copper (300 mg). The filtrate was cooled and then filtration gave 40 mg (9.3%) of biacenedione. The filtrate was concentrated under vacuum, and the residue was triturated with petroleum ether (bp 38–50°) (20 ml) to give pale yellow crystals. Recrystallization from methanol gave 565 mg (65%) of **7** as colorless prisms.

Spiro[acenaphthenone-2,3′-tricyclo[3.2.1.0$^{2',4'}$]octane-6′,7′-dicarboxylic anhydride] (**8**).—A solution of **1** (580 mg, 3 mmol) and bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (660 mg, 4 mmol) in benzene (30 ml) was refluxed for 40 hr. Concentration of the solution was followed by addition of methanol (20 ml). After standing overnight, the product was collected by filtration. Recrystallization from chlorobenzene gave 250 mg (25%) of **8**, mp 274–276° dec, as colorless prisms: ir (KBr) 1845, 1770, 1708 cm^{-1} (C=O); mass spectrum *m/e* 330 (M$^+$).

Anal. Calcd for $C_{21}H_{14}O_4$: C, 76.35; H, 4.27. Found: C, 76.32; H, 4.32.

Reaction of 1 with Phenylacetylene.—After a solution of **1** (580 mg, 3 mmol) and phenylacetylene (2.0 g, 19.6 mmol) in benzene (25 ml) was refluxed for 48 hr, the solvent was removed under vacuum to leave a semicrystalline residue. A solution of the residue in 20 ml of petroleum benzine (bp 42–60°) was heated under reflux for 30 min and then allowed to stand overnight. Filtration gave yellow crystals, which on two recrystallizations from ethanol afforded 200 mg of **9**, mp 243–244°, as pale yellow needles. The petroleum benzine filtrate was concentrated under vacuum, and the residue was chromatographed over alumina (elution with benzene and chloroform), giving 400 mg of **1** and 20 mg of **9**: yield of **9**, 220 mg (25%); ir (KBr) 1710 cm^{-1} (C=O); mass spectrum *m/e* (rel intensity) 296 (100), 268 (34), 267 (12), 240 (21), 239 (70), 238 (11), 237 (18), 120 (10).

Anal. Calcd for $C_{20}H_{12}N_2O$: C, 81.06; H, 4.08; N, 9.45. Found: C, 81.12; H, 4.10; N, 9.35.

Reaction of 1 with Diethyl Acetylenedicarboxylate.—After a solution of **1** (970 mg, 5 mmol) and diethyl acetylenedicarboxylate (1.2 g, 7 mmol) in benzene (20 ml) was refluxed for 16 hr, the same procedure as above gave crude **10**. Two recrystallizations from ethyl acetate gave 1.45 g (80%) of pure **10**, mp 147.5–148.5°, as pale yellow prisms: ir (KBr) 1742, 1712 cm^{-1} (C=O); mass spectrum *m/e* (rel intensity) 364 (39), 320 (15), 291 (25), 258 (26), 257 (26), 221 (26), 220 (100), 180 (31), 152 (20).

Anal. Calcd for $C_{20}H_{16}N_2O_5$: C, 65.93; H, 4.43; N, 7.69. Found: C, 65.65; H, 4.49; N, 7.70.

Registry No.—**1**, 2008-77-7; **3a**, 27544-92-9; **3b**, 27544-93-0; **3c**, 27610-03-3; **3d**, 27610-04-4; **4a**, 27544-94-1; **4b**, 27544-95-2; **4c**, 27544-96-3; **5**, 27544-97-4; **6**, 27544-98-5; **8**, 27544-99-6; **9**, 27545-00-2; **10**, 27545-01-3.

Synthesis of 3-Substituted 1,4-Pentadiyn-3-ols

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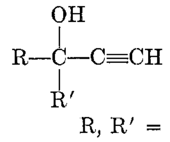
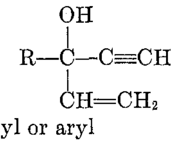
A convenient synthesis of 3-substituted 1,4-pentadiyn-3-ols is described. This synthesis employs the treatment of a phenyl ester with a metal acetylide in liquid ammonia, using dichloromethane as cosolvent. Triethynylmethanol was synthesized by a similar method.

