2,2,7,7-Tetranitro-1,8-octanediol (XIV).—The procedure was the same as for the preparation of compound IX (method a) except that 8.8 g. (0.05 mole) of 1,6-dinitrohexane[8,10] was employed. This procedure afforded 14.7 g. (90% crude yield) of the diol, m.p. 140–157° dec. After two recrystallizations from dilute ethanol there was obtained 12.2 g. (75% yield) of the pure diol as feathery needles, m.p. 157–159° dec. The decomposition point depends on the rate of heating and the extent of subdivision of the sample; values ranging from 155–158° for a powdered sample to 164–166° for large crystals placed in the bath at 150° were obtained (capillary tube).

Anal. Calcd. for $C_8H_{14}O_{10}N_4$: C, 29.44; H, 4.29; N, 17.17. Found: C, 29.45; H, 4.40; N, 16.99.

1,8-Diacetoxy-2,2,7,7-tetranitroöctane, m.p. 93–94°, was obtained after two recrystallizations from dilute ethanol.

Anal. Calcd. for $C_{12}H_{18}O_{12}N_4$: C, 35.12; H, 4.39; N, 13.65. Found: C, 35.39; H, 4.23; N, 13.50.

1,1,6,6-Tetranitrohexane (VII). (a) From 1,6-Dinitrohexane (V).[13]—To a solution of 4.14 g. (0.1 mole; 97% assay) of sodium hydroxide in 50 ml. of water was added with stirring at 0–5° 8.8 g. (0.05 mole) of 1,7-dinitrohexane. After solution was attained, 6.9 g. (0.1 mole) of sodium nitrite was added all at once and after 15 min., a solution of 34 g. (0.1 mole) silver nitrate in 50 ml. of water was introduced. The reaction mixture immediately thickened and became dark in color. After continued stirring for 2 more hr. at 0°, the precipitate was filtered, washed with 100 ml. of water, and dried *in vacuo* for 48 hr. Continuous extraction of the dry solid with dry ether for 24 hr. and removal of the solvent *in vacuo* gave 11 g. (84% yield) of compound VII, m.p. 63–65°. Recrystallization with chloroform gave m.p. 66–67°; when mixed with compound VII prepared from XIV the melting point was undepressed.

(b) **From 1,6-Dibromo-1,1,6,6-tetranitrohexane.**[13]—To a solution of potassium iodide (6.3 g., 0.38 mole) in 150 ml. of 50% methanol was added 4.24 g. (0.01 mole) of 1,6-dibromo-1,1,6,6-tetranitrohexane (see preparation below). The mixture was stirred for 8 hr. at 26° and was then cooled and acidified with dilute hydrochloric acid and extracted with ether. The ether layer was washed with sodium thiosulfate solution, then reduced in volume to precipitate sulfur. The solution was filtered and the filtrate concentrated to dryness under reduced pressure, yielding 2.26 g. (85%) of 1,1,6,6-tetranitrohexane (VII), m.p. 64–65°. When mixed with an authentic sample, the melting point was not depressed.

1,6-Dibromo-1,1,6,6-tetranitrohexane.[13]—To a solution of 0.76 g. (0.0185 mole, 97% assay) sodium hydroxide in 150 ml. of water at 0–5° was added 2.0 g. (0.0075 mole) of 1,1,6,6-tetranitrohexane. The mixture was stirred until it became homogeneous; 2.5 g. (0.0138 mole) of bromine was then added dropwise, causing a yellow precipitate to form. The mixture was stirred for 2 hr. and then filtered. The product was crystallized first from hexane and then from aqueous ethanol to yield colorless crystals, m.p. 120–121°.

Anal. Calcd. for $C_6H_8N_4O_8Br_2$: C, 16.98; H, 1.88; N, 13.20. Found: C, 16.83; H, 2.03; N, 13.23.

1,7-Dibromo-1,1,7,7-tetranitroheptane.[13]—1,7-Dinitroheptane (9.5 g., 0.05 mole) was oxidatively nitrated by the same procedure employed with 1,6-dinitrohexane (VII) (procedure b, above) to yield 12.5 g. of a yellow oil, $n^{20}D$ 1.4800, believed to contain principally 1,1,7,7-tetranitroheptane (VIII); 89% yield calculated as (VIII). Attempts to crystallize the material failed. An attempted molecular distillation of the product resulted in its decomposition.

