variety of polysubstituted cyclopentanes will be described separately.<sup>1</sup>

An earlier attempt to synthesize this amine XVI was to have proceeded via chemical reduction of the oxime<sup>17</sup> of 3-cyclopenten-1-one. In the more direct of the reported<sup>17,18</sup> syntheses of 3-cyclopenten-1-one, Dashkevich<sup>17</sup> claimed that it was obtained in 26.9% yield from the pyrolysis of calcium acrylate. Our attempts to reproduce his results gave only small amounts of complex oils.

### Experimental

Melting points are uncorrected. Evaporations were conducted under reduced pressure. Liquid products were distilled through a small  $(1.3 \times 10 \text{ cm.})$  Vigreux column. Solids were pressed with potassium bromide for infrared spectral determinations.

Mixture: Diethyl Cyclopent-3-ene-1,1-dicarboxylate (III) and Diethyl 2-Vinylcyclopropane-1,1-dicarboxylate (IV).—2-Butyne-1,4-diol was catalytically semihydrogenated to cis-2butene-1,4-diol,<sup>19,20</sup> 78% yield, b.p. 103°/0.5 mm,  $n^{24}$ p 1.4755 (lit.,<sup>19</sup> b.p. 134–135°,/15 mm.  $n^{26}$ p 1.4760). Subsequent treatment with thionyl chloride and pyridine in ether gave cis-1,4-dichloro-2-butene,<sup>9</sup> 78%, b.p. 70–72°/35 mm.,  $n^{24}$ p 1.4868 (lit.,<sup>8</sup> b.p. 59–62°/22 mm.,  $n^{25}$ p 1.4891.)

A hot solution of \$9.7 g. (3.90 g.-atoms) of sodium in 1600 ml. of absolute ethanol was stirred during the addition in a thin stream from a separatory funnel of 304.4 g. (1.90 moles) of diethyl malonate. After 5 min. the mixture was sucked up into the separatory funnel, then added at a fast drip during 1.5 hr. to 237.5 g. (1.90 moles) of cis-1,4-dichloro-2-butene. Stirring and heating at  $65-75^{\circ}$  was continued both during the addition and for another 4 hr. The resulting mixture was not basic to phenolphthalein. (Crystallization of the sodio malonate mixture in the separatory funnel was prevented by heating with an electrical immersion heater suspended just above the stopcock.) The mixture was allowed to stand overnight, the finely divided sodium chloride was removed by filtration, the filtrate evaporated and the residual oil distilled: 270.2 g. (67%), b.p.  $71-76^{\circ}/0.5 \text{ mm}$ ,  $n^{24}$ D 1.4488.

Anal. Caled. for  $C_{11}H_{16}O_4$ : C, 62.25; H, 7.60. Found: C, 62.16; H, 7.57.

The undistilled residue partially crystallized. It was washed with heptane until free of gummy material. The remaining solid was agitated with about 100 ml. of chloroform, some sodium chloride was removed by filtration, and the filtrate was evaporated to dryness. Crystallization of

(19) A. W. Johnson, J. Chem. Soc., 1014 (1946).

<sup>(6)</sup> R. R. Russel and C. A. VanderWerf, J. Am. Chem. Soc., 69, 11 (1947).

<sup>(7)</sup> S. F. Birch, R. A. Dean, and N. J. Hunter, J. Org. Chem., 23, 1390 (1958).

 <sup>(8)</sup> L. H. Amundsen, et al., J. Am. Chem. Soc., 73, 2118 (1951);
 J. Org. Chem., 25, 2230 (1960).

<sup>(9)</sup> K. Mislow and H. M. Hellman, J. Am. Chem. Soc., 73, 244 (1951).

 $<sup>(10)\,</sup>$  An apparent absence of olefinic groups in this compound suggests that it has a bi- or tricyclic structure.

<sup>(11)</sup> M. Tiffeneau and B. Tchoubar, Compt. rend., 212, 581 (1941).

<sup>(12)</sup> H. de V. Finch, S. A. Ballard, and T. W. Evans, U.S. Patent 2,454,047 (1948).

<sup>(13)</sup> H. T. Clarke and T. F. Murray, Org. Syn., Coll. Vol. I, 523 (1948).