Reports in the literature on the preparation of tertiary ethynyl carbinols have been numerous, and a wide variety of reagents and reaction conditions have been described. For compounds having an unsubstituted terminal acetylenic group, the most familiar method has involved the use of a metal acetylide in liquid ammonia.[1,2] These include monoethynyl carbinols with various alkyl or aryl substituents on the α carbon.

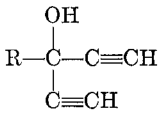


$$R-\overset{OH}{\underset{R'}{C}}-C\equiv CH$$

R, R′ = alkyl or aryl



$$R-\overset{OH}{\underset{CH=CH_2}{C}}-C\equiv CH$$



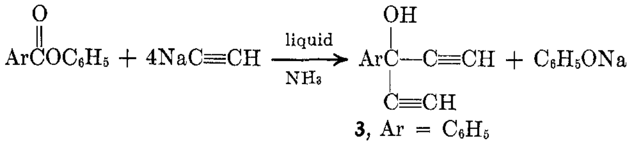
$$R-\overset{OH}{\underset{C\equiv CH}{C}}-C\equiv CH$$

1, R = H
2, R = CH_3
3, R = C_6H_5

Although several diethynyl carbinols that are terminally substituted on the triple bond have been described,[3] only a few examples of diethynyl carbinols that are not substituted at this position have been reported. Jones, *et al.*,[4] developed the ethynyl Grignard reagent which was reacted with EtO_2CH to give **1**. The methyl derivative **2** was obtained by treating diethynyl ketone with MeMgBr or by reacting 3-butyn-2-one with ethynylmagnesium bromide.[5] The phenyl compound **3** was obtained similarly from phenyl ethynyl ketone.[6] All of these methods employ the ethynyl Grignard which is not always successful.

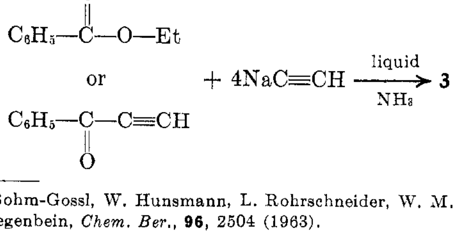
We wish to report a convenient synthesis of tertiary diethynyl carbinols using a metal acetylide in liquid ammonia. Earlier work in these laboratories has shown that CH_2Cl_2 is a very effective cosolvent in ethynylation reactions involving liquid ammonia.[7] Use of this cosolvent in the ethynylation of appropriately substituted phenyl esters proved to be beneficial in obtaining a large variety of 3-substituted 1,4-pentadiyn-3-ols.

3-Aryl-1,4-pentadiyn-3-ols.—Phenyl benzoate dissolved in CH_2Cl_2 was added to 4 equiv of sodium acetylide in liquid ammonia to give 3-phenyl-1,4-pentadiyn-3-ol (**3**) in 20–30% yield. Lithium acetylide



$$Ar\overset{O}{\overset{\|}{C}}OC_6H_5 + 4NaC\equiv CH \xrightarrow[NH_3]{liquid} Ar\overset{OH}{\underset{C\equiv CH}{C}}-C\equiv CH + C_6H_5ONa$$

3, Ar = C_6H_5



$$\left.\begin{array}{c} C_6H_5-\overset{O}{\overset{\|}{C}}-O-Et \\ \text{or} \\ C_6H_5-\underset{O}{\underset{\|}{C}}-C\equiv CH \end{array}\right. + 4NaC\equiv CH \xrightarrow[NH_3]{liquid} \mathbf{3}$$

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[1] K. N. Campbell, B. K. Campbell, and L. T. Eby, *J. Amer. Chem. Soc.*, **60**, 2882 (1938).

[2] W. M. McLamore, M. Harfenist, A. Bavley, and S. Y. P'An, *J. Org. Chem.*, **19**, 570 (1954).

