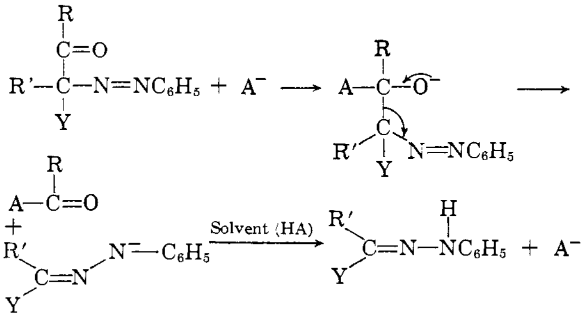
TABLE III

N-METHYLPHENYLHYDRAZONES

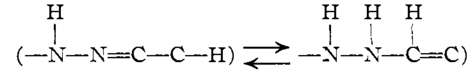
Compound prepared	B.p., °C. (mm.)	λ_{max} 1, mμ	log E_{m_1}	λ_{max} 2, mμ	log E_{m_2}	Formula	—Nitrogen, %— Calcd.	Found
2,3-Butanedione mono-N-methylphenylhydrazone (XVII)	128–130 (5)	298	3.62	335	3.86	$C_{11}H_{14}N_2O$	14.74	14.91
Benzil mono-N-methylphenylhydrazone (XVIII)	59–60 (m.p.)	..	..	335	4.06	$C_{21}H_{18}N_2O$	8.93	9.01
Ethyl pyruvate N-methylphenylhydrazone (XIX)	144–146 (4)	293	3.97	315	3.80	$C_{12}H_{16}N_2O_2$	12.70	12.66
Pyruvanilide N-methylphenylhydrazone (XX)	99 (m.p.)	285	3.95	334	3.89	$C_{16}H_{17}N_3O$	15.71	15.90

densation of phenylhydrazine with the corresponding ketone.

That the hydrazone form is more stable than the azo form has been demonstrated in many coupling reactions of a diazonium salt to a methyl or methylene carbon.[5] A possible course, analogous to that customarily assumed for the cleavage of β-dicarbonyl compounds, for the conversion of azo to hydrazone in the cleavage of azo-compound is depicted as



While not germane to the acyl cleavage, the possibility of ene–hydrazine tautomerism



$$(\text{—}\overset{\displaystyle H}{\overset{|}{N}}\text{—N=C—C—H}) \rightleftarrows \text{—}\overset{\displaystyle H}{\overset{|}{N}}\text{—}\overset{\displaystyle H}{\overset{|}{N}}\text{—}\overset{\displaystyle H}{\overset{|}{C}}\text{=C)}$$

exists in the cleavage products.[4] Such isomerization has not been excluded by the evidence. The spectroscopic data may actually indicate this isomerization, since in a few cases no absorption was noted in the 285 to 295 mμ region. This is particularly noteworthy with the spectrum of the benzil derivative XVIII where ene-hydrazine tautomerism cannot occur. The possibility of ene–hydrazine tautomerism in these cleavage products is being studied with the hope that a correlation with spectral data may be obtained.

Acknowledgment.—The authors are greatly indebted to Edward Ferlauto for the spectroscopic data, Ronald Mangravite, Mrs. Barbara Artman and Mrs. Constance Morris for the microanalyses and to Professor N. Kornblum of Purdue University for his encouragement and guidance.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLA.]

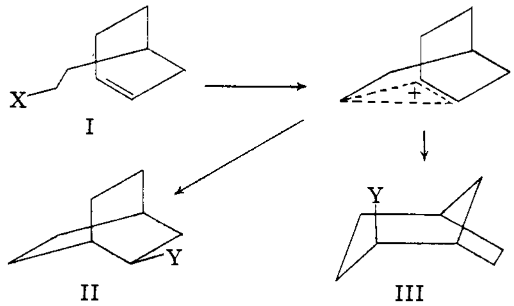
A Remarkably Facile Ring Closure Through Double Bond Participation[1]

BY WERNER HERZ AND GERALD CAPLE

RECEIVED MARCH 16, 1962

The conversion of the mesylate of 1-methyl-1-(2-hydroxyethyl)-1,2-dihydronaphthalene (VIIc) to *exo*-1-methyl-2,3-benzbicyclo(3,2,1)-4-octanol on treatment with alumina and wet benzene is reported.