The crude 1,1,7,7-tetranitroheptane was converted into its dibromo derivative by the same procedure used for preparing 1,6-dibromo-1,1,6,6-tetranitrohexane (see above). The crude product was an oil which was first crystallized from hexane (m.p. 32–34°) and then from aqueous ethanol; m.p. 42.5–43°.

Anal. Calcd. for $C_7H_{10}N_4O_8Br_2$: C, 19.17; H, 2.28; N, 12.78. Found: C, 19.09; H, 2.40; N, 12.69.

Acknowledgment.—Support of this work by the Office of Naval Research is gratefully acknowledged.

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[13] We are indebted to Dr. R. Miller for carrying out this experiment.

Reactions of Acetylenes. II. Some Reactions of β-Ethynylcarboxylic Acids

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The alkylation of malonic esters with *tert*-acetylenic chlorides leads to substituted malonic esters, $HC\equiv C—C(R^1R^2)—C(R^3)(COOC_2H_5)_2$. These compounds have been used to prepare a wide variety of other products, notably saturated and unsaturated carboxylic acids, levulinic acids, pyrrolidones, pyrrolidines, and amines of novel structures. The facile hydration of the acetylenic group under alkaline conditions is pointed out.

The preparation[1] of 3,3-dimethyl-4-pentynoic acid (VI) from diethyl malonate in these laboratories some years ago suggested a reinvestigation and extension of the reaction involved. It is well known that sodiomalonic esters cannot be alkylated in the usual manner with *tert*-aliphatic halides since the latter are much too sensitive to elimination of hydrogen halide in strongly alkaline media. The *tert*-acetylenic halides $[R^1R^2C(Cl)\text{-}C\equiv CH]$, however, react in alkaline solutions by a unique mechanism[2,3] involving an electrophilic zwitterion-carbene, ($R^1R^2\overset{\oplus}{C}—C\equiv\overset{\ominus}{C} \longleftrightarrow R^1R^2C=C=C:$), which has been shown to be capable of alkylating sterically hindered nucleophiles.[2]

In agreement with the earlier report[1] it has now been found that *tert*-acetylenic halides successfully alkylate sodiomalonic esters and their monoalkyl derivatives, thus providing a simple route to the

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[1] O. K. Behrens, J. Corse, D. E. Huff, R. G. Jones, Q. F. Soper, and C. W. Whitehead, *J. Biol. Chem.*, **175**, 788 (1948).

[2] (a) G. F. Hennion and R. S. Hanzel, *J. Am. Chem. Soc.*, **82**, 4908 (1960); (b) G. F. Hennion and A. P. Boisselle, *J. Org. Chem.*, **26**, 2677 (1961).

[3] H. D. Hartzler, *J. Am. Chem. Soc.*, **83**, 4990 (1961).