<sup>(15)</sup> P. A. S. Smith, Org. Reactions, III, 337 (1946).

<sup>(16)</sup> C. F. H. Allen and A. Bell, Org. Syn., Coll. Vol. III, 846 (1955).
(17) B. N. Dashkevich, Dokl. Akad. Nauk, S.S.S.R., 107, 700

<sup>(1956).</sup> 

<sup>(18)</sup> K. Alder and F. H. Flock, Chem. Ber., 89, 1732 (1956).

<sup>(20) 2-</sup>Butene-1,4-diol ("predominantly cis") from the General Aniline and Film Co. proved to be equally satisfactory.

the residue from methanol gave 10.4 g. (2.6%) of plates, m.p. 160-161°. Recrystallization did not change the melting point. This substance did not decolorize dilute solutions of either bromine in ether or potassium permanganate in acetone.

Anal. Calcd. for C<sub>11</sub>H<sub>16</sub>O<sub>4</sub>: C, 62.25; H, 7.60. Found: C, 62.50; H, 7.84.

3-Cyclopentene-1,1-dicarboxylic Acid (VI).--A solution of 215 g. of potassium hydroxide and 270 g. of the above mixture of diesters (III + IV) in 2400 ml. of 80% ethanol was heated under reflux for 11 hr., then evaporated to dryness. A solution of the residual solid in 500 ml. of water was kept cold with an ice bath during gradual acidification with 194 ml. of concentrated sulfuric acid. The resulting slurry was extracted thrice with 1-l. portions of ether, the ethereal extracts were dried (magnesium sulfate), and the ether was almost all removed by distillation over the steam bath, heating no longer than necessary. The residual oil was dissolved in 1450 ml. of toluene (preheated to 90°). This solution, clarified by filtration through Celite<sup>21</sup> and allowed to stand overnight, deposited 61.9 g. (31%) of massive rods, m.p. 164-169° dec. (The mother liquor was reserved for the isolation of 2-vinylcyclopropane-1,1-dicarboxylic acid, VII, described below.) Recrystallization from ether-toluene did not raise the melting point although the product from another saponification conducted on a smaller scale had a m.p. of 170-172° dec. Analyses were obtained from the latter sample. The infrared spectrum of the former sample showed no sign of contamination by the cyclopropane isomer and pyrolysis gave 3-cyclopentene-1-carboxylic acid (IX, below) of high purity.

Anal. Caled. for C<sub>7</sub>H<sub>8</sub>O<sub>4</sub>: C, 53.84; H, 5.16. Found: C, 53.97; H, 5.33.

2-Vinylcyclopropane-1,1-dicarboxylic Acid (VII).-A. The mother liquor from the above preparation was set aside at  $-5^{\circ}$ . It deposited 61.1 g. of fluffy needles, m.p. 98–102°. In other preparations this by-product separated when such mother liquors were allowed to stand for several days at room temperature. In one case a mixture of plates and large rosettes was obtained. One of these rosettes (m.p. 108-109°) recrystallized from toluene at  $\leq 90^{\circ}$ , gave needles, m.p. 111–112°, with gassing from 120°. The melting point was unchanged after admixture with 2-vinylcyclopropane-1,1dicarboxylic acid of m.p. 115-116° (below). The infrared spectra of the two samples were identical.

B. The condensation of 128.4 g. of trans-1,4-dibromo-2butene<sup>3,4</sup> (I) with 90 ml. of diethyl malonate according to the procedure of Skinner, et al., 3 gave 68.2 g. (53%) of diethyl 2-vinylcyclopropane-1,1-dicarboxylate (IV), b.p./0.8 mm. 88-92°, n<sup>24</sup>D 1.4508. (Kierstead, et al., reported<sup>5</sup> b.p. 69-72°/0.5 mm., n<sup>25</sup>D 1.4502.) Saponification of 42.4 g. of this diester in 80% ethanol as described above for the synthesis of VI gave 23.7 g. (76%) of needles, m.p. 104-107°. The melting point of the last crystals to be deposited was 108-109°; lit.<sup>5</sup> m.p. 107-108°

Anal. Caled. for C<sub>7</sub>H<sub>8</sub>O<sub>4</sub>: C, 53.84; H, 5.16. Found: C, 53.75; H, 5.58.

