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]

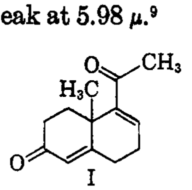
MELVIN S. NEWMAN, S. RAMACHANDRAN, S. K. SANKARAPPA, AND S. SWAMINATHAN

Received July 6, 1960

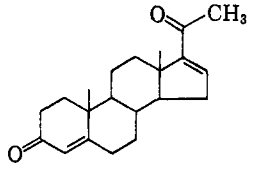
The conversion of 1-ethynyl-1β-hydroxy-6-oxo-8a-methyl-1,2,3,4,6,7,8,8a-octahydronaphthalene (VI) to the title compound (I) is described.

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.

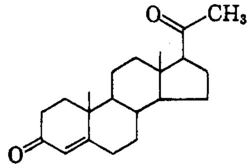
I has an absorption maximum at 235 mμ (ε 19,900). The wave length is about that to be expected, as $\Delta^{4,16}$-pregnadiene-3,20-dione, II, absorbs[7] at 234 mμ (ε 25,100), the intensity being about the sum of the intensities for the unsaturated ketone systems III (ε 15,850) and IV (ε 8,900) at 234 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]



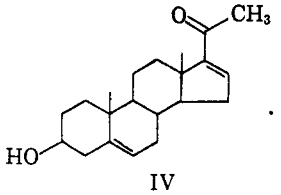
I



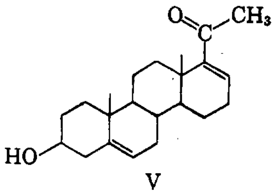
II



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.

---

[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).

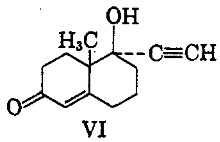
[7] A. Butenandt and J. Schmidt-Thomé, *Ber.*, **72**, 182 (1939).

[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).

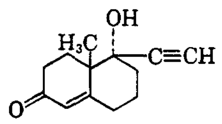
[9] K. Dobriner, E. R. Katzenellenbogen, and R. N. Jones, *Infrared Absorption Spectra of Steroids—An Atlas*, Vol. I, Interscience Publishers, Inc., N. Y., (1953); curve no. 121.

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

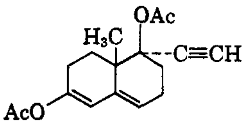
[11] I. N. Nazarov and I. A. Gurvich, *Zhur. obshchei. Khim.*, **25**, 956 (1955); *Chem. Abstr.*, **50**, 3351*b* (1956).



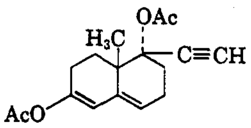
VI
(m.p. 172°)



VII
(m.p. 184°)

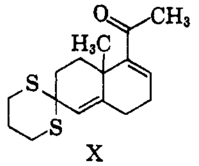


VIII

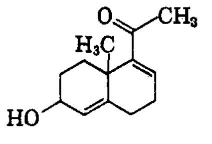


IX

On treatment with hot 90% formic acid VIII gave in about 40% yield a crystalline product, m.p. 97–98°, which furnished infrared, ultraviolet, NMR[13] and analytical data consistent with the structure I. Compound I furnished a red mono-2,4-dinitrophenylhydrazone which still retains the infrared peak at 6.0 μ characteristic of I but of relatively low intensity. Compound I was further characterized by its crystalline 1-acetyl-6-oxo-8a-methyl-3,4,6,7,8,8a-hexahydronaphthalene-6-trimethylenethioketal,[14] X. Reduction of I with sodium borohydride yielded a compound, m.p. 115–117°, which is probably 1-acetyl-6β-hydroxy-8a-methyl-3,4,6,7,8,8a-hexahydronaphthalene, XI,[12] on the basis of its spectral characteristics.