Participation of the double bond, with formation of non-classical ions, has been invoked to explain rates and products observed during the solvolysis of Δ^3-cyclopentenylethyl arenesulfonates[2,3] and cycloheptenylmethyl bromobenzenesulfonate.[4] In a recent communication[5] Winstein and Carter have summarized these results and provided evidence for the participation of the double bond in the solvolysis of Δ^3-cyclohexenyl bromobenzenesulfonate (I) which leads to bicyclo(2,2,2)octanol (II) and *trans*-bicyclo(3,2,1)octanol-2 (III), presumably through intervention of the non-classical ion.



We have independently observed an instance of double bond participation in a system analogous to I, but under unprecedentedly mild conditions, and hereby report our results.

For reasons which need not be detailed here we undertook the synthesis of 1-methyl-1-vinyl-1,2-

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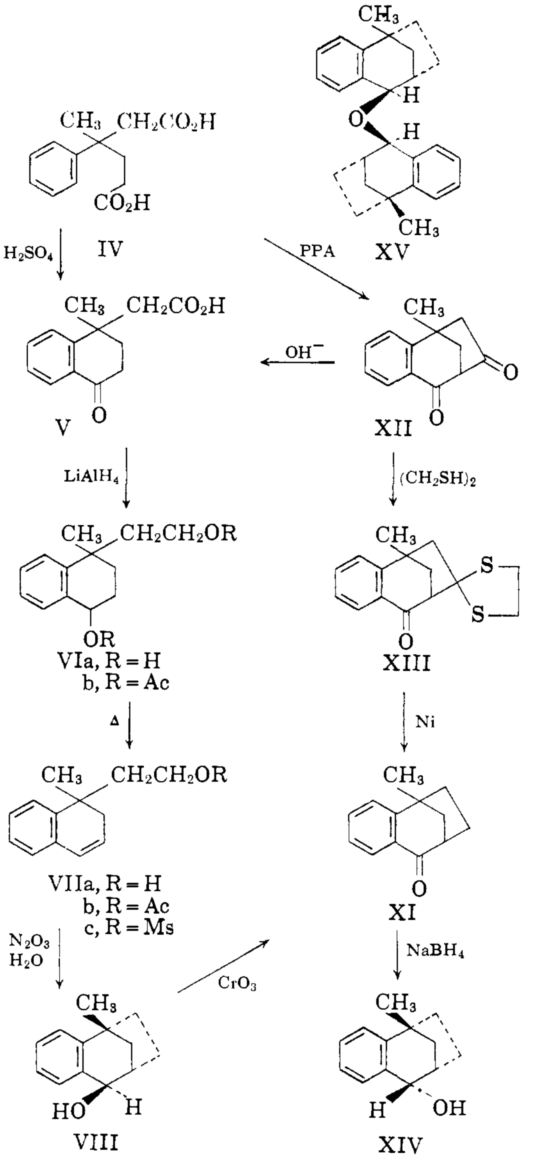
[1] Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in partial support of this research.

[2] R. G. Lawton, *J. Am. Chem. Soc.*, **83**, 2299 (1961).

[3] P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961).

[4] G. Le Ny, *Compt. rend.*, **251**, 1526 (1960).

[5] S. Winstein and P. Carter, *J. Am. Chem. Soc.*, **83**, 4485 (1961).



dihydronaphthalene (X).[6] One of several schemes studied involved the preparation of X by way of 1-methyl 1-(2-hydroxyethyl)-1,2-dihydronaphthalene (VIIa) *via* the route outlined below. Friedel-Crafts condensation of 4-methyl-4-(carbethoxymethyl)-butyrolactone[7] with benzene gave a 78% yield of 3-methyl-3-phenyladipic acid (IV). Cyclization of this substance with sulfuric acid on a steam-bath afforded 1-methyl-1-carboxymethyl-4-tetralone (V) which was reduced with lithium aluminum hydride. The resulting mixture of epimers (VIa) could not be dehydrated satisfactorily and was therefore converted to the diacetate VIb.

