Anal. Calcd. for $C_{18}H_{22}NCl$: C, 75.11; N, 7.70; N, 4.48. Found: C, 74.98; H, 7.71; N, 4.50.

1,6-Diphenyl-5,6-dihydro-2-pyridone (XXXIII). 2-Styrylacrylic acid (IX) (70 g., 0.4 mole) was heated under reflux with 1500 ml. of aniline for 1 day. At the end of this period the solution was evaporated under reduced pressure and with heating to a syrupy residue. The residue was heated on an oil bath at 185° for 3 hr., cooled slightly, and dissolved in 1 l. of hot benzene. The benzene solution was extracted with three 200-ml. portions of 10% sodium hydroxide solution, three 200-ml. portions of 10% hydrochloric acid solution, and once with 200 ml. of water. The organic layer was dried over anhydrous calcium sulfate, filtered, and the benzene removed on a steam bath under a stream of nitrogen. The resulting amber colored oily solid was dissolved in 300 ml. of hot methanol, filtered, and cooled. After standing at −10° for 3 hr. crystallization began and was completed after 1 week. The solution was then filtered and the solid washed with a small amount of cold methanol and dried on the funnel to yield 12 g. (12%) of pale yellow crystalline solid; m.p. 165—170°. The crude material was purified by recrystallization from methanol to give 11.2 g. (11%) of cream colored crystals; m.p. 181–187°. Three additional recrystallizations from methanol netted a white crystalline analytic sample; m.p. 187–188°.

Anal. Calcd. for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.58; H, 6.07; N, 5.50.

UNIVERSITY PARK, PA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Preparation of *t*-Acetylenic Chlorides[1]

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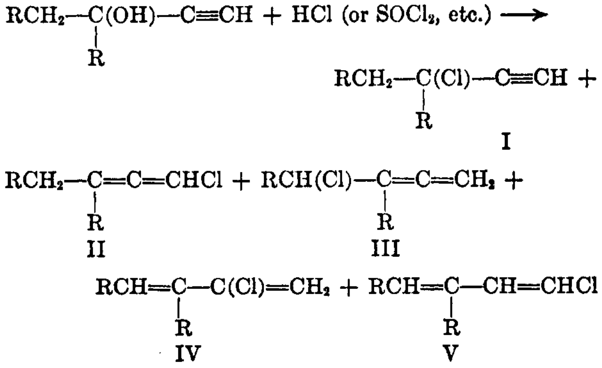
t-Acetylenic chlorides, $RR'C(Cl)—C\equiv CH$, were prepared from the corresponding *t*-carbinols by reaction with excess cold concentrated hydrochloric acid containing calcium and cuprous chlorides. The procedure described is the best developed to date with respect to yields and isomer purity of the products.

Earlier work in this laboratory has shown that the *t*-acetylenic chlorides, $RR'C(Cl)—C\equiv CH$, are versatile intermediates in organic syntheses.[3] Unfortunately, only a few chlorides of this type have been prepared in good yield and acceptable purity. Where R and R′ are small alkyl groups (water and acid soluble *t*-carbinols), chlorides may be prepared in 50–60% yields by treatment of the carbinols with concentrated hydrochloric acid containing calcium chloride.[3] This method has not proved satisfactory, however, where R and (or) R′ are larger than ethyl. The difficulty arises largely from the fact that rearrangement products are obtained at the expense of the desired *t*-chloride as shown in the following equation.



$$RCH_2—\underset{R}{C}(OH)—C\equiv CH + HCl\ (\text{or } SOCl_2\text{, etc.}) \longrightarrow$$

$$\underset{\text{I}}{RCH_2—\underset{R}{C}(Cl)—C\equiv CH} +$$

$$\underset{\text{II}}{RCH_2—\underset{R}{C}=C=CHCl} + \underset{\text{III}}{RCH(Cl)—\underset{R}{C}=C=CH_2} +$$

$$\underset{\text{IV}}{RCH=\underset{R}{C}—C(Cl)=CH_2} + \underset{\text{V}}{RCH=\underset{R}{C}—CH=CHCl}$$