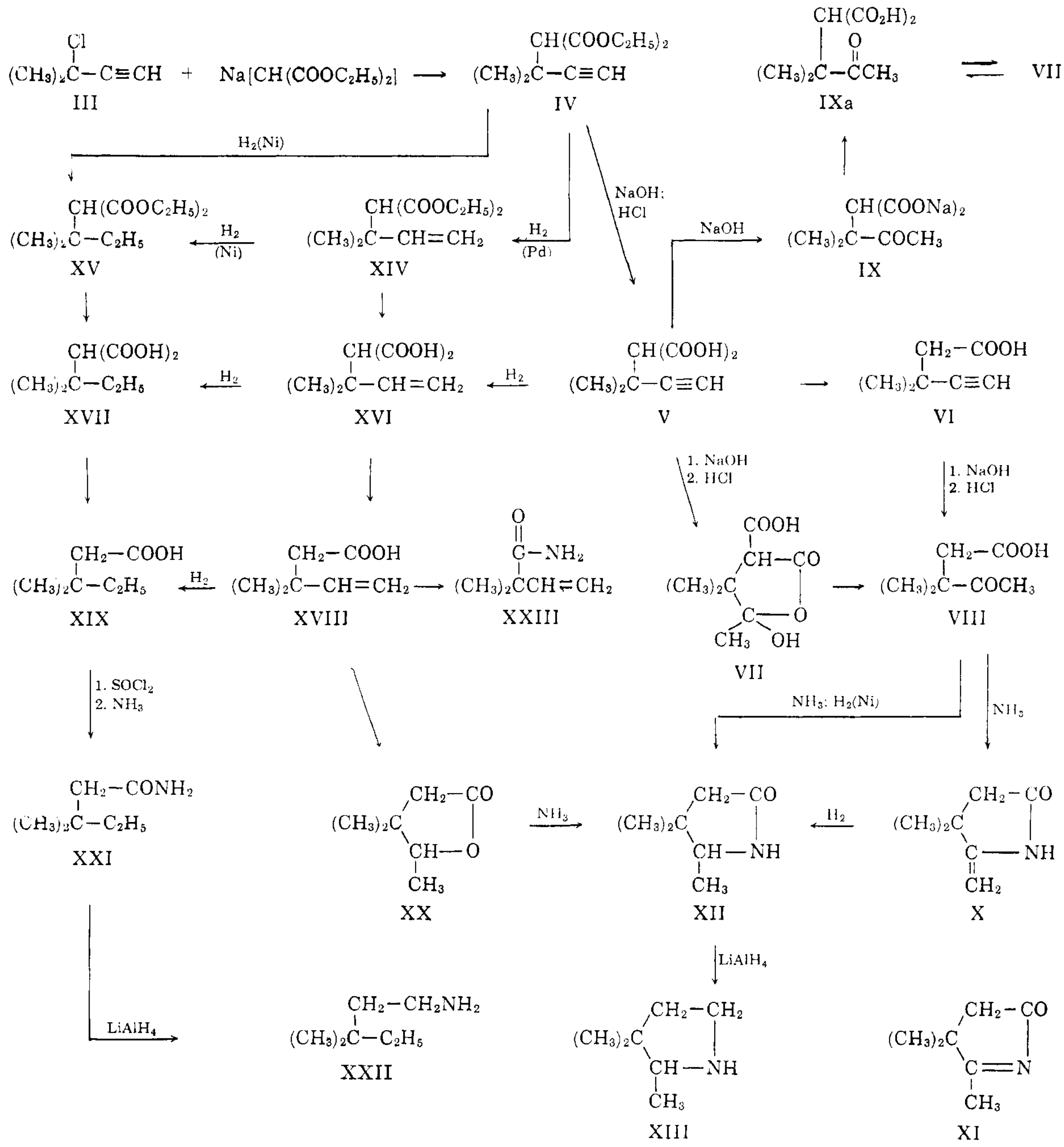
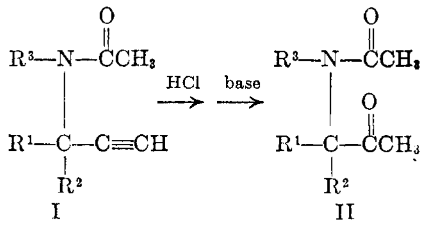


Fig. 1.—Syntheses from diethyl 1,1-dimethylpropargylmalonate.

highly substituted products, $HC\equiv C—C(R^1R^2)—C(R^3)(COOC_2H_5)_2$. These compounds may be used, as shown in Fig. 1, for the preparation of substituted pyrrolidines and various saturated and unsaturated acids and amines. In addition to this application we were interested also in studying the hydration of the acetylenic acids. Recent work in these laboratories[4] has demonstrated a remarkable facilitation of hydration in acetylenes containing α-acetamido groups (I), so it was of interest to investigate other acetylenes with similarly situated oxygen atoms.



The method of synthesis[1] involved treatment of 3-chloro-3-methyl-1-butyne with diethyl sodiomalonate to give the substituted malonic ester IV. Hydrolysis of the diester IV under the described conditions[1] gave the acetylenic acid V accompanied by a small amount of a new compound. Analysis of this new material indicated that a mole of

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[4] N. R. Easton, R. Dillard, M. Livezey, D. E. Morrison, and G. F. Hennion, Am. Chem. Soc. Meeting, New York, 1960, Abstracts 44-O.

water had been added to the acid V. Since a facile hydration of the triple bond had been expected,[2] the new compound was believed to be the ketone IXa. The infrared spectrum, however, indicated the presence of a alcoholic hydroxyl group and the absence of ketonic carbonyl suggesting structure VII. Conversion to the sodium salt eliminated the hydroxy group with release of the ketone carbonyl. It thus appears that VII and IXa are tautomeric, VII representing the crystalline state of the free acid, IX the structure of the sodium salt, and IXa the open chain γ-keto acid. When the diester IV was treated under more strenuous conditions, either by using a higher temperature or a longer heating time, the product was nearly all VII. Compound VII was also obtained from the acid V by refluxing in 25% sodium hydroxide. Thus, facile hydration of the triple bond had taken place under alkaline conditions.