After 10 months this material had become gummy, m.p. 90-105°. Recrystallization from toluene gave needles, m.p.  $115 - 116^{\circ}$ 

 $\gamma$ -Vinyl- $\gamma$ -butyrolactone (X).—2-Vinylcyclopropane-1,1dicarboxylic acid (VII) (25.6 g.) was pyrolyzed with the aid of an oil bath heated gradually from 120–170°; effervescence was gentle and steady. Distillation of the residue gave 13.0 g. (71%) of an oil, b.p. 113°/17 mm., n<sup>22</sup>D 1.4601, insoluble in cold, 1 N sodium hydroxide. The reported<sup>6</sup> constants for  $\gamma$ -vinyl- $\gamma$ -butyrolactone are b.p. 75°/2 mm.  $n^{25}$ D 1.4603. Anal. Calcd. for C<sub>6</sub>H<sub>8</sub>O<sub>2</sub>: C, 64.27; H, 7.19. Found:

C, 64.15; H, 7.46.  $\lambda_{\text{max}}^{\text{KBr}}$  3.24, 6.09, 7.02, 10.19, 11.00 (vinyl), and 5.64  $\mu$  ( $\gamma$ -lactone).

3-Cyclopentene-1-carboxylic Acid (IX).--A flask contain-

ing 30.79 g. of 3-cyclopentene-1,1-dicarboxylic acid (VI) was connected with a condenser arranged for distillation. The diacid was heated with an oil bath initially at 180°, finally at 170°. After 1 hr. gas evolution had ceased. The residual oil was distilled in vacuo. All of the volatile product was collected as a single fraction: 20.6 g. (93%), b.p. 83-84°/2 mm., n<sup>23</sup>D 1.4673.

Anal. Calcd. for C<sub>6</sub>H<sub>8</sub>O<sub>2</sub> (112.12): C, 64.27; H, 7.19. Found: C, 64.46; H, 7.44; neut. equiv., 120; pK, 6.0 (determined potentiometrically in 50% aqueous ethanol).

Racemic  $3\alpha$ ,  $4\beta$ -Dibromocyclopentane- $1\alpha$ -carboxylic Acid (V).—After the addition of 0.160 g. (1.0 mmole) of bromine to a solution of 0.112 g. (1.0 mmole) of 3-cyclopentene-1carboxylic acid (IX) in 1 ml. of cyclohexane there rapidly separated 0.200 g. (74%) of leaflets, m.p. 118-121°. Recrystallization from cyclohexane raised the m.p. to 120-122°. Anal. Calcd. for C<sub>6</sub>H<sub>8</sub>O<sub>2</sub>Br<sub>2</sub>: C, 26.50; H, 2.97; Br,

58.77. Found: C, 26.77; H, 3.06; Br, 59.02.

Oxidation of 3-Cyclopentene-1-carboxylic Acid (IX) to Tricarballylic Acid (VIII).-A solution of 1.01 g. (9.0 mmoles) of 3-cyclopentene-1-carboxylic acid (IX) in 9 ml. of 1 N sodium hydroxide was chilled with an ice bath and agitated during the portionwise addition of a solution of 3.80 g. (2.4 mmoles) of potassium permanganate in 50 ml. of water. The resulting, thick mixture was warmed at 40° for 10 min., then heated at 100° to coagulate the manganese dioxide present. Solids were removed by filtration, the filtrate was acidified with hydrochloric acid, treated with decolorizing charcoal, filtered again, evaporated to dryness, then evaporated to dryness twice more with 20-ml. portions of t-butyl alcohol. Extraction of the solid residue with acetone, evaporation of the extracts, trituration of the resulting solid with dry ether, and collection of the solid by filtration gave 1.04 g. (66%) of product, m.p. 154-160°. Crystallization from acetone-toluene followed by recrystallization from water raised the m.p. to 160-161° (lit.,<sup>18</sup> m.p. 160-161°). A comparison of infrared spectra and a mixture m.p. determination (160-161°) showed that the product was identical with a commercial sample of tricarballylic acid.

Anal. Caled. for C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>: C, 40.91; H, 4.58. Found: C, 41.15; H, 4.69.