[3] H. G. Viehe, *Chem. Ber.*, **92**, 1950 (1959); K. Hess and W. Weltzien, *Ber.*, **54B**, 2511 (1921).

[4] E. R. H. Jones, L. Skattebol, and M. C. Whiting, *J. Chem. Soc.*, 4765 (1956); E. R. H. Jones, H. H. Lee, and M. C. Whiting, *ibid.*, 3483 (1960).

[5] T. Bohm-Gossl, W. Hunsmann, L. Rohrschneider, W. M. Schneider, and W. Ziegenbein, *Chem. Ber.*, **96**, 2504 (1963).

[6] J. G. Noltes and G. J. M. Van der Kerk, *Recl. Trav. Chim. Pays-Bas*, **81**, 41 (1962).

[7] It was noted in these laboratories that ethynylation of diaryl ketone in liquid NH_3-CH_2Cl_2 solvent consistently gave complete conversions to the 1,1-diaryl-2-propynyl-1-ols which was not the case when NH_3-ether solvent was employed.

TABLE I
3-ARYL-1,4-PENTADIYN-3-OL, ArC(OH)$(C{\equiv}CH)_2$

Compd no.	Ar	Mp or bp (mm), °C	% yield	Formula	Calcd, %		Found, %	
					C	H	C	H
3	C_6H_5	58–60	20	$C_{11}H_8O$	84.59	5.16	84.21	5.26
4	4-FC_6H_4	68–70 (0.2)	32	$C_{11}H_7FO$	75.85	4.05	75.92	4.37
5	4-ClC_6H_4	85–88 (0.08)	27	$C_{11}H_7ClO$	69.30	3.70	69.14	3.81
6	3,4-$Cl_2C_6H_3$	94–96 (0.05)	14	$C_{11}H_6Cl_2O$	58.69	2.68	58.84	2.75
7	4-$CH_3C_6H_4$	86–90 (0.15)	12	$C_{12}H_{10}O$	84.68	5.92	84.41	6.19
8	3-$CF_3C_7H_4$	80–85 (0.2)	45	$C_{12}H_7F_3O$	64.28	3.14	64.27	3.38
9	4-$CH_3OC_6H_4$	111–114 (0.08)	11	$C_{12}H_{10}O_2$	77.40	5.41	77.32	5.71
10	2-$C_{10}H_7$	145–155 (0.2)	23	$C_{15}H_{10}O$	87.35	4.89	86.97	4.96
11	3-C_5H_4N	120–122	3	$C_{10}H_7NO$	76.42	4.49	76.69	4.70
12	2-C_4H_3S	107–111 (4)	1.7	C_9H_6OS	66.67	3.73	66.44	4.25
13	2-(5-BrC_4H_2O)	76–80 (0.01)	7.4	$C_9H_5BrO_2$	48.03	2.23	48.28	2.49