An attempt to pyrolyze VIb did not yield X, but furnished a mixture of methylnaphthalene, monoacetate VIIb and starting material. Formation of VIIb was effected satisfactorily by heating VIb at 200°, but it, too, decomposed to methylnaphthalene at the temperatures employed for pyrolyses, nor was it possible to dehydrate alcohol VIIa satisfactorily.

It was then decided to proceed through the mesylate VIIc. On chromatography of the crude product in wet benzene–petroleum ether over alumina, the ether eluate after one crystallization furnished 54% (based on VIIa) of a saturated secondary alcohol (VIII), m.p. 80–82°, isomeric with VIIa. Purification of the mesylate could be accomplished by chromatography using anhydrous solvents, but subsequent treatment with alumina and benzene saturated with water again caused conversion to VIII.

The following evidence establishes VIII as the structure of the new alcohol. Its n.m.r. spectrum[8] exhibited a sharp doublet at 4.21 p.p.m. ($J = 2.8$ c.p.s.), intensity one proton. The chemical shift is characteristic of a proton on carbon carrying a hydroxyl group which, in the present instance, is spin coupled to only one adjacent hydrogen atom. Other signals include the benzene resonance centered at 7.15 (4 protons, approx. A_2B_2), the hydroxyl hydrogen at 3.01, the methyl singlet at 1.46, the methine (C_5) hydrogen centered at 2.5 p.p.m. and a complex system of bands, total intensity six protons, for the methylene hydrogens at C_6, C_7 and C_8.

A benzbicyclo(2,2,2) formula (IX) was thus rendered quite improbable, a conclusion which was confirmed by oxidation of VIII to the α-tetralone XI which had an infrared band at 1680 cm.$^{-1}$ and yielded a red dinitrophenylhydrazone. This substance exhibited the typical *peri*-hydrogen resonance of α-tetralones (doublet of triplets centered at 8 p.p.m., due to deshielding by the adjacent carbonyl group) which appears to have diagnostic value.[9]

An independent synthesis of XI was carried out through the interesting diketone XII which was encountered fortuitously in our attempts to cyclize IV through the agency of polyphosphoric acid. Incidentally, this reaction provides another example of the acid-catalyzed intramolecular Claisen acylation studied previously in this Laboratory.[10] Hydrolytic cleavage of XII proceeded entirely in the direction of V, presumably because of the greater thermodynamic stability of the corresponding enolate ion.

The cyclopentanone carbonyl group of XII was converted selectively to the thioketal XIII which on nickel desulfurization furnished a sample of 1-methyl-2,3-benzbicyclo(3,2,1)-4-octanone (XI) identical with the material prepared by oxidation of VIII.

The stereochemistry assigned to VIII is suggested by its mode of formation (*trans*-diaxial attack) and is supported by the sodium borohydride reduction of XI, which presumably proceeds from the less hindered *exo* side. There was formed a new epimeric alcohol XIV, m.p. 60°, whose n.m.r.

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(6) This and related work will form the subject of a future communication.

(7) T. Kubota and T. Matsuura, *J. Inst. Polytech. Osaka City Univ., Ser. C*, **4**, 112 (1953); *C. A.*, **49**, 2407 (1955).

(8) N.m.r. spectra were run at 60 m.c. on a Varian HR-60 spectrometer in deuteriochloroform solution. Tetramethylsilane served as internal standard. Frequencies were determined by the side-band technique. Funds for the purchase of the n.m.r. spectrometer were provided by the Institute of Molecular Biophysics.

(9) It is also found in the n.m.r. spectra of V, XII, XIII and a number of other α-tetralones synthesized in related work.

(10) W. Herz, *J. Am. Chem. Soc.*, **79**, 5011 (1957).

spectrum exhibited a doublet at 4.95 p.p.m. (J = 5 c.p.s.) characteristic of the assigned structure.[11]

A minor product during the chromatograms of the mesylate VIIIc with dry solvents was the ether XV. Presumably this results from nucleophilic attack of the alcohol VIII, formed by small amounts of adsorbed moisture, on the mesylate VIIc.