Such complex mixtures are easily explained. The carbonium ion ($RR'\overset{+}{C}—C\equiv CH \longleftrightarrow RR'C=C=\underset{+}{C}H$) derived from the alcohol may lead directly to I and II. Dehydration of the alcohol yields the conjugate eneyne hydrocarbon which is converted to III and IV by addition of hydrogen chloride (1,4- and 1,2- addition, respectively). Prototropic rearrangement of II yields V. That mixtures of products are encountered has long been recognized in individual cases.[4]

Favorskaya and co-workers[4] first noted that cuprous chloride has a marked effect on the course of the reaction of the lower *t*-acetylenic carbinols with hydrochloric acid and emphasized that this substance promotes rearrangement of *t*-chlorides

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[1] (1) Paper No. 73 on substituted acetylenes; previous paper, G. F. Hennion and C. A. Lynch, *J. Org. Chem.*, **25**, 1330 (1960).

[2] (2) Eli Lilly Company Fellow, 1958–60. Abstracted in part from the Ph.D. Dissertation of A. P. B.

[3] (3)(a) G. F. Hennion and D. E. Maloney, *J. Am. Chem. Soc.*, **73**, 4735 (1951); (b) G. F. Hennion and E. G. Teach, *J. Am. Chem. Soc.*, **75**, 1653, 4297 (1953); (c) G. F. Hennion and J. M. Campbell, *J. Org. Chem.*, **21**, 761 (1956); (d) G. F. Hennion and K. W. Nelson, *J. Am. Chem. Soc.*, **79**, 2142 (1957); (e) G. F. Hennion and R. S. Hanzel, *J. Am. Chem. Soc.*, **82**, 4908 (1960).

[4] (4)(a) A. Favorskii and T. Favorskaya, *Compt. rend.*, **200**, 839 (1935); (b) T. Favorskaya, *J. Gen. Chem. U. S. S. R.*, **9**, 386 (1939); (c) T. Favorskaya and A. Zakharova, *J. Gen. Chem. U. S. S. R.*, **10**, 446 (1940); (d) T. Favorskaya and I. Favorskaya, *J. Gen. Chem. U. S. S. R.*, **10**, 451 (1940); (e) T. Favorskaya, *J. Gen. Chem. U. S. S. R.*, **11**, 1246 (1941); (f) I. Favorskaya, *J. Gen. Chem. U. S. S. R.*, **18**, 52 (1948); (g) C. D. Hurd and W. McPhee, *J. Am. Chem. Soc.*, **71**, 398 (1949); (h) G. F. Hennion, J. Sheehan, and D. Maloney, *J. Am. Chem. Soc.*, **72**, 3542 (1950); (i) E. Bergmann and D. Herrman, *J. Am. Chem. Soc.*, **73**, 4013 (1951); (j) Y. Bhatia, P. Landor, and S. Landor, *J. Chem. Soc.*, 24 (1959); (k) G. F. Hennion and C. A. Lynch, *J. Org. Chem.*, **25**, 1330 (1960).

TABLE I

t-Acetylenic Chlorides, RR′C(Cl)—C≡CH

No.	R	R′	Formula	Yield,[a] %	Isomer Purity	B.P. °C.	Mm.	n_D^{25}	Cl, % Calcd.	Cl, % Obsd.
1	CH_3—	CH_3—	C_5H_7Cl	65	Good[b]	73–76		1.4156		
2	CH_3—	C_2H_5—	C_6H_9Cl	78	Good[b]	53–56	128	1.4302		
3	C_2H_5—	C_2H_5—	$C_7H_{11}Cl$	83	Good[b]	70–72	100	1.4389		
4	CH_3—	*i*-C_3H_7—	$C_7H_{11}Cl$	77	83%[c]	66–68	100	1.440[d]	27.15	26.71[d]
5	CH_3—	*i*-C_4H_9—	$C_8H_{13}Cl$	53[e]	Good[b]	53–56	25	1.4358	24.51	24.61
6	—$CH_2(CH_2)_3CH_2$—		$C_8H_{11}Cl$	81	Good[b]	54–56	12	1.4782	24.86	24.52
7	CH_3—	*i*-C_5H_{11}—	$C_9H_{15}Cl$	82	Good[b]	57–59	15	1.4381	22.34	22.01
8	*i*-C_3H_7—	*i*-C_3H_7—	$C_9H_{15}Cl$	88	Poor[b,c]	57–60	15	1.4559[f]	22.34	22.48[f]
9	CH_3—	*n*-C_6H_{13}—	$C_{10}H_{17}Cl$	76	Good[b]	76–80	12	1.4427	20.53	20.12
10	C_2H_5—	C_5H_{11}—[g]	$C_{10}H_{17}Cl$	79	Poor[b,c]	49–56	3	1.458[h]	20.53	19.94[h]