Decarboxylation of VII gave VIII which is probably a mixture of the open and cyclic forms. Compound VIII could also be prepared directly by vigorous treatment of the acetylenic acid VI with strong base. Treatment of the keto acid (VIII) with ammonia gave the 2-methylenepyrrolidone (X). The nuclear magnetic resonance spectrum shows that this compound has the exocyclic double bond as in structure X, rather than the endocyclic double bond as in XI. Treatment of VIII with ammonia and hydrogen over Raney nickel catalyst gave the pyrrolidone XII; treatment of the pyrrolidone with lithium aluminum hydride gave the pyrrolidine XIII.

The availability of the substituted malonic ester (IV) prompted us to consider further syntheses from this starting material. Either partial or complete hydrogenation of the acetylenic group was easily accomplished to give the esters XIV and XV. These could be hydrolyzed and decarboxylated to the acids XVIII and XIX. The unsaturated acid XVIII could be cyclized under acidic conditions to give the lactone (XX) which on treatment with ammonia gave the pyrrolidone XII. The saturated acid (XIX) could be readily converted to the amine XXII.

These reactions were extended to cover substituted malonic esters and various other acetylenic chlorides.

Experimental

Melting points are uncorrected and were taken in a capillary tube.

The tertiary acetylenic chlorides were prepared by the method of Hennion, *et al.*[5]

Diethyl (1,1-Dimethylpropargyl)malonate (IV), (1,1-Dimethylpropargyl)malonic Acid (V), and 3,3-Dimethyl-4-pentynoic Acid (VI).—These compounds were prepared according to ref. 1.

2-Carboxy-3,3-dimethyl-4-hydroxy-4-pentanolactone (VII).—A mixture of 17 g. (0.06 mole) of diethyl (1,1-dimethylpropargyl)malonate[1] and 200 ml. of 10% sodium hydroxide was refluxed overnight. The solution was concentrated to dryness at reduced pressure. The residue was dissolved in water and cooled; the solution was then made acidic with concentrated hydrochloric acid. The resulting mixture was extracted with benzene and with chloroform. The organic layers were combined, dried over magnesium sulfate, and concentrated at reduced pressure. The residue was recrystallized from benzene, giving 6 g. (50%) of product, m.p. 120–122°.

Anal. Calcd. for $C_8H_{12}O_5$: C, 51.06; H, 6.43. Found: C, 51.09; H, 6.37.

The same compound could be prepared by refluxing a solution of the malonic acid V in 10% sodium hydroxide for 16 hr.

3,3-Dimethyllevulinic Acid (VIII).—The 3-carboxy-4,4,5-trimethyl-5-hydroxy-2-furanone (VII), (25 g., 0.133 mole), was heated at 155° for 1 hr. The resulting liquid was then cooled and distilled. The 3,3-dimethyllevulinic acid (12 g., 63%) boiled at 79° at 0.02 mm.

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.31; H, 8.39. Found: C, 58.41; H, 8.54.

The same compound could be prepared from the acid VI by refluxing a basic solution for 16 hr.

4,4-Dimethyl-5-methylene-2-pyrrolidone (X).—A mixture of 25 g. (0.133 mole) of 3,3-dimethyllevulinic acid, ammonia, and ethanol was heated in an autoclave at 185° for 5 hr. The mixture was concentrated at reduced pressure, and the residue was distilled, b.p. 110–115° at 4 mm., giving 10 g. (59%) of product. It was crystallized from low-boiling petroleum ether, m.p. 72–74°.

Anal. Calcd. for $C_7H_{11}NO$: C, 67.17; H, 8.85. Found: C, 66.91; H, 8.82.

4,4,5-Trimethyl-2-pyrrolidone (XII).—The 3,3-dimethyllevulinic acid, 70 g. (0.5 mole), was heated at 135° for 5 hr. in an autoclave with ethanol, ammonia, and Raney nickel under 2000 p.s.i. of hydrogen. The mixture was filtered and the ethanol distilled at reduced pressure. The product (46 g., 72%) boiled at 85° at 0.2 mm.

Anal. Calcd. for $C_7H_{13}NO$: N, 11.01. Found: N, 10.94.

This compound was also prepared by hydrogenation of X.