This facile preparation of the bicyclo(3,2,1) system may have value in synthesis and we are studying its general applicability.

Experimental[12]

4-Methyl-4-(carbethoxymethyl)-butyrolactone.—A mixture of 360 g. of ethyl levulinate, 290 ml. of ethyl bromoacetate and 1.5 l. of dry benzene was added with stirring to 190 g. of activated zinc covered with dry ether at such a rate that rapid reflux was maintained. Refluxing was continued overnight, after which the cooled mixture was hydrolyzed with 1 l. of 10% hydrochloric acid and extracted thoroughly with ether. The ether extract was washed with saturated sodium chloride solution, dried and distilled; yield 245 g. (53%), b.p. 122–126° (1 mm.), infrared bands at 1770 and 1740 cm.$^{-1}$.

3-Methyl-3-phenyladipic Acid (IV).—To a cold (0°) mixture of 450 g. of aluminum chloride and 500 ml. of dry benzene was added with stirring and cooling a solution of 151 g. of the preceding lactone in 400 ml. of dry benzene in the course of 75 minutes. After stirring overnight at room temperature, the mixture was poured over ice–hydrochloric acid, the benzene layer separated and the aqueous layer extracted with ether. The combined organic extracts were washed with water and extracted thoroughly with 15% potassium hydroxide solution. The basic extracts were combined with 50 g. of potassium hydroxide and 100 ml. of ethanol, refluxed for 8 hr., cooled and poured over ice-hydrochloric acid. The solid was filtered, dried and recrystallized from ethyl acetate; wt. 151 g. (78%), m.p. 153–155°.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 66.36; H, 7.12.

1-Methyl-2,3-benzbicyclo-(3,2,1)-octane-4,6-dione (XII).—A mixture of 20 g. of IV and 250 ml. of polyphosphoric acid was heated on a steam-bath for 1 hour, poured over ice and filtered. The solid material was dried, dissolved in benzene–petroleum ether and chromatographed over 70 g. of alumina. The eluate was concentrated and the residue crystallized from ethyl acetate–petroleum ether; yield 8 g. (46%), m.p. 109–111°, infrared bands at 1750 (cyclopentanone) and 1685 cm.$^{-1}$ (α-tetralone). The n.m.r. spectrum had signals at 7.95 (doublet of triplets, *peri*-hydrogen), 7.45 (complex, three benzene protons), 3.63 (doublet, J = 5 c.p.s., H_5 deshielded by two adjacent carbonyls whose coupling constant to one of the adjacent protons appears to be 0), 2.3–2.64 (complex system of lines, intensity four protons, corresponding to H_7 and H_8) and 1.7 p.p.m. (singlet C_1–methyl). The signal of the methyl group appears at unusually low field (see also the n.m.r. spectrum of XIII).

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 77.98; H, 6.04. Found: C, 77.42; H, 6.21.

A mixture of 3 g. of XII, 1.4 g. of ethanedithiol and 12 ml. of boron trifluoride etherate was allowed to stand overnight, poured over ice and extracted with ethyl ether. The ether extract was dried and evaporated and the gummy residue taken up in benzene–petroleum ether and chromatographed over alumina. The eluate crystallized on standing. Recrystallization from ethanol–water gave colorless needles (XIII), m.p. 66–68°, infrared band at 1685 cm.$^{-1}$ (α-tetralone), n.m.r. signals at 8.02 (doublet of triplets, *peri*-hydrogen) 7.40 (3 protons, benzene resonance), 3.48 (5 protons, H_5 and methylene protons of thioketal?), 2.60 (2 protons, doublet, J = 4, H_7), 2.45 (2 protons, doublet, J = 2.5, H_8) and 1.77 p.p. m. (C_1–methyl).

Anal. Calcd. for $C_{15}H_{16}OS_2$: C, 64.18; H, 5.84. Found: C, 64.50; H, 5.97.