TABLE II
3-ALKYL-1,4-PENTADIYN-3-OLS, RC(OH)$(C{\equiv}CH)_2$

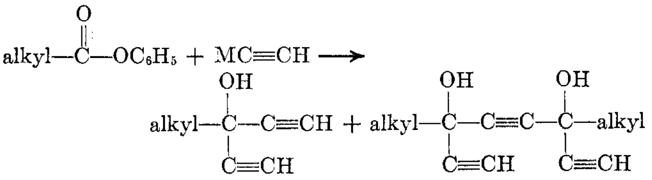
Compd no.	R	Mp or bp (mm), °C	% yield	Formula	Calcd, %		Found, %	
					C	H	C	H
14	CH_3CH_2	54–56	6.0	C_7H_8O	77.75	7.46	77.65	7.64
15	$(CH_3)_2CH$	63–65	21.0	$C_8H_{10}O$	78.65	8.25	78.60	8.26
16	$(CH_3)_3C$	48–52 (4)	50.0	$C_9H_{12}O$	79.37	8.88	79.33	9.04
17	$CH_3(CH_2)_4$	102–106 (4)	8.1	$C_{10}H_{14}O$	79.95	9.39	79.94	9.35
18	$CH_3(CH_2)_2CH(CH_3)$	28–30	16.4	$C_{10}H_{14}O$	79.95	9.39	79.77	9.38
19	Cyclopropyl	50–52	23.0	C_8H_8O	79.97	6.71	79.75	6.58
20	Cyclobutyl	86–88	35.6	$C_9H_{10}O$	80.56	7.51	80.46	7.46
21	Cyclopentyl	50–52	1.6	$C_{10}H_{12}O$	81.04	8.16	80.81	8.19
22	Cyclohexyl	73–75	52.0	$C_{11}H_{14}O$	81.44	8.70	81.23	8.92
23	1-Methylcyclohexyl	39–40	32.0	$C_{12}H_{16}O$	81.77	9.15	81.53	9.31
24	1-Cyclohexenyl	86–88	17.0	$C_{11}H_{12}O$	82.46	7.55	82.40	7.47
25	1-Adamantyl	113–115	17.0	$C_{15}H_{18}O$	81.77	9.15	81.53	9.31

was as effective as sodium acetylide. Phenyl esters of substituted aromatic acids (see Table I), including the heteroaromatics **11**, **12**, and **13**, on this treatment gave the appropriately substituted carbinols. Yields ranged from 2 to 45%.

Ethyl benzoate was treated with NaC≡CH as described above, and **3** was isolated in 40% yield (yields were erratic when the ethyl esters were used). Use of phenyl ethynyl ketone[8] with NaC≡CH resulted in only a 9% yield of **3**. When *p*-chlorophenyl ethynyl ketone was treated with sodium acetylide, no corresponding diethynyl carbinol could be isolated.

3-Alkyl-1,4-pentadiyn-3-ols.—The ethynylation was extended to the phenyl alkanoates to give the 3-alkyl-1,4-pentadiyn-3-ols (see Table II). It was noted that the amount of substitution on the α carbon atom of the ester greatly influenced the yields. The methyl compound could not be isolated using this method, whereas the ethyl (**14**) was isolated in 6% yield, isopropyl (**15**) in 20.5%, and *tert*-butyl (**16**) in 50% yield. The cycloaliphatics (**19**–**25**) worked quite well in this ethynylation.

In two cases, alkyl being *tert*-butyl (**26**) or 1-methylcyclohexyl (**27**), the diacetylenic glycols were isolated in addition to the expected carbinols.

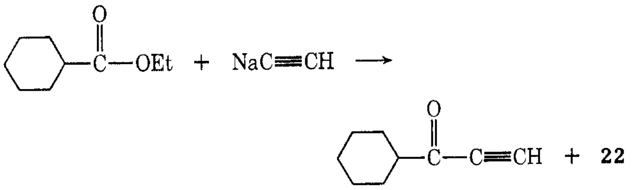


$$\text{alkyl}-\overset{\overset{\displaystyle O}{\|}}{C}-OC_6H_5 + MC{\equiv}CH \longrightarrow \text{alkyl}-\underset{\underset{\displaystyle C{\equiv}CH}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-C{\equiv}CH + \text{alkyl}-\underset{\underset{\displaystyle C{\equiv}CH}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-C{\equiv}C-\underset{\underset{\displaystyle C{\equiv}CH}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-\text{alkyl}$$

26, alkyl = *tert*-butyl
27, alkyl = 1-methylcyclohexyl

In order to determine which of the metal acetylides was superior in this reaction, phenyl cyclohexanecarboxylate was treated with lithium, sodium, potassium, and calcium acetylide in liquid ammonia with isolated yields of 40, 52, 60, and 0%, respectively. In general, for cycloalkyl derivatives the use of potassium acetylide gives the highest yields.

The ethyl ester of cyclohexanecarboxylic acid was treated with sodium acetylide to give, in addition to 5% of the expected diethynyl carbinol, cyclohexyl ethynyl ketone (**28**) in 10% yield. Use of other ethyl esters gave erratic results, and the reaction mixtures were usually contaminated with starting esters.