2,3,3-Trimethylpyrrolidine (XIII).—A mixture of 4 g. (0.031 mole) of 4,4,5-trimethylpyrrolidone (XII) and 2.3 g. (0.06 mole) of lithium aluminum hydride in 250 ml. of diethyl ether was refluxed overnight. The excess reducing agent was destroyed with a 20% solution of sodium hydroxide. The ether layer was dried over magnesium sulfate and concentrated at reduced pressure. The residue was distilled; the product (2 g., 53%) boiled at 65° at 85 mm. The hydrochloride was prepared and crystallized from ethyl acetate, m.p. 148–150°.

Anal. Calcd. for $C_7H_{16}ClN$: C, 56.17; H, 10.78. Found: C, 56.03; H, 10.82.

Diethyl 1,1-Dimethylallylmalonate (XIV).—The diethyl 1,1-dimethylpropargylmalonate (226 g., 1.0 mole) was hydrogenated over 5% palladium on carbon with petroleum ether as the solvent under a pressure of approximately 40 p.s.i. of hydrogen. The mixture was filtered and the solvent distilled at reduced pressure. The residue was then distilled; 180 g. (79%) of product boiling at 52–54° at 0.05 mm. was obtained.

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 63.06; H, 8.73.

1,1-Dimethylallylmalonic Acid (XVI).—A mixture of 180 g. (0.8 mole) of diethyl 1,1-dimethylallylmalonate, 128 g. (3.2 moles) of sodium hydroxide, and 1 l. of water was refluxed overnight. The mixture was concentrated at reduced pressure and then acidified with concentrated hydrochloric acid; 1.5 l. of clear solution was obtained. On standing overnight, 86 g. (83%) of 1,1-dimethylallylmalonic acid separated. After recrystallization from a mixture of benzene and ethyl acetate, it melted at 104–106°.

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(5) G. F. Hennion, J. J. Sheehan, and D. E. Maloney, *J. Am. Chem. Soc.*, **72**, 3542 (1950).

Anal. Calcd. for $C_8H_{12}O_4$: C, 55.80; H, 7.03. Found: C, 55.54; H, 7.12.

3,3-Dimethyl-4-pentenoic Acid (XVIII).—The 1,1-dimethylallylmalonic acid (85 g., 0.63 mole) was heated at 157° for 3 hr., filtered, and distilled. The material boiling at 47–48° at 0.1 mm. (n^{25}D 1.4226) weighed 40 g. (50%).

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.55; H, 9.60.

3,3-Dimethyl-4-pentanolactone (XX).—A mixture of 10 g. (0.078 mole) of 3,3-dimethyl-4-pentenoic acid (XVIII) in 50 ml. of concentrated sulfuric acid was stirred for 10 min. and poured over 200 g. of ice. The mixture was extracted with ether; the ether solution was dried over magnesium sulfate and concentrated at reduced pressure. The residue was distilled and 8 g. (80%) of product boiling at 50° at 0.5 mm. was collected; it was insoluble in dilute sodium hydroxide.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.53; H, 9.71.

Diethyl *t*-Amylmalonate (XV).—A solution of 19 g. (0.084 mole) of the acetylenic ester (IV) in ethanol was hydrogenated over Raney nickel catalyst at approximately 40 p.s.i. of hydrogen. The catalyst was filtered and the solvent removed at reduced pressure. The residue was distilled under 4 mm. of pressure. A yield of 13 g. (68%) of diethyl *t*-amylmalonate, boiling at 92–92.5° at 4 mm. (n^{25}D 1.4287), was obtained.

Anal. Calcd. for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 62.34; H, 9.63.

***t*-Amylmalonic Acid (XVII).**—A mixture of 15 g. (0.65 mole) of diethyl *t*-amylmalonate, 12 g. (0.3 mole) of sodium hydroxide, 30 ml. of water, and 25 ml. of ethanol was refluxed for 4 hr. The mixture was concentrated at reduced pressure, and the residue, after washing with ether, was made acidic with sulfuric acid. The mixture was extracted with ether, the ether layer dried over magnsium sulfate, and concentrated at reduced pressure. The residue was recrystallized from benzene, giving 6 g. (53%) of product melting at 120–122°.

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.06; H, 8.19.

3,3-Dimethylpentanoic Acid (XIX).—The malonic acid (XVII), 160 g. (0.92 mole), was heated at 157–160° for 4 hr. and distilled. The product (88 g., 73%) was collected at 54–57° at 0.3 mm.

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.58; H, 10.85. Found: C, 64.83; H, 10.56.