1-Methyl-1-carboxymethyl-4-tetralone (V).—A mixture of 1.25 g. of XII and 70 ml. of 10% potassium hydroxide solution was allowed to stand for 20 hours, acidified and extracted with ether. The washed and dried ether extract yielded a viscous oil which was recrystallized from petroleum ether-ethyl acetate (9:1); yield 0.5 g. (36%) of V, m.p. 91–92°, infrared bands at 1710 (carboxyl) and 1685 cm.$^{-1}$ (α-tetralone), n.m.r. signals at 8.02 (doublet of triplets), 7.41 (benzene resonance), 2.73 (complex band system of 4 protons, H_2 and α-methylene of side chain) and 1.52 p.p.m. (C_1–methyl).

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.02; H, 6.44.

The dinitrophenylhydrazone was recrystallized from ethanol; m.p. 259°.

Anal. Calcd. for $C_{19}H_{17}O_6N_4$: C, 57.28; H, 4.55; N, 14.07. Found: C, 57.03; H, 4.56; N, 13.74.

Compound V was prepared more conveniently by cyclization of 24 g. of 3-methyl-3-phenyladipic acid with 250 ml. of concentrated sulfuric acid. After 30 minutes on a steam-bath, the temperature had risen to 86°. The mixture was poured onto ice and the solid which formed on standing was filtered and washed with brine. Recrystallization from petroleum ether–ethyl acetate yielded 11 g. of V, m.p. 91–92° (50%).

Acetate of 1-Methyl-1-(2-hydroxyethyl)-1,2-dihydronaphthalene (VIIb).—A solution of 28 g. of V in 250 ml. of dry ether was added dropwise to 13 g. of lithium aluminum hydride and 150 ml. of dry ether. After stirring overnight, the mixture was hydrolyzed with water and filtered to remove salts. The organic layer was separated, dried and concentrated. The residue was heated at 70° with 200 ml. of acetic anhydride and 4 ml. of pyridine for 10 hours, concentrated *in vacuo*, heated at 200° until the evolution of acetic acid ceased and distilled at reduced pressure, b.p. 115–118° (0.3 mm.), yield 20.8 g. (71%), infrared band at 1740 cm.$^{-1}$ (acetate), n.m.r. signals at 7.38 (4 protons, benzene resonance), 6.50, 6.40, 6.08, 5.90 (2 protons, triplets, H_3 and H_4), 3.98 (2 protons, triplet, J = 8.3, $-CH_2-O-$), 2.27 and 2.18 (2 doublets, H_2), 1.90 (acetate methyl superimposed on several bands of 1-methylene protons) and 1.27 p.p.m. (C_1–methyl).

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 77.93; H, 8.05.

Pyrolysis of 1 g. of VIIb was carried out by passing the acetate over glass helices at 500° in a stream of nitrogen. The product was collected in a Dry Ice trap and passed through the furnace again, taken up in ether, washed with dilute base, water, dried and distilled. The fraction boiling at 80–90° (1.2 mm.) was identified as 1-methylnaphthalene by its n.m.r. spectrum and by conversion to the picrate, m.p. 139°, no depression on admixture of an authentic sample.

1-Methyl-1-(2-hydroxymethyl)-1,2-dihydronaphthalene (VIIa).—A solution of 16 g. of VIIb, 15 g. of potassium hydroxide, 50 ml. of water and 150 ml. of methanol was refluxed for 12 hours, cooled, diluted with water and extracted with ether. The ether extract was washed, dried, concentrated and distilled. The fraction, b.p. 130–132° (1.2 mm.), was collected, yield 10 g. (75%), n.m.r. signals at 7.16 (4 protons, center of benzene resonance), 6.53, 6.42, 6.08, 5.92 (2 protons, triplets, H_3 and H_4), 3.41 (2 protons, triplets, J = 7, $-CH_2-O$), 2.22 and 2.16 (2 protons, doublets, H_2), 1.79 (2 protons, slightly split triplet, J = 7, 1-methylene) and 1.27 p.p.m. (C_1–methyl).

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.93; H, 8.59. Found: C, 82.68; H, 8.55.