3-Cyclopentene-1-carbonyl Chloride (XII).---A solution of 18.7 g. of 3-cyclopentene-1-carboxylic acid (IX) in 15 ml. of thionyl chloride was protected with a calcium chloride tube and allowed to stand overnight. A buildup of the heat of reaction was prevented with a pan of cool water. Excess thionyl chloride was removed by evaporation during 1 hr. at about 15 mm. and 25°. Distillation of the residue gave 20.7 g. (95%) of a colorless liquid, b.p. 95-96°/55 mm., n<sup>23</sup>D 1.4746.

Anal. Caled. for C<sub>6</sub>H<sub>7</sub>OCl: C, 55.19; H, 5.40. Found: C, 54.88; H, 5.70.

3-Cvclopentene-1-carboxanilide (XI).—A solution of 0.372 g. (4.0 mmoles) of aniline in 5 ml. of dry ether was cooled with an ice bath and agitated during the dropwise addition of a solution of 0.238 g. (2.0 mmoles) of 3-cyclopentene-1carbonyl chloride (XII) in 5 ml. of dry ether. The resulting solid was removed by filtration and washed with methylene chloride. The combined filtrate and washes were evaporated to dryness and the residue crystallized from benzene to give 0.246 g. (66%) of a solid, m.p. 139-140°. Recrystallization from benzene raised the m.p. to  $140^{\circ}$  (lit.,<sup>11</sup> m.p.  $140^{\circ}$ ). This compound crystallized as transparent leaflets which soon became chalklike in appearance when set aside to dry, indicating the loss of solvent of crystallization.

Anal. Calcd. for C<sub>12</sub>H<sub>13</sub>NO: C, 76.97; H, 7.00; N,

7.48. Found: C, 76.85; H, 7.09; N, 7.60. 3-Cyclopenten-1-ylamine (XVI) Hydrochloride via 3-Cyclopentene-1-carbonyl Azide (XIV) and 3-Cyclopenten-1-yl Isocyanate (XV).—A well stirred solution of 3.82 g. (58.8 mmoles) of sodium azide in 12 ml. of water was maintained at < 6° during the gradual addition of a solution of 5.00 g. (38.3 mmoles) of 3-cyclopentene-1-carbonyl chloride (XII) in 12 ml. of acetone. The mixture was stirred another 0.5

<sup>(21)</sup> Celite is acid-washed, diatomaceous earth sold by the Johns-Manville Corp.

hr. at  $0^{\circ}$ , the aqueous layer was washed twice with 10-ml. portions of benzene, then discarded. The organic layer, kept cold during the interim, was combined with the benzene washes, dried with magnesium sulfate, filtered, then heated under reflux for 0.5 hr., until the evolution of nitrogen was complete. Decomposition of the acyl azide began at about 60°. Only enough heat was applied to maintain a modestly brick evolution of gas. A few drops of the resulting, sharpsmelling isocyanate solution was used for the preparation of a phenylurea derivative (below). The remaining solution was cooled and 20 ml. of concentrated hydrochloric acid was added. The mixture was stirred, slowly at first and then more rapidly until the vigor of evolution of carbon dioxide was much diminished (15 min.). The mixture was heated under reflux with vigorous stirring for just 5 min., when a droplet of saturated barium hydroxide solution no longer became turbid when suspended in the effluent gas stream. The mixture was evaporated to dryness, the residue agitated with 10 ml. of absolute ethanol, then evaporated to dryness again to remove the last of the water and hydrogen chloride. The resulting solid was agitated with acetone, collected by filtration, and washed with acetone to yield 3.77 g. (82%) of

hygroscopic needles, m.p. 219–221°. Recrystallization from absolute ethanol did not raise the melting point.

Anal. Caled. for C<sub>5</sub>H<sub>10</sub>NCl: C, 50.21; H, 8.43; N, 11.71. Found: C, 49.87; H, 8.52; N, 12.18.

In a similar experiment where the isocyanate solution and concentrated hydrochloric acid were refluxed for a longer period  $(1 \text{ hr.})^{15}$  the product was obtained in only 51% yield, m.p. 217–219°. The acetone washes were found to contain a considerable amount of another crude hydrochloride.