3,3-Dimethylpentanamide (XXI).—A mixture of 26 g. (0.2 mole) of 3,3-dimethylpentanoic acid and 119 g. (1.0 mole) of thionyl chloride in 500 ml. of benzene was refluxed overnight. The solvent and excess thionyl chloride were removed at reduced pressure, and the residue was distilled under 50 mm. of mercury; the material (20 g.) boiling at 72–74° (n^{25}D 1.4318) was collected. This material was dissolved in 250 ml. of benzene, and anhydrous ammonia was bubbled in for 2 hr. The mixture was stirred for 1 hr. and 250 ml. of toluene was added. The mixture was treated with carbon and filtered, and the filtrate was concentrated to dryness at room temperature. The residue after being recrystallized from methyl cyclohexane melted at 70–72° (10 g., 38%).

Anal. Calcd. for $C_7H_{15}NO$: C, 65.07; H, 11.70. Found: C, 64.96; H, 11.79.

3,3-Dimethylpentylamine (XXII).—A mixture of 6 g. (0.05 mole) of 3,3-dimethylpentanamide (XXI) and 5.7 g. (0.15 mole) of lithium aluminum hydride in 500 ml. of ether was refluxed overnight. The mixture was decomposed with a solution of sodium hydroxide. The ether layer was separated and dried over magnesium sulfate. Dry hydrogen chloride was added to the filtered ether solution. The solid hydrochloride was recrystallized from a mixture of ethyl acetate and methyl ethyl ketone, giving 2 g. (26%) of product. It decomposed above 260°.

Anal. Calcd. for $C_7H_{18}ClN$: C, 55.43; H, 11.96. Found: C, 55.68; H, 12.13.

3,3-Dimethyl-4-pentenamide (XXIII).—This procedure was similar to that for the saturated compound (XXII), m.p. 66–68°.

Anal. Calcd. for $C_7H_{13}NO$: C, 66.10; H, 10.30. Found: C, 66.27; H, 10.22.

Diethyl ethyl(1,1-dimethylpropargyl)malonate was prepared from 772.88 g. (4.0 moles) of diethyl ethylmalonate and 205 g. (2.0 moles) of 3-chloro-2-methyl-1-butyne according to ref. 1, giving 127 g. (25%) of product, b.p. 70–72° at 0.1 mm., n^{25}D 1.4514.

Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 65.90; H, 8.55.

2-Carboxy-2-ethyl-3,3-dimethyl-4-hydroxy-4-pentanolactone was prepared from 50.8 g. (0.2 mole) of diethyl ethyl-1,1-dimethylpropargylmalonate by method for VII, giving 11 g. (25%) of product, m.p. 152–153°.

Anal. Calcd. for $C_{10}H_{16}O_5$: C, 55.54; H, 7.64. Found: C, 55.60; H, 7.63.

2-Ethyl-3,3-dimethyllevulinic acid was prepared from 11 g. (0.051 mole) of 3-carboxy-3-ethyl-4,4,5-trimethyl-5-hydroxy-2-furanone by method for VIII, giving 6 g. (70%) of product, b.p. 84–85° at 0.1 mm.

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.76; H, 9.36. Found: C, 62.66; H, 9.36.

Diethyl (1-ethynylcyclohexyl)malonate was prepared according to ref. 1 from 2 moles of 1-ethynylcyclohexyl chloride, giving 114 g. (21%) of product, b.p. 93–94° at 0.03 mm.

Anal. Calcd. for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 67.86; H, 8.62.

(1-Ethynylcyclohexyl)malonic acid was prepared according to ref. 1 from 0.22 mole of diethyl (1-ethynylcyclohexyl)malonate, giving 20 g. (44%) of product, m.p. 145–147°.

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 62.93; H, 7.00.

(1-Ethynylcyclohexyl)acetic acid was prepared according to ref. 1 from 0.12 mole of (1-ethynylcyclohexyl)malonic acid, giving 14 g. (70%) of product, m.p. 45–48°.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.22; H, 8.36.

3,3-Pentamethylenelevulinic Acid.—A mixture of 14 g. (0.085 mole) of (1-ethynylcyclohexyl)acetic acid and 100 ml. of 20% sodium hydroxide solution was refluxed overnight, cooled, and then made acidic with concentrated hydrochloric acid. The mixture was extracted with ether, the ether solution dried over magnesium sulfate, filtered, and the ether removed from the filtrate under reduced pressure. The residue was crystallized from a mixture of ether–petroleum ether, giving 6.5 g. (41.6%) of product melting at 65–67°.

Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.24; H, 8.72.

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