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Skipped Diynes. V. Secondary Diethynylcarbinols, a Base-Catalyzed Ynol to Enol Rearrangement, and Ultraviolet Spectra and Conjugation[1]

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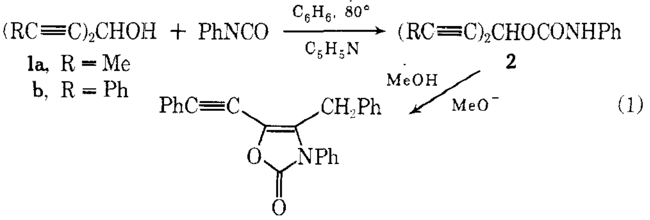
Bis(1-propynyl)methanol (**1a**), bis(phenylethynyl)methanol (**1b**), and tetrakis(1-propynyl)ethane-1,2-diol (**10**) are highly activated propargyl alcohols. Because of their sensitivity to acid, conversions of **1** to carbamate, ester, ether, and halide best proceed under neutral or basic conditions. Even so, disruptions of the diyne system are common, *e.g.*, the formation of 4-bromo-2,5-heptadiyne and 2-bromo-2,3-heptadien-5-yne from **1a**, thermal cleavage of **10**, and a base-catalyzed ynol to enone rearrangement of **1b** to 1,5-diphenylpent-1-en-4-yn-3-one (**14**). It is shown that the conversion of 1,3-diphenylpropynol (**15**) to 1,3-diphenylpropenone (**16**) in the presence of base is another example of this rearrangement and that reactions which appear to be characteristic of the ynol (**1b, 15**) are probably those of the enone (**14, 16**). The question of conjugation in skipped 1,4-diynes is discussed in the context of the uv spectra of several series and it is concluded that, in the diethynylmethanes, -carbinols, and ketones, the central function at the 3 carbon does transmit conjugation. The trialkylethynylcarbinols are anomalous in that their uv absorption bands are decidedly hypsochromic relative to all members of the diethynyl families.

In a skipped diyne, a methylene or other functionality is interposed between the two triple bonds. Such compounds could conceivably display properties that result from reciprocal effects of the alkyne and the middle group. Elsewhere we have reported on diethynylmethanes,[2] diethynyl ketones,[3] triethynylcarbinols, and related allenes.[4] Here we examine the chemistry of the diethynylcarbinols (**1**).

Relatively few (*ca.* 12) skipped diynols are known.[5,6] In their reactions, *e.g.*, hydration or hydrogenation of the triple bond and oxidation or functional exchange of the hydroxy group, these compounds appear to be unexceptional propargyl alcohols.[5,6] However, because the "propargylic" effect has been enhanced and vulnerable sites abound, we also find that competing processes are easily initiated. After describing a few "standard" processes we shall describe an unusual rearrangement of certain ethynylcarbinols.

Carbinol Reactions. Reaction of **1** with phenyl isocyanate yielded the expected urethanes (**2**).[7]



(1)

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Efforts to cyclize bis(1-propynyl)methyl *N*-phenylcarbamate either thermally (*ca.* 130°) or under basic conditions (*ca.* 60°) led only to intractable tars or recovery of unreacted carbamate. Likewise, bis(phenylethynyl)methyl *N*-phenylcarbamate did not cyclize in refluxing xylene but formed 4-benzyl-3-phenyl-5-phenylethynyl-4-oxazolin-2-one (**3**) in refluxing methanolic sodium methoxide.[7a] This product presumably arises from the base-catalyzed isomerization of the initially formed adduct, 4-benzylidene-3-phenyl-5-phenylethynyl-2-oxazolidinone (eq 1).

We have also prepared esters of **1** under basic or neutral conditions, which preclude possible acid-catalyzed Meyer–Schuster rearrangements of ethynylcarbinols to α,β-unsaturated ketones.[8] It was possible to esterify **1b** with acetyl chloride by refluxing them in benzene containing sufficient pyridine to neutralize the hydrochloric acid formed (eq 2), although **1a** was only partially esterified by benzoyl chloride under these conditions. However, the alkylation of preformed dipropynylmethyl alkoxide with a suitable acid chloride was successful and we were able to prepare bis(1-propynyl)methyl *m*-bromobenzoate (**5**) in fair yield (eq 3).