X



XI

From treatment of VI with hot 90% formic acid three isomeric compounds have been reported.[5,6] Two of these, m.p. 92–93° and 95–96° were undoubtedly impure I, as on repetition of the experiments fractions having similar melting ranges were obtained and shown to be impure I. The third compound,[6] m.p. 181–182°, was undoubtedly impure α-hydroxyethynylcarbinol VII, as we have made pure VII by treatment of VI in methylene chloride solution with boron fluoride–etherate,[15] and found it to melt at 184–185°. The 184° isomer, VII, can also be isomerized to VI by similar treatment. Infrared, ultraviolet, and NMR[13] analyses leave no doubt that VI, m.p. 172–173°, and VII, m.p. 184–185°, are the epimeric ethynylcarbinols.[12] Further, VII can also be converted *via* formic acid treatment of its diacetate, IX, to I. The only remaining doubt about VI and VII is the α- and β-assignment for the hydroxyl groups.[12]

On treatment of the ethynylcarbinol, VI, m.p. 172°, in aqueous methanol at about 60° with mercuric sulfate, an isomeric compound XII, m.p. 122–123°, λ_{max} at 257 mμ (ϵ 10,900), was obtained.[6] This compound was claimed[6] to be I. We have repeated this experiment and obtained a compound, m.p. 124.4–126.0°, isomeric with VI, which was undoubtedly the same compound. XII was obtained in a slightly better yield using a boron fluoride—mercuric oxide catalyst.[16] While the ultraviolet data agreed with that quoted, the infrared spectrum, not reported earlier,[6] revealed the presence of an hydroxyl group. This fact alone rules out structure I for XII. Certain reduction products[6] of XII also await a new formulation. The liquid product[4] described as I also needs reinvestigation.

Extensive decomposition of I, observed during attempted chromatographic purification on neutral Aluminum Oxide Woelm, prompted study of the action of base on I. When I was treated with sodium hydroxide in methanol for twelve hours at room temperature,[17] an isomeric compound, XIII, m.p. 116–117°, λ_{max} 279 mμ (ϵ 25,600), infrared absorption at 5.82 (s), 6.02 (s), 6.14 (v.s), 6.26 (s) μ, was obtained in 33% yield after purification on acid-washed alumina. NMR analysis[13] revealed that a deep seated change had occurred. No further work on XIII has been done.

EXPERIMENTAL[18]

1,6-Dioxo-8a-methyl-1,2,3,4,6,7,8,8a-octahydronaphthalene,[19] XIV. The starting material for VI was prepared by

---

[12] Using the prefix α- and β- in the same sense as in the steroid series, Nazarov[11] considered the ethynylcarbinol, m.p. 172°, to have an α-hydroxy group (VII). We have assigned[4,10] the β-hydroxy structure VI to the 172° isomer as addition of metal acetylides to 17-ketosteroids yields β-hydroxy compounds.

[13] We thank Dr. G. V. D. Tiers, Minnesota Mining Manufacturing Co., Minneapolis, Minn., for this determination and interpretation.

[14] Propane-1,3-dithiol has been shown to give higher yields of cyclic thioketals than ethanedithiol. See H. Hauptmann and M. M. Campos, *J. Am. Chem. Soc.*, **72**, 1405 (1950).

[15] The presence of small amount of ethanol is necessary for this isomerization. A similar observation was made in the hydrogen chloride catalyzed isomerization of 6β,21-diacetoxy-Δ^4-pregnene-3,20-dione to the 6α-epimer. P. Th. Herzig and M. Ehrenstein, *J. Org. Chem.*, **16**, 1050 (1951).

[16] G. F. Hennion, D. B. Kilian, T. H. Vaughn, and J. A. Nieuwland, *J. Am. Chem. Soc.*, **56**, 1130, 1384 (1934).

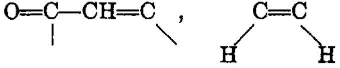
[17] Under similar conditions, II yields (*ca.* 30%) 16α-methoxyprogesterone. D. K. Fukushima and T. F. Gallagher, *J. Am. Chem. Soc.*, **73**, 196 (1951).