The mesylate was prepared by cooling 5 g. of VIIa and 30 ml. of dry pyridine to 0°, adding 6 ml. of methanesulfonyl chloride and stirring at room temperature for 18 hours. Decomposition with ice, extraction with ether, washing and drying of the ether extracts yielded on evaporation a gum which did not crystallize. Chromatography over acid-washed alumina (solvent anhydrous benzene–petroleum ether) resulted in a waxy solid (VIIc), infrared band at 1350 cm.$^{-1}$ (methanesulfonate), which could not be recrystal-

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(11) Dreiding models indicate that this shift—relative to VIII—is not due to a change in orientation of the C_4-proton relative to the benzene ring with its diamagnetic anisotropy, but arises because shielding by the methylene bridge is less than by the ethylene bridge.

(12) M.p.'s and b.p.'s are uncorrected. Analyses by Dr. F. Pascher, Bonn, Germany.

lized satisfactorily and gave poor carbon values, perhaps because of contamination by the ether XV which sometimes cannot be separated satisfactorily from the mesylate.

Anal. Calcd. for $C_{14}H_{18}O_3S$: C, 63.14; H, 6.81; S, 12.20. Found: C, 64.95; H, 6.99; S, 11.75.

exo-**1-Methyl-2,3-benzbicyclo(3,2,1)-4-octanol (VIII).**—A solution of unpurified mesylate, prepared from 5 g. of alcohol VIIa, in wet benzene–petroleum ether was chromatographed over basic alumina. Elution with diethyl ether yielded crystalline material which was recrystallized from ligroin; total yield of once-recrystallized material 2.7 g. (54%), m.p. 80–82°.

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 83.14; H, 8.79.

A solution of 1.09 g. of mesylate, previously chromatographed over acid-washed alumina using anhydrous solvents was chromatographed over basic alumina. Benzene–petroleum ether eluted 0.190 g. of a non-polar fraction which was recrystallized from ethanol, m.p. 165–168°, and shown to be the ether XV by infrared (no hydroxyl or mesylate bands) and n.m.r. spectrum (benzene resonance at 7.15, doublet at 4.38, J = 2, –CH–O–, complex band system for methylene and methine protons, and 1.47 p.p.m., (C_1–methyl).

Anal. Calcd. for $C_{26}H_{30}O$: C, 87.10; H, 8.44; O, 4.46. Found: C, 87.24; H, 8.27; O, 4.59.

Elution with diethyl ether resulted in recovery of 0.725 g. of mesylate.

1-Methyl-2,3-benzbicyclo(3,2,1)-4-octanone (XI).—Oxidation of 1.5 g. of VIII with chromic oxide–pyridine complex[13] yielded after decomposition with ice, extraction with ether, washing, drying of the ether extract, 1.2 g. (80%) of XI, b.p. 91–93° (0.2 mm.), infrared band at 1680 cm.$^{-1}$, n.m.r. signals at 8.01 (1 proton, doublet of triplets, *peri*-hydrogen), 7.38 (3 protons, benzene resonance), 3.12 (1 proton, doublet of doublets), methylene and methine hydrogens (total intensity 6 protons) and 1.63 p.p.m. (C_1–methyl).

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.68; H, 7.60.

The dinitrophenylhydrazone, scarlet needles from ethanol–ethyl acetate, melted at 228–230°.

Anal. Calcd. for $C_{19}H_{18}N_4O_4$: C, 62.28; H, 4.95; N, 15.29. Found: C, 61.90; H, 4.96; N, 15.39.

The ketone XI was also prepared by desulfurization of 0.3 g. of the thioketal XIII with W-2 Raney nickel in absolute ethanol. The identity was established by conversion to the dinitrophenylhydrazone, m.p. and mixed m.p. and infrared spectra.

endo-**1-Methyl-2,3-benzbicyclo(3,2,1)-4-octanol (XIV).**—Reduction of 1 g. of XI with 1 g. of sodium borohydride in 95% ethanol in the usual fashion yielded, after hydrolysis, extraction with ether, drying and removal of solvent, material which was recrystallized from petroleum ether; m.p. 59–62°, yield 0.5 g., n.m.r. signals at 7.18 (4 protons, center of benzene resonance), 4.95 (1 proton, doublet, J = 5, H_4), 2.85 (–OH), 2.45 (1 proton, complex multiplet, H_5), 1.65 (6 protons, center of complex system, H_6, H_7 and H_8) and 1.37 p.p.m. (C_1–methyl).