$$\mathbf{1b} + \text{MeCOCl} \xrightarrow[C_6H_6\text{-}C_5H_5N]{} \underset{\mathbf{4}}{(\text{PhC}{\equiv}\text{C})_2\text{CHOCOMe}} \qquad (2)$$

$$\mathbf{1a} \xrightarrow[2.\ 3\text{-BrC}_6H_3\text{COCl}]{1.\ \text{NaH-THF}} \underset{\mathbf{5}}{(\text{MeC}{\equiv}\text{C})_2\text{CHOCOC}_6H_3\text{-3-Br}} \qquad (3)$$

Ether formation was patterned on the ester syntheses and an example given by Liang.[6]

$$\mathbf{1a} \xrightarrow[2.\ \text{MeI}]{1.\ \text{Na-}C_6H_6} \underset{\mathbf{6}}{(\text{MeC}{\equiv}\text{C})_2\text{CHOMe}} \qquad (4)$$

The diethynylhalomethanes could possibly lead to polyethynylated methanes, ethanes, or ethylenes. A recent report, for example, describing the conversion of bis(phenylethynyl)methyl bromide into tetrakis(phenylethynyl)ethylene in the presence of potassium *tert*-butoxide was encouraging.[9] We were able to prepare bis(phenylethynyl)methyl bromide (**7b**) by treating **1b** with phosphorus tribromide in absolute ether at 0° (eq 5). This bromide was a yellow solid which decomposed to a red tar upon standing for several hours at 25°. It was, however, found to be stable indefinitely at −78°. Compound **1a** and phosphorus tribromide in absolute ether at 0° yielded an unstable oil which decomposed to a black tar within several hours at 25°. Spectral analysis indicated that the oil was a mixture of 4-bromo-2,5-heptadiyne (**7a**, 98%) and 2-bromo-2,3-heptadien-5-yne (**8a**, 2%). If the bromination was carried out in the presence of pyridine, the ratio of the two products changed to 1:1. Similar acetylene–allene rearrangements are known.[10]

$$1 + PBr_3 \xrightarrow[0°]{Et_2O} \underset{7}{(RC\equiv C)_2CHBr} + \underset{8}{RBrC{=}C{=}CHC\equiv CR} \quad (5)$$

a, R = Me
b, R = Ph

Attempts to separate the bromides (*e.g.*, distillation or column chromatography) resulted only in their decomposition and partial hydrolysis to **1a**, although they could be stored at −78° for several weeks without detectable decomposition.

We record observations on two of several reactions attempted with **7**. The bromides from **1a** reacted only slowly with magnesium metal in ether at 25°. An aqueous quench of the reaction mixture after 24 hr gave starting bromides and small amounts of 2,5-heptadiyne (**9**) and **8a**. When the reaction was repeated with **7b**, a yellow solid containing at least three compounds (one major product and two minor products) precipitated from the reaction mixture after 1 hr. Since mass spectral analysis showed that the heaviest fragment had *m/e* 430 and the base peak had *m/e* 215, it is probable that the major product in the mixture was a species of molecular weight 430, perhaps 1,1,2,2-tetrakis(phenylethynyl)ethane, which cleaves into two identical fragments of *m/e* 215 upon electron impact. The coupling process would then be

$$Mg + 7b \longrightarrow \underset{m/e\ 430}{(PhC\equiv C)_2CHCH(C\equiv CPh)_2} + \text{other products} \quad (6)$$

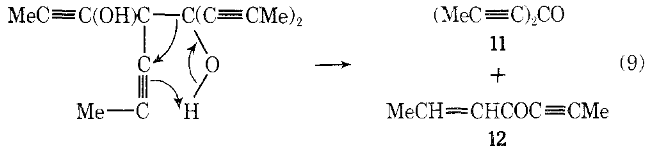
With another reductant, namely Cr(II),[11] **7a** gave 2,5-heptadiyne, and **7b** gave a yellow solid, identical in all respects with that of eq 6.

$$7a + CrSO_4 \longrightarrow \underset{9}{(MeC\equiv C)_2CH_2} \quad (7)$$

Tetraethynylglycols are analogs of **1** which were of interest to us as possible precursors of tetraethynylethylene. The sensitivity of **10**, one of the two known glycols[12] in this class (eq 8), precluded certain conversions.