[18] (a) Melting points reported are uncorrected. (b) Microanalyses carried out by Galbraith Laboratories, Knoxville, Tenn., or Schwarzkopf Microanalytical Laboratory, N. Y., are indicated by superscripts g and s. (c) Ultraviolet spectra were obtained in 95% alcohol. (d) Infrared spectra were obtained using potassium bromide pellets and peaks reported in microns with the usual notation to indicate intensity. (e) Acid-washed alumina supplied by Merck and Co., Inc., Rahway, N. J., was used for chromatography. (f) "Treated as usual" means the organic layer was washed with 5% hydrochloric acid or 5% sodum bicarbonate solution as indicated, water, saturated brine and dried by dripping through a funnel containing magnesium sulfate. The solvent was then removed by distillation at atmospheric or reduced pressure.

the following simplified procedure. A mixture of 63.1 g. (0.5 mole) of 2-methyl-1,3-cyclohexanedione,[20] XV, 52.6 g. (0.75 mole) of technical grade methyl vinyl ketone, about 0.25 g. (3 pellets) of potassium hydroxide, and 250 ml. of absolute methanol was refluxed for 3 hr. After removal of solvent and excess methyl vinyl ketone under reduced pressure,[21] 3 ml. of pyrrolidine (or piperidine) and 250 ml. of benzene were added. This solution was refluxed into a phase-separating head until separation of water ceased. The dark reaction mixture was cooled, diluted with an equal volume of ether, washed with dilute acid, and treated as usual. The crude liquid (82–85 g.) was distilled and the fraction (68 g.), b.p. 117–145° at 0.5 to 1 mm. was collected, diluted with 10 ml. of ether, and allowed to crystallize in an ice box. A first crop of 50–53 g. of the crystalline product was collected by filtration and washed with ether. Redistillation of the mother liquor and the washings and crystallization gave a further 4 to 6 g. of product giving a net yield of 56–58 g. (63–65% based on XV) of XIV, m.p. 47–50°.

1-Ethynyl-1β-hydroxy-6-oxo-8a-methyl-1,2,3,4,6,7,8,8a-octahydronaphthalene, VI. Pure VI, m.p. 172–173°, λ_{max} 242 mμ (ε 13,800), infrared 2.96 (s), 3.06 (s), 4.80 (w), 6.00 (s), 6.16 (m) μ, was prepared[11] in 85% yield in 1-mole runs by reacting an ether solution of XIV with a solution of lithium acetylide in liquid ammonia for 1 hr. and decomposing with saturated aqueous ammonium chloride. Longer reaction periods gave lower yields of VI and a liquid product[2,4,11] of unknown nature.

Conversion of VI *to* XII. Hydration of 4 g. of VI in the presence of mercuric sulfate in methanol solution as described[6] furnished 600 mg. (15%) of product, m.p. 124–126°. The same compound could be obtained in 30–35% yield by using Nieuwland's catalyst.[16] Two crystallizations from a mixture of ether and petroleum ether (b.p. 40–60°) furnished pure XII, m.p. 124.4–126.0°; λ_{max} 257 mμ (ε 11,000); infrared 2.86 (s), 6.00 (s), 6.06 (s), 6.12 (s), 6.24 (m) μ. The NMR spectrum[13] revealed the presence of —OH,



$\mathrm{O{=}\underset{|}{C}{-}CH{=}C}{<}$, ${>}\mathrm{\underset{H}{C}{=}\underset{H}{C}}{<}$ and the absence of $\mathrm{{-}C{\equiv}C}$ and $\mathrm{O{=}C{-}CH_3}$ groups.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.4; H, 7.9. Found:[8] C, 76.4, 76.6; H, 8.0, 8.1.

XII does not give a ferric chloride test and the ultraviolet spectrum is not changed by alkali. This excludes an enol or a phenol. Acid catalyzed reaction with acetic anhydride gives a mono acetate, m.p. 122.0–122.6°; λ_{max} 256 (ε 15,000); infrared 5.76 (s), 6.00 (s), 6.06 (s), 6.12 (s), 6.24 (m) μ.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.1; H, 7.4. Found[8]: C, 72.8, 72.7; H, 7.6, 7.7.

XII gives a 2,4-dinitrophenylhydrazone,[22] m.p. 222–223° (reported[6] for the mono-2,4-dinitrophenylhydrazone, 218.5–219.5°).

1-Ethynyl-1β,6-diacetoxy-8a-methyl-1,2,3,7,8,8a-hexahydronaphthalene, VIII. A mixture of 5 g. of VI, 25 ml. of acetic anhydride and 0.5 g. of *p*-toluenesulfonic acid was left at room temperature for 16 hr. On pouring the solution into iced-water, an oil that separated solidified in 0.5 hr. and was collected by filtration, washed with water and dried; yield 6.5 g. (92%). Reproducible yields were obtained in larger runs. One crystallization from ethanol afforded, with negligible loss, colorless crystals of VIII, m.p. 92–93°; λ_{max} 235 mμ (ε 18,600); infrared 3.09 (s), 5.70 (s), 5.76 (s), 6.00 (m), 6.10 (m) μ.