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Although the aryl and alkyl diethynyl carbinols are quite stable, once purified, precaution should be taken in working with crude reaction mixtures. In most cases, the crude product was distilled at reduced pressure until evidence of decomposition was noted, and the source of heat was then removed. The crude reaction mixture of the *p*-nitrophenyl derivative exploded during attempted distillation. Redistillation of these compounds afforded no problems. In some instances column chromatography was used. Usually, the products were solids and could be recrystallized from benzene and low-boiling petroleum ether mixtures. In none of

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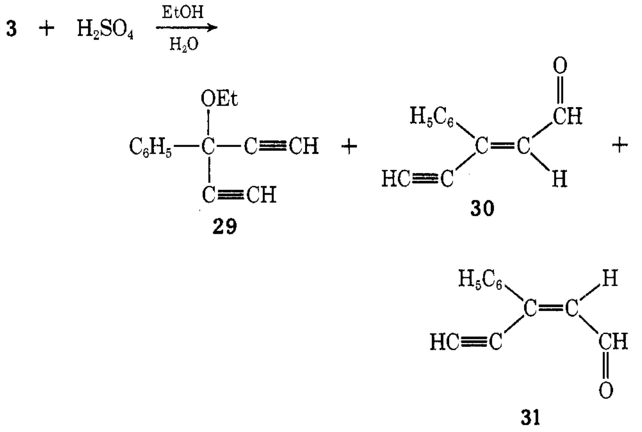
[8] When phenyl ethynyl ketone was treated with ethynylmagnesium,[6] **3** was obtained in 15% yield.

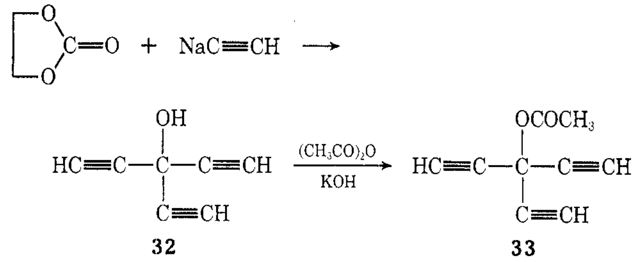
the above reactions using the phenyl esters were any starting phenyl esters isolated.

Treatment of **3** with H_2SO_4 in aqueous EtOH at room temperature gave on distillation, as a major product, the ethyl ether **29**. The minor components, based on the nmr and ir spectra (see Experimental Section), were



cis- (**30**) and *trans*- (**31**) β-ethynylcinnamaldehydes. By treating **3** with H_2SO_4 in aqueous EtOH at reflux temperature for a brief time, **31** could be isolated in 33% yield. (Neither **29** nor **30** was present.) Heating for longer times gave only intractable tars. The formation of the cinnamaldehydes from **3** is related to the Meyer-Schuster rearrangement,[9] involving allenization of the triple bond.

Triethynylmethanol.—Although terminally substituted triethynylmethanols have been reported,[10] **32** has not been described in the literature. Utilizing our synthetic method, several attempts were made to prepare this compound. The only intermediate that



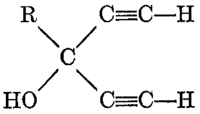
proved successful was ethylene carbonate. When the latter compound was added to 5 equiv of sodium acetylide in liquid NH_3, **32** was isolated upon neutralization with NH_4Cl by first column chromatography and then distillation in 1–8% yields. The material was a low-melting solid that showed the expected nmr and ir spectra. The compound exploded on combustion for elemental analyses. Attempted recrystallization of this material was unsuccessful. However, its acetate (**33**) crystallized readily from a benzene–petroleum ether mixture.

Nmr Spectra. It was noted that the chemical shifts of the acetylenic protons varied depending upon the substitution at the 3 position of the pentadiynols. The fact that the acetylenic protons are shifted downfield in **32** relative to **16**, contrary to expectations based on acetylenic anisotropy, indicates that other screening mechanisms are probably operative. Presumably, the acetylenic π electrons increase the conjugation of the system, allowing the 3 substituent to affect the electronic density at the terminal acetylenic carbons.