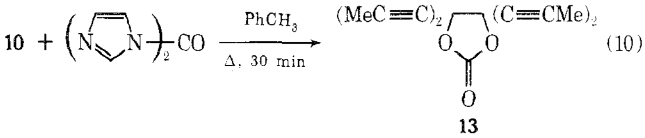
$$MeC\equiv CMgX + (COOEt)_2 \longrightarrow \underset{10}{[(MeC\equiv C)_2COH]_2} \quad (8)$$

In dilute aqueous acid the glycol was destroyed. Reaction of **10** with phosphorus tribromide gave only a complex mixture of vinyl allenes, glycols, etc. Attempted esterification with pyridine and benzyol chloride did not yield the expected diester but rather mixtures of the glycol and half-esters; alternatively, treatment of **10** with butyllithium at −40° followed by addition of acetyl chloride at 0° gave only small amounts of the desired diacetate along with large quantities of tarry materials. In an attempt to condense **10** with benzaldehyde, their solution in toluene was heated at 110° over molecular sieves for several hours. From this mixture only dipropynyl ketone was isolable. This product may have formed by an oxy-Cope rearrangement, for which there is precedent among the diacetylenic glycols.[13]



The presence of the second predicted product from this reaction, hept-2-en-5-yn-4-one (**12**), in the reaction mixture was inferred from the ir and nmr spectra of the product solution.

Even if diesters or dihalides are excluded, several attractive routes from a 1,2-glycol to an alkene are known. In one of these, our attempts to prepare the intermediate thionocarbonate from the glycol and 1,1′-thiocarbonyldiimidazole[14] did not succeed. On the other hand, the carbonate formed readily but could not be converted to the alkene by the usual techniques.[15]



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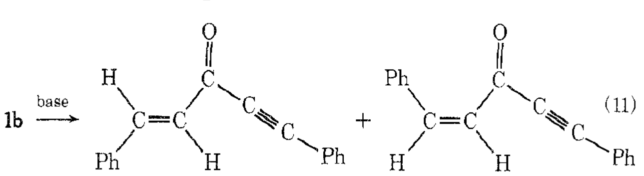
Base-Catalyzed Rearrangements. Although base-catalyzed rearrangements of propargylic compounds are familiar in acetylene chemistry,[2,10,16] we were rather surprised to find the following.



trans-14 (J_{HH} = 16.1 Hz) *cis*-14 (J_{HH} = 12.3 Hz)

One must credit Nineham and Raphael and Lappin with the discovery of this rearrangement (eq 12, 13), even though Lappin was unable to isolate the phenyl aroyl ketone (eq 13).[17] We have since located one other example (eq 14).[18]

$$PhCHOHC\equiv CCO_2CH_3 \xrightarrow{base} PhCOCH{=}CHCO_2CH_3 \quad (12)$$

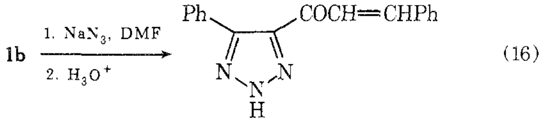
$$\underset{15,\ Ar = Ph}{PhC\equiv CCHOHAr} \xrightarrow{base} \underset{16,\ Ar = Ph}{(PhCH{=}CHCOAr)} \longrightarrow PhCHO + CH_3COAr \quad (13)$$

$$HC\equiv CC\equiv CCHOHCH_3 \xrightarrow{base} [HC\equiv CCH{=}CHCOCH_3] \quad (14)$$

Earlier, Liang had reported that, in the presence of alcoholic potassium hydroxide, **1b** is converted into bis(phenylacetyl)methanol, $(C_6H_5CH_2CO)_2CHOH$,[6] an altogether implausible transformation. Moreover, these reactions are clearly different from the known acid-catalyzed Meyer–Shuster rearrangement.[8b]

$$1b \xrightarrow{H_3O^+} \underset{17}{PhCOCH{=}CHC\equiv CPh} \quad (15)$$

The first indication that **1b** might undergo a base-catalyzed rearrangement arose during the triazole synthesis of eq 16.[19] It was established that phenylethynyl β-styryl ketone (**14**) yields the same triazole under similar conditions and that various bases, *e.g.*, hydroxide, acetate, azide, and triethylamine, catalyzed the isomerization of **1b** to **14**. In order to be sure that isomerization of **1b** actually preceded triazole formation, we monitored reactions 11 and 16 by ir or nmr. The $\nu_{C\equiv C}$ bands are diagnostic in that $\nu_{C\equiv C}$ (2205 cm^{-1}) of **1b** is lost early in the reaction while $\nu_{C\equiv C}$ (2255 cm^{-1}) of **14** appears, then disappears. Thus it is probable that isomerization of **1b** to **14** is faster



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