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.8; H, 7.0. Found[8]: C, 70.7; H, 7.1.

1-Acetyl-6-oxo-8a-methyl-3,4,6,7,8,8a-hexahydronaphthalene, I. A solution of 90 g. of VIII in 200 ml. of 90% formic acid was refluxed under nitrogen for 2 hr. After removal of formic acid under aspirator pressure, the residue was dissolved in methylene chloride, washed free of acid with a minimum quantity of 5% aqueous sodium bicarbonate, and treated as usual. The crude product on cooling yielded 17.3 g. of light yellow crystals of I, m.p. 90–96°. Chromatography of the mother liquor on alumina and elution with Skellysolve F[23] and benzene gave another 11.8 g. of I, m.p. 92–96°. Further elution of the column with ether gave about 20 g. of a liquid, which has not been studied, besides 0.75 g. of VI and 0.7 g. of VII eluted in that order. One recrystallization of crude I from ether gave 28.3 g. (43.4%) of product, m.p. 94–96°. The persistent light yellow color could not be removed by charcoal treatment. The analytical sample of I, prepared by rechromatography on alumina[24] and crystallization from ether, formed colorless plates, m.p. 97–98°; λ_{max} 235 mμ (ε 19,500); infrared 6.00 (v.s.), 6.10 (s), 6.15 (s) μ. The NMR spectrum[13] was consistent with the proposed structure as no unexpected peaks were present.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.4; H, 7.9. Found[8]: C, 76.6, 76.7; H, 8.2, 8.2.

I gives a red mono-2,4-dinitrophenylhydrazone.[22] Two crystallizations from ethanol furnished the analytical sample, m.p. 198.6–199.6°.

Anal. Calcd. for $C_{19}H_{20}N_4O_5$: C, 59.4; H, 5.2; N, 14.6. Found[8]: C, 59.6, 59.6; H, 5.4, 5.2; N, 14.8, 14.9.

1-Ethynyl-1α-hydroxy-6-oxo-8a-methyl-1,2,3,4,6,7,8,8a-octahydronaphthalene, VII. (a) A solution of 1 g. of VI in 12 ml. of 90% formic acid was refluxed for 1.5 hr. and the formic acid removed under vacuum. A methylene chloride solution of the residue was washed with 5% aqueous sodium bicarbonate and treated as usual. The crude product in a small volume of methylene chloride was chromatographed on alumina. Elution with a 3:2 mixture of petroleum ether (b.p. 35–55°) and benzene gave 10 mg. of I. Further elution with ether gave 25 mg. of VI followed by 15 mg. of a third crystalline compound that proved to be VII. These compounds were found to be identical with the corresponding authentic samples as checked by mixed melting point determination and infrared spectral analysis.

(b) A solution of 42 g. of VI, m.p. 172–173°, in 1 l. of methylene chloride, 22 ml. of boron fluoride–etherate and 15 ml. of ethanol[15] was refluxed for 6 hr. and left at room temperature for 10 hr. The dark solution was washed with saturated aqueous sodium bicarbonate, treated as usual and concentrated to a volume of about 250 ml. A first crop of 12 g. of light yellow crystals, m.p. 182–184°, after charcoal treatment of an ethyl acetate solution gave 11.3 g. (27%) of VII, m.p. 184–185°, mixed m.p. with VI, 145–180°; λ_{max} 242 mμ (ε 15,500); infrared 2.99 (s), 3.09 (s), 4.80 (w), 6.00 (s), 6.18 (m) μ.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.4; H, 7.9. Found[8]: C, 76.2; H, 7.8.