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 83.59; H, 8.59.

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[13] G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE, THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL

Unsaturated Macrocyclic Compounds. XXV.[1] The Synthesis of Bisdehydro-[20]annulene,[2] [20]Annulene, Tridehydro-[30]annulene and [30]Annulene from 1,5,9-Decatriyne

BY FRANZ SONDHEIMER AND YEHIEL GAONI

RECEIVED APRIL 26, 1962

Two syntheses of 1,5,9-decatriyne (V) are described. The oxidative coupling of this triacetylene with cupric acetate in pyridine yielded the cyclic dimer IX and cyclic trimer XII, as well as the linear dimer VIIIa and linear tetramer VIIIb. The cyclic dimer IX was rearranged with potassium *t*-butoxide in *t*-butyl alcohol to bisdehydro-[20]annulene (*e.g.*, X), which was converted by partial hydrogenation to [20]annulene (*e.g.*, XI). Similarly, the cyclic trimer XII was rearranged to tridehydro-[30]annulene (*e.g.*, XIII), which on partial hydrogenation produced [30]annulene (*e.g.*, XIV).

It has been shown previously that the oxidative coupling of aliphatic α,ω-diacetylenes may give rise to large-ring polyacetylenes[3,4] and that linear 1,5-diacetylenes are rearranged by means of potassium *t*-butoxide to conjugated polyen-ynes.[5] In part XXI of this series[2] we described the use of a combination of both of these types of reactions for the synthesis of a number of fully conjugated macrocyclic polyene-polyynes (dehydro-annulenes), 1,5-hexadiyne being subjected to the coupling reaction, followed by prototropic rearrangement of the resulting cyclic products. An alternative route to large-ring polyacetylenes made up of 1,5-diyne units, suitable for rearrangement to dehydro-annulenes, appeared to involve the oxidative coupling of the hitherto unknown 1,5,9-decatriyne (V). In the present paper we report the synthesis of this compound,[6a] its coupling to the cyclic dimer IX[6c] and trimer XII,[6a] and the prototropic rearrangement of these substances[7] to bisdehydro-[20]annulene (*e.g.*, X)[6c] and tridehydro-[30]annulene (*e.g.*, XIII).[6a] These dehydro-annulenes were then converted by partial hydrogenation to [20]annulene (*e.g.*, XI)[6c] and [30]annulene (*e.g.*, XIV),[6b] respectively.

Two different syntheses of 1,5,9-decatriyne (V) were developed. The preferred method was modeled on the synthesis of 1,5-hexadiyne from

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[1] For Part XXIV, see F. Sondheimer and Y. Gaoni, *J. Am. Chem. Soc.*, **83**, 4863 (1961).

[2] For the nomenclature employed, see F. Sondheimer and R. Wolovsky, *ibid.*, **84**, 260 (1962).

[3] (a) F. Sondheimer and Y. Amiel, *ibid.*, **79**, 5817 (1957); (b) F. Sondheimer, Y. Amiel and R. Wolovsky, *ibid.*, **79**, 6263 (1957); (c) F. Sondheimer, Y. Amiel and R. Wolovsky, *ibid.*, **81**, 4600 (1959).

[4] G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, 889 (1959).

[5] F. Sondheimer, D. A. Ben-Efraim and Y. Gaoni, *J. Am. Chem. Soc.*, **83**, 1682 (1961).

[6] For preliminary communications, see (a) F. Sondheimer, R. Wolovsky and Y. Gaoni, *ibid.*, **82**, 754 (1960); (b) F. Sondheimer, R. Wolovsky and Y. Gaoni, *ibid.*, **82**, 755 (1960); (c) F. Sondheimer and Y. Gaoni, *ibid.*, **83**, 1259 (1961).

[7] The prototropic rearrangement of 1,5,9-decatriyne (V) itself with potassium *t*-butoxide has been described in part XVIII of this series.[5]