In comparing the chemical shifts in Table III, it seems that the greater the polarizability of R, the greater the shift to lower field, *i.e.*, the greater the deshielding.

TABLE III

CHEMICAL SHIFTS OF ACETYLENIC PROTONS



Compd no.	R	Chemical shifts of acetylenic protons, τ
16	*tert*-Butyl	7.43
19	Cyclopropyl	7.38
24	1-Cyclohexenyl	7.35
3	C_6H_5	7.27
8	$3\text{-}CF_3C_6H_4$	7.20
32	HC≡C—	7.25

Experimental Section

All melting points are uncorrected and were obtained in an open capillary tube. The ir spectra were determined in $CHCl_3$ with a Perkin-Elmer spectrophotometer, Model 21. The nmr spectra were determined in $CDCl_3$ on a Varian A-60 nmr spectrometer, using tetramethylsilane as an internal standard. Chemical shifts are reported using the τ scale.

Preparation of 3-Substituted 1,4-Pentadiyn-3-ols. General Procedure.—To 2 mol of sodium acetylide prepared by usual methods in 2.5 l. of liquid NH_3 was added dropwise over a 1-hr period 0.5 mol of the phenyl ester in 500–1000 ml of CH_2Cl_2. The NH_3 was allowed to evaporate as the reaction proceeded. After 4 hr, 1.5 l. of ether was added, the remaining ammonia was evaporated, and the mixture was decomposed with ice and water (total volume, 1.5 l.). The organic layer was separated, and the aqueous phase was extracted three times with ether. The combined organic solvents were washed three times with 200-ml portions of water and dried ($MgSO_4$), and the solvent was removed. The residue was distilled (Vigreux) at reduced pressure until decomposition was evident. The distillates that solidified were recrystallized from mixtures of benzene and petroleum ether (bp 35–60°). The distillates that remained oils were redistilled. In some cases column chromatography was used (Florisil). Yields are reported in Tables I and II.

The nmr spectra of the aliphatic and cycloaliphatic derivatives gave singlets (2 H) for the acetylenic protons in the range τ 7.46–7.42. The signals for each particular substituent were those expected. For the aromatic derivatives the singlets for the acetylenic protons were in the range τ 7.32–7.20.

The ir spectra of these compounds showed a sharp absorption peak at 3.02–3.05 μ and a weak absorption peak at 4.7–4.8 μ for the acetylenic group, and a sharp OH peak at 2.8–2.85 μ.

Treatment of Phenyl Pivalate with Sodium Acetylide.—Using the previously described reaction conditions, 0.5 mol of phenyl pivalate was allowed to react with 2 mol of sodium acetylide. Distillation of the crude reaction mixture gave a 50% yield of **16** (see Table II), bp 48–52° (4 mm). The portion that did not distil was crystallized from benzene–petroleum ether (bp 35–60°) to give 7.1 g of the acetylenic glycol **26**, mp 103–105°. *Anal.* Calcd for $C_{16}H_{22}O_2$: C, 78.00; H, 9.00. Found: C, 78.16; H, 9.10.

Phenyl 1-methylcyclohexanecarboxylate (0.27 mol) was treated similarly with sodium acetylide to give 12.5 g (26%) of **23** (see Table II) and 5 g of 3,6-bis(1-methylcyclohexyl)-1,4,7-octatriyne-3,6-diol (**27**), mp 114–116° (crystallized from petroleum ether, bp 60–71°). *Anal.* Calcd for $C_{22}H_{30}O_2$: C, 80.92; H, 9.26. Found: C, 81.16; H, 9.21.

Reaction of Ethyl Cyclohexanecarboxylate with Sodium Acetylide.—Ethyl cyclohexanecarboxylate (0.5 mol) was treated

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[9] K. H. Meyer and K. Schuster, *Ber.*, **55**, 819 (1922); G. F. Hennion and B. R. Fleck, *J. Amer. Chem. Soc.*, **77**, 3253 (1955).