From the mother liquor a further 24 g. (57%), of solid, m.p. 149–175° was obtained. This mixture could not be separated into individual components by fractional crystal-

---

(19) (a) P. Wieland and K. Miescher, *Helv. Chim. Acta*, **33**, 2215 (1950); (b) N. L. Wendler, H. L. Slates, and M. Tishler, *J. Am. Chem. Soc.*, **73**, 3816 (1951); (c) ref. 4; (d) I. N. Nazarov, S. I. Zavyalov, M. S. Bermistrova, I. A. Gurvich, and L. I. Shmonia, *Zhur. Obshchei. Khim.*, **26**, 441 (1956); *Chem. Abstr.*, **50**, 13847c (1956).

(20) A. B. Mekler and M. S. Newman, *J. Am. Chem. Soc.*, **82**, 4039 (1960).

(21) The residue on distillation after work up gives 2-methyl-2-(3′-oxobutyl)-1,3-cyclohexanedione in 85% yield. See C. B. C. Boyce and J. S. Whitehurst, *J. Chem. Soc.*, 2022 (1959).

(22) This was obtained following the procedure in *The Systematic Identification of Organic Compounds* by R. L. Shriner, R. C. Fuson, and D. Y. Curtin, 4th edition, John Wiley and Sons, Inc., N. Y., p. 219.

(23) Petroleum hydrocarbon fraction (b.p. 35–55°).

lization. Chromatography of 1 g. of this mixture on alumina[24] and elution with ether and methylene chloride gave 0.75 g. of VI, m.p. 172–173° followed by[25] 0.18 g. of VII, m.p. 184–185°. Thus 24 g. of the mixture has roughly 4:1 composition of VI and VII giving an estimated net yield of 15.6 g. (37%) of VII and 18 g. (43%) of VI. The remaining crude reaction product was chromatographed to obtain 6 g. of a liquid, which lacked —OH and —C≡CH bands (infrared) and showed saturated and α,β-unsaturated carbonyl bands. This liquid has not been further examined.

While 1 g. of pure VII could be obtained from 4.2 g. of VI under conditions described in (b), the starting material was recovered unchanged when ethanol was omitted in another experiment. When 1 g. of 17α-ethynyltestosterone,[26] m.p. 264–266°, was treated as in (b) the starting material was recovered unchanged.

Epimerization of VII *to* VI. Treatment of 2.16 g. of pure VII, m.p. 184–185°, as in (b) above yielded 0.4 g. (18.5%) of VI, m.p. 172–173°, and 1.5 g. (69.4%) of VII, m.p. 184–185°, by crystallization and chromatography.

1-Ethynyl-1α,6-diacetoxy-8a-methyl-1,2,3,7,8,8a-hexahydronaphthalene, IX. Treatment of 2.3 g. of VII, m.p. 184–185°, at room temperature with 15 ml. of acetic anhydride containing 100 mg. of *p*-toluenesulfonic acid yielded 2.0 g. of product, m.p. 110–114° after a work up as above. One crystallization from ether-petroleum ether (b.p. 35–55°) afforded 1.8 g. (55.4%) of IX, m.p. 113–114°; λ_{max} 234 mμ (ε 19,950); infrared 3.04 (s), 4.80 (w), 5.70 (s), 5.76 (s), 6.00 (m), 6.10 (m) μ.

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.8; H, 7.0. Found: C, 71.0, 71.0; H, 7.0, 7.1.

Conversion of IX *to* I. A solution of 1.43 g. of IX in 5 ml. of 90% formic acid was refluxed for 1.5 hr. and worked up as described in the preparation of I from VIII. Chromatography of the crude liquid yielded 330 mg. (32.6%) of I, m.p. and mixed m.p. with product from VIII, 97–98°.

1-Acetyl-6-oxo-8a-methyl-3,4,6,7,8,8a-hexahydronaphthalene-6-trimethylenethioketal, X. To a suspension of 1.8 g. of I in a mixture of 5 ml. of ether and 2 ml. of boron fluoride-etherate cooled in ice bath, 1 ml. of propane-1,3-dithiol was added dropwise. The suspension soon turned to a clear solution and in 2 hr. set to a mass of needles. The mixture was dissolved in ether, washed with 10% aqueous sodium bicarbonate and treated as usual. The crude liquid deposited 2.2 g. of crystals which on recrystallization from ether afforded 2.0 g. (75%) of X, m.p. 119.5–120.0°; λ_{max} 230 mμ (ε 12,300)[27]; infrared 6.00 (s), 6.18 (m) μ both of relatively diminished intensity as compared to same peaks in I.