[a] Yields are for once distilled material (through a 60 × 1 cm. helix-packed column) of given boiling range. [b] From infrared spectrum. [c] From gas liquid chromatography (10 ft. × 1/4 in. column, silicone oil, General Electric, SF-96, flow rate of 40 ml. of helium per minute, temperatures 100–140°). [d] Redistilled sample, 92% *t*-chloride (by gas liquid chromatography). [e] A 15% yield of 1-chloro-3,5-dimethyl-1,2-hexadiene, b.p. 50–52° at 12 mm. was obtained also. [f] Analytical sample, center fraction from redistillation. [g] 2-Methylbutyl, $C_2H_5(CH_3)CHCH_2$—. [h] Redistilled sample; infrared spectrum indicated gross contamination by isomeric 1-chloro-1,2-diene.

(I) to the isomers II and V. This was confirmed in this laboratory where it was also observed that superior yields of the lower *t*-chlorides are obtained when the *t*-acetylenic carbinols are treated with cold concentrated hydrochloric acid containing calcium chloride.[4h] More recently it was observed that a small amount of copper bronze powder, employed along with calcium chloride and hydrochloric acid, has a marked beneficial effect on the yield and quality of the *t*-chloride formed. It was also learned that cuprous chloride, when used in considerable amount along with hydrochloric acid, has a pronounced effect on the yield of 1-ethynylcyclohexyl chloride from 1-ethylcyclohexanol.[3d] Apparently, cuprous chloride complexes with acetylenic carbinols and effects solution in hydrochloric acid for conversion to the *t*-chlorides.

We wish to report now that a variety of *t*-acetylenic carbinols may be converted to their *t*-chlorides by treatment, in the cold, with excess hydrochloric acid containing calcium chloride, cuprous chloride, and copper bronze powder. The general procedure described is superior to all other methods previously reported, in that higher yields and purer products are produced. The *t*-chlorides are described in Table I. Compounds 1, 2, 3, 5, and 6 have been reported previously.[3d,4b–d,4h]

EXPERIMENTAL

The *t-acetylenic carbinols* were provided (one exception) by the Air Reduction Chemical Company, New York, and were used as received. Diisopropylethynylcarbinol was prepared by the reaction of diisopropyl ketone with sodium acetylide in liquid ammonia; b.p. 67–68° at 25 mm., n_D^{20} 1.4466 (lit.[5] b.p. 162–164°, n_D^{20} 1.4470).