[10] Yu. Yu. Tsmur and B. N. Dashkevich, *Zh. Obshch. Khim.*, **33**, 1357 (1963); D. D. Coffman, J. C.-Y. Tsao, L. E. Schniepp, and C. S. Marvel, *J. Amer. Chem. Soc.*, **55**, 3792 (1933); M. Siemiatycki, *Ann. Chim. (Paris)*, **2**, 189 (1957).

with 2 mol of $NaC{\equiv}CH$ as previously described; after the NH_3 had evaporated, the mixture was decomposed with 800 ml of water; and solid CO_2 was added until the pH of the solution was approximately 8. The ether layer was separated and dried ($MgSO_4$), and the solvent was removed. Distillation of the residue gave two fractions. The first fraction, bp 64–66° (4 mm), weight 7.5 g (10%), was cyclohexyl ethynyl ketone (**28**): nmr ($CDCl_3$) τ 6.65 (1 H, s, $\equiv$C–H), 8.42 (11 H, broad m, cyclohexyl); ir ($CHCl_3$) 3.02 ($\equiv$C–H), 4.76 ($C{\equiv}C$), 6.0 μ (CO). *Anal.* Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.21; H, 8.86.

The higher boiling fraction crystallized from petroleum ether (bp 35–60°) to give 3.5 g of solid with ir and nmr spectra identical with those of **22**.

Treatment of 3 with H_2SO_4. A.—A solution of 10 g (0.064 mol) of **3** in 250 ml of EtOH was cooled with an ice–water bath, and 25 ml of concentrated H_2SO_4 in 100 ml of water was added slowly. The mixture was allowed to stir for 5 days at room temperature. After being diluted with water, the mixture was extracted with ether. The ether solution was washed several times with water and dried ($MgSO_4$); distillation gave 8 g of oil, bp 60–65° (0.05 mm).

An analysis of the nmr spectrum of this oil indicated 72% 3-ethoxy-3-phenyl-1,4-pentadiyne (**29**), 16% *cis*-β-ethynylcinnamaldehyde (**30**), and 12% trans isomer (**31**).[11]

The ether **29** was purified by column chromatography (Florisil, benzene) and distillation: bp 54° (0.01 mm); nmr ($CDCl_3$) τ 8.75 (3 H, t, methyl), 6.20 (2 H, q, methylene), 8.96 (2 H, s, $C{\equiv}CH$), and 2.56 and 2.26 (5 H, 2 m, phenyl); ir ($CHCl_3$) 3.06 μ ($C{\equiv}CH$). *Anal.* Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.47; H, 6.47.

B.—To 10 g (0.064 mol) of **3** in 150 ml of EtOH was added 25 ml of H_2SO_4 in 100 ml of H_2O; the resulting mixture was heated to reflux temperature. A vigorous reaction ensued, and after 5 min, the mixture was worked up as above. The crude oil was distilled, bp 74–84° (0.03 mm). The distillate (**31**) which solidified was crystallized twice from petroleum ether (bp 60–71°): weight 3.5 g; mp 64–66°; nmr ($CDCl_3$) τ 6.21 (1 H, s, $C{\equiv}CH$), 3.85 (1 H, d, J = 8 Hz, vinyl), −0.33 (1 H, d, J = 8 Hz, adlehyde), and 2.53 and 2.30 (5 H, 2 m, phenyl); ir ($CHCl_3$) 3.05 ($C{\equiv}CH$), 4.75 ($C{\equiv}C$), 6.0 μ (CO). *Anal.* Calcd for $C_{11}H_8O$: C, 84.59; H, 5.16. Found: C, 84.86; H, 5.45.