Anal. Calcd. for $C_{16}H_{22}OS_2$: C, 65.3; H, 7.5; S, 21.8. Found[8]: C, 65.1, 65.3; H, 7.6, 7.6; S, 21.6, 21.8.

1-Acetyl-6β-hydroxy-8a-methyl-3,4,6,7,8,8a-hexahydronaphthalene, XI. A solution of 1 g. (5.0 mmoles) of I, 200 mg. (5.3 mmoles) of sodium borohydride and 1 ml. of water in 10 ml. of *t*-butyl alcohol was stirred for 1 hr. at room temperature. The excess borohydride was destroyed by adding a few drops of glacial acetic acid and the mixture evaporated to dryness. After the usual treatment the crude liquid gave 0.5 g. of crystals, m.p. 111–114°, and the mother liquor on chromatography afforded a further 120 mg. of crystals. Two crystallizations from ether-methanol yielded 0.58 g. (58%) of colorless XI, m.p. 115–117°, λ_{max} 231 mμ (ε 11,900)[27]; infrared 2.86 (s), 6.03 (s), 6.16 (m).

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.7; H, 8.8. Found[8]: C, 75.8, 75.8; H, 8.9, 9.0.

Conversion of I *to* XIII. To a solution of 1.1 g. of I in 10 ml. of dry methanol was added 0.13 g. of sodium hydroxide. The initially colorless solution turned dark red instantaneously on adding the alkali. After 12 hr. at room temperature, the reaction mixture was acidified with a few drops of glacial acetic acid and evaporated to dryness under aspirator pressure. The residue dissolved in methylene chloride was treated as usual. The crude liquid was chromatographed on alumina and eluted with 1:1 ether-benzene mixture to obtain 490 mg. of crystals, m.p. 115.0–116.5°. Charcoal treatment of an ether solution furnished 370 mg. (33.6%) of colorless XIII, m.p. 116–117°; λ_{max} 279 mμ (ε 25,600); infrared 5.82 (s), 6.02 (s), 6.14 (v.s.), 6.26 (s) μ.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.4; H, 7.9. Found[8]: C, 76.3, 76.4; H, 7.7, 7.6.

COLUMBUS 10, OHIO
MADRAS 25, INDIA

---

(24) When the commercial neutral Aluminum Oxide Woelm was used, extensive loss due to decomposition occurred.

(25) According to the generalization of D. H. R. Barton and R. C. Cookson, *Quart. Rev.*, 10, 44 (1956) the ethynyl alcohol, m.p. 172–173°, eluted first, should have an axial hydroxyl group. This assignment would indicate structure VII for the 172° isomer as proposed by Nazarov.[11] However, as factors responsible for adsorption of the epimeric alcohols, VI and VII, might be complicated by the proximity of the α,β-unsaturated carbonyl function, a definite assignment cannot be made without further evidence. We have preferred the structures given for reasons mentioned.[12]

(26) We wish to thank the Upjohn Co., Kalamazoo, Mich., for this sample.

(27) We believe that the methyl ketonic function is free in X for two reasons: (a) the absorption maximum for XIV, VI, and VII is at 242 mμ; (b) the λ_{max} for 1-acetyl-1-cyclohexene types is at 232 mμ. See J. D. Chanley, *J. Am. Chem. Soc.*, 70, 244 (1948).

[CONTRIBUTION FROM THE RESEARCH AND ENGINEERING DIVISION, MONSANTO CHEMICAL CO.]

Steric Effects in the Gomberg Reaction[1]

HAROLD WEINGARTEN

Received June 10, 1960

The influence of substitution *ortho* to the radical site in homolytic aromatic arylation was investigated. Steric effects were found to be insignificant.

Although the Gomberg reaction has been known in the literature[2] for nearly forty years, it has been investigated quantitatively only during the last ten.[3] The bulk of these quantitative studies describe the ratio of biphenyl products

---

(1) Presented at the 135th Meeting of the American Chemical Society at Boston, Mass., April 1959, Abstr., p. 47-O.

(2) M. Gomberg and W. E. Bachman, *J. Am. Chem. Soc.*, 46, 2339 (1924).