N-(3-Cyclopenten-1-yl)-N'-phenylurea (XIII).—A little of the solution of 3-cyclopenten-1-yl isocyanate (XV) from the above experiment was combined with aniline. The resulting solid was washed with benzene. It crystallized from ethanol as needles, m.p. 218°.

Anal. Caled. for  $C_{12}H_{14}N_2O$ : C, 71.26; H, 6.98; N, 13.85. Found: C, 70.98; H, 7.12; N, 14.03.

Acknowledgment.—The authors wish to thank Mr. Louis Brancone and his group for the elemental analyses and Mr. William Fulmor and his coworkers for the spectral data.

# Hydrogenation-Hydrogenolysis Studies of Symmetrically Substituted 1,4-Acetylenic Glycols

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#### Received January 24, 1962

The formerly difficult hydrogenation of 1,4-acetylenic glycols to the corresponding olefinic and saturated glycols at low pressures with palladium catalysts has been accomplished in high yield and purity. Hydrogenolysis side reactions at the tertiary hydroxyl groups, previously responsible for poor yields and quality of product have been eliminated by the novel use of very small amounts of base during the hydrogenation. The route through which hydrogenolysis takes place has been established.

The hydrogenation of 1,4-acetylenic glycols at low pressures to the corresponding olefinic and saturated diols was studied extensively by Zal'kind<sup>1-4</sup> and Du Pont<sup>5,6</sup> using both palladium and platinum catalysts. Both investigators found that on complete hydrogenation of acetylenic diols to the saturated derivatives extensive hydrogenolysis at the tertiary hydroxyl groups was encountered yielding a mixture of saturated carbinol, saturated hydrocarbon, and a minor amount of the desired 1,4-saturated glycol. Zal'kind believed hydrogenolysis to originate from further hydrogenation of the saturated diol but no experimental proof was offered to support this view.

Raney nickel has been recommended<sup>7,8</sup> as a

Y. S. Zal'kind, J. Russ. Phys. Chem. Soc., 45, 1875, 1896 (1913);
 Chem. Abstr., 8, 1419 (1914).

(2) Y. S. Zal'kind and I. G. Bezsonova, J. Russ. Phys. Chem. Soc., 53, 279 (1921); Chem. Abstr., 18, 2327 (1924).

(3) Y. S. Zal'kind, et al., J. Russ. Phys. Chem. Soc., 47, 680 (1915); Chem. Abstr., 9, 2510 (1915).

(4) A. W. Johnson, "Acetylenic Compounds, Vol. I, the Acetylenic Alcohols," Edw. Arnold Co., London, 1946, pp. 188, 195, 207.
(5) G. DuPont, Ann. Chim., 30, 485 (1913).

(6) G. DuPont, Compt. rend., 156, 1623 (1913); Chem. Abstr., 7, 3112 (1913).

(7) G. DuPont, Bull. soc. chim. (5), 3, 1030 (1936).

(8) N. Lozac'h, Ecole Normale Superieure, Publications des Laboratoires Chemie, Vol. III, p. 30 (1945). selective catalyst for the preparation of olefinic glycols. Its use with small amounts of base as promoter was claimed by Vaughn<sup>9</sup> to result in a selective hydrogenation which halted exactly at the olefinic stage. Experiments in this laboratory<sup>10</sup> have shown that at low to moderate pressures Raney nickel, while resulting in less hydrogenolysis than palladium catalyst, does not completely hydrogenate the acetylenic diols to the corresponding saturated diols and is not selective for semihydrogenation with base promoters.

The need for a low pressure, efficient, selective process<sup>11</sup> for hydrogenating 1,4-acetylenic glycols to the corresponding olefinic and saturated diols in high yield and purity arose in this laboratory. Consequently, both the mechanism and route by which hydrogenolysis takes place and its inhibition were studied. Zal'kind's original contention that hydrogenolysis arose from the saturated diols was found erroneous since both the saturated diols and their analogous carbinols were found completely stable to hydrogenolysis showing no pressure drop

(10) J. Casey, unpublished work. Air Reduction Co., Murray Hill, N. J.

(11) R. J. Tedeschi; U.S. Patent 2,992,278, July 11, 1961.

<sup>(9)</sup> T. H. Vaughn, U.S. Patent 2,157,365, May 9, 1939.