Triethynylmethanol (32).—Ethylene carbonate (0.4 mol) dissolved in 300 ml of CH_2Cl_2 was treated with 2 mol of sodium acetylide in 2.5 l. of liquid NH_3 as before, and, after evaporating the NH_3, dry NH_4Cl (150 g), followed by ice and water (2 l.), was added. The mixture was allowed to stand for 30 min, and the aqueous layer was separated. The ether layer was washed with water (difficult emulsion) and dried ($MgSO_4$), and the ether was removed at reduced pressure. The residue was passed over a Florisil column with 9:1 C_6H_6–EtOAc, and the eluate was distilled, bp 50–55° (4 mm). This distillate solidified on cooling, mp 28–30°. Yields of 1–8% were obtained. Elemental analysis was not possible on this compound because of its explosive nature when combustion is attempted.

The nmr spectrum showed two peaks, 7.25 (3 H, s, acetylenic protons) and 6.70 (1 H, s, OH, D_2O exchangeable).

The ir spectrum had peaks at 3.05 μ for the acetylenic CH, 4.7 μ for the triple bond, and 2.84 μ for the OH (no peaks in the carbonyl region).

Triethynylmethyl Acetate (33).—An ethereal solution of **32** (0.05 mol) was added to a suspension of 30 g of powdered KOH in 500 ml of ether, cooling with an ice–ethanol bath and vigorously stirring. At −5° 20.2 g (0.2 mol) of acetic anhydride in an equal volume of ether was added dropwise over 20 min. Stirring and cooling were maintained for 45 min, and 500 ml of water was added. The ether solution was separated, washed twice with water, and dried ($MgSO_4$), and the ether was removed at reduced pressure. The residue was recrystallized from benzene–petroleum ether (bp 35–60°) to give 1.6 g (23%) of product, mp 88–89°. *Anal.* Calcd for $C_9H_6O_2$: C, 73.96; H, 4.14. Found: C, 73.93; H, 4.33.

Registry No.—**3**, 27410-03-3; **4**, 27410-04-4; **5**, 27410-05-5; **6**, 27410-06-6; **7**, 27410-07-7; **8**, 27410-08-8; **9**, 27410-09-9; **10**, 27410-10-2; **11**, 27410-11-3; **12**, 27410-12-4; **13**, 27410-13-5; **14**, 27410-14-6; **15**, 27410-15-7; **16**, 27410-16-8; **17**, 27410-17-9; **18**, 27410-18-0; **19**, 27410-19-1; **20**, 27410-20-4; **21**, 27410-21-5; **22**, 27410-22-6; **23**, 27410-23-7; **24**, 27410-24-8; **25**, 27410-25-9; **26**, 27410-26-0; **27**, 27410-27-1; **28**, 7560-69-2; **29**, 27410-29-3; **31**, 27390-88-1; **32**, 27410-30-6; **33**, 27410-31-7.

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[11] The nmr spectra of pure samples of **29** and **31** are described below. The assignment of the cis compound **30** was based on the presence of two additional doublets centered at τ 4.52 and 0.03 (J = 8 Hz). Isolation of this compound was not attempted.

A New Method for the Preparation of α,β-Unsaturated Carbonyl Compounds

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A unique preparation of α,β-unsaturated aldehydes and ketones from the corresponding saturated analogs is reported. The procedure involves a homogeneous liquid-phase oxidative dehydrogenation by air or oxygen in the presence of a group VIII metal [preferably Pd(II)] catalyst and a cocatalyst. Particular attention is given to the synthesis of 2-cyclohexen-1-one (2). The scope and limitations of this reaction are discussed. In addition, probable and alternative mechanisms of this selective dehydrogenation technique are examined.

The preparation of α,β-unsaturated ketones and aldehydes customarily involves allylic oxidation of olefins,[1] elimination reactions on α substituted carbonyl compounds,[2] or dehydration of aldols.[3] Most methods either involve several steps or are often complicated by low yields and unwanted by-products. Typical of an excellent, but several-step synthesis of an α,β-unsaturated ketone is that pictured in Scheme I for 2-cyclohexen-1-one (2) from dihydroresorcinol.[4] Since no short and easy synthetic scheme was available for the preparation of a highly versatile compound such as 2, it was advantageous to develop a one-step dehydrogenation of the corresponding saturated ketone or aldehyde. In contrast to the present liquid-phase reaction, only

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