Preparation of higher t-acetylenic chlorides. A 1-l. 3 neck flask provided with mechanical stirrer, thermometer, and dropping funnel was charged with 56 g. (0.5 mole) calcium chloride, 40 g. (0.4 mole) cuprous chloride, 0.2–0.5 g. copper bronze powder and 430 ml. (5 moles) of cold, concentrated hydrochloric acid. The mixture was cooled (ice bath) with stirring, and 1 mole of *t*-acetylenic carbinol was added dropwise within 30 min. Stirring was continued for 1 hr. (inside temperature 0–5°). The upper layer was separated (both layers very dark, illumination needed) and washed immediately with two 100-ml. portions of cold, concentrated hydrochloric acid, and then with three 100-ml. portions of distilled water. The product, now nearly colorless, was dried superficially (in the separatory funnel) with anhydrous potassium carbonate and then thoroughly with fresh potassium carbonate. Distillation *in vacuo* from a small amount of powdered anhydrous potassium carbonate[6] was accomplished with use of a 60 × 1 cm. helix-packed, electrically heated column. The infrared spectra showed no bands (μ) near 2.8 (—OH absent); —C≡CH bands at 3.05 and near 4.75 were present as expected. In two instances (Table I, Nos. 8 and 10) a band at 5.1 indicated contamination by the chloroallene isomer (RR′C=C=CHCl). In two other instances (Nos. 4 and 8) bands at 6.2 showed the presence of conjugate diene impurity. In these cases (Nos. 4, 8, and 10) purification could be achieved only partially by careful refractionation *in vacuo*. In No. 4, for example, gas liquid chromatography showed that the once distilled product was 83% *t*-chloride; redistillation raised the purity to 92%. In compound No. 8, gas liquid chromatography did not resolve the mixture completely and quantitative determination of the *t*-chloride content could not be made. Compound No. 10 was badly decomposed during gas liquid chromatography.

When the procedure described above was employed with 3,5-dimethyl-1-hexyne-3-ol, a 53% yield of 3-chloro-3,5-dimethyl-1-hexyne (Table I, No. 5) and a 15% yield of the isomeric 1-chloro-3,5-dimethyl-1,2-hexadiene were obtained. The two products were separable by fractional distillation, and each was obtained pure. It was learned subsequently that the latter compound could be prepared in good yield as described below.

Preparation of 1-chloro-3,5-dimethyl-1,2-hexadiene. One-half mole (63 g.) of 3,5-dimethyl-1-hexyne-3-ol was stirred with 215 ml. (2.5 moles) of concentrated hydrochloric acid containing 20 g. of cuprous chloride and 0.5 g. copper bronze powder for 10 hr. at ice bath temperature. The organic layer was then separated, washed, and dried as described

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(5) W. J. Hickinbottom, A. A. Hyatt, and M. B. Sparke, *J. Chem. Soc.*, 2529 (1954).

(6) All *t*-acetylenic chlorides are thermally sensitive, especially in the presence of acids, even in trace amounts. Distillations should be carried out from a small amount of powdered anhydrous sodium or potassium carbonate and the pressure should be adjusted so that the boiling point does not exceed *ca.* 75°.

above. Two distillations (60-cm. column) gave 3.6 g. (5% yield) of 3-chloro-3,5-dimethyl-1-hexyne, b.p. 53–55° at 25 mm., n_D^{25} 1.4365, and 43.2 g. (60% yield) of 1-chloro-3,5-dimethyl-1,2-hexadiene, b.p. 51–52° at 10 mm., 62–64° at 25 mm., n_D^{25} 1.4695. Infrared bands were absent at 2.8, 3.05, and 4.7 μ; strong at 5.1, and very weak at 6.2 μ.

Anal. Calcd. for $C_8H_{13}Cl$: Cl, 24.52. Found: Cl, 25.04.

Acknowledgment. The authors express their sincere thanks to Air Reduction Company, New York, for generous samples of *t*-acetylenic carbinols, to W. L. Brown of the Lilly Research Laboratories, Indianapolis, for the analytical work and to Eli Lilly and Company for financial support. The gas chromatography unit (Aerograph, Model A-90) used in this work was acquired under National Science Foundation Grant G-4058.

NOTRE DAME, IND.

[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY AND THE DEPARTMENT OF ORGANIC CHEMISTRY, UNIVERSITY OF MADRAS)

1-Acetyl-6-oxo-8a-methyl-3,4,6,7,8,8a-hexahydronaphthalene[1]

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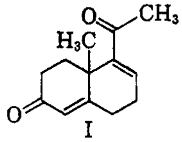
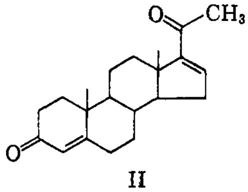
The conversion of 1-ethynyl-1β-hydroxy-6-oxo-8a-methyl-1,2,3,4,6,7,8,8a-octahydronaphthalene (VI) to the title compound (I) is described.

The title compound (I), a possible intermediate for steroid syntheses,[2,3] has been described as a liquid[2,4,5] and as a solid,[6] m.p. 122–123°. As the spectral properties reported[4,6] for I were not consistent with those to be expected, a reexamination of the synthesis of I was undertaken. In this paper, the synthesis of authentic I, m.p. 97–98°, is described.

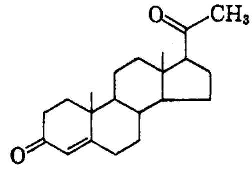
I has an absorption maximum at 235 mμ (ε 19,900). The wave length is about that to be expected, as $\Delta^{4,16}$-pregnadiene-3,20-dione, II, absorbs[7] at 234 mμ (ε 25,100), the intensity being about the sum of the intensities for the unsaturated ketone systems III (ε 15,850) and IV (ε 8,900) at 234 mμ.[8] The intensity of absorption of I (ε 19,900) is less than expected (ε *ca.* 25,000). Possibly the proximity of the two α,β-unsaturated ketone systems in I is responsible for the lower intensity. The infrared absorption at 6.0 μ of I is also that to be expected since II has a single peak at 5.98 μ.[9]



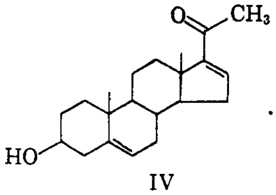
I



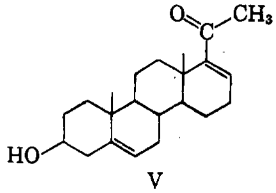
II



III



IV



V

The starting material for our synthesis of I was the ethynylcarbinol,[4,10,11] VI, prepared essentially as described.[11] By shortening the reaction time high yields of VI were obtained. There was no evidence of the formation of the epimeric alcohol VII in these experiments.[12]

VI was converted in excellent yield to the diacetate VIII. The ultraviolet and infrared absorption data leave no doubt as to the structure of VIII.

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[1] This research was supported in part by a grant (CY-3184) from the U. S. Public Health Service for which we express our appreciation.

[2] C. A. Friedmann and R. Robinson, *Chem. and Ind.*, 777, 1117 (1951).

[3] S. Swaminathan and M. S. Newman, U. S. Patent 2,673,872 (1954).

[4] S. Swaminathan and M. S. Newman, *Tetrahedron*, 2, 88 (1958).

[5] Ref. 4 mentions in the experimental section an isomeric solid (m.p. 92–93°) as a minor product in the reaction of hot formic acid on VI and described as "presumably I" in the absence of supporting evidence to establish its identity or nonidentity with the liquid product described as I in the same paper.

[6] I. N. Nazarov and I. A. Gurvich, *Zhur. obshchei. Khim.*, 25, 1723 (1955); *Chem. Abstr.*, 50, 5600^e (1956).

[7] A. Butenandt and J. Schmidt-Thomé, *Ber.*, 72, 182 (1939).

[8] The fact that V absorbs at 233 mμ (ε 8,930) shows that the intensity of absorption of the chromophore in both IV and V is the same whether the unsaturation is in a 5- or 6-membered ring. R. M. Dodson, P. B. Sollman, and B. Riegel, *J. Am. Chem. Soc.*, 75, 5132 (1953).

[9] K. Dobriner, E. R. Katzenellenbogen, and R. N. Jones, *Infrared Absorption Spectra of Steroids—An Atlas*, Vol. I, Interscience Publishers, Inc., N. Y., (1953); curve no. 121.

[10] M. S. Newman and S. Swaminathan, U. S. Pat. 2,714,615 (1955); *Chem. Abstr.*, 50, 13095a (1956).

[11] I. N. Nazarov and I. A. Gurvich, *Zhur. obshchei. Khim.*, 25, 956 (1955); *Chem. Abstr.*, 50, 3351*b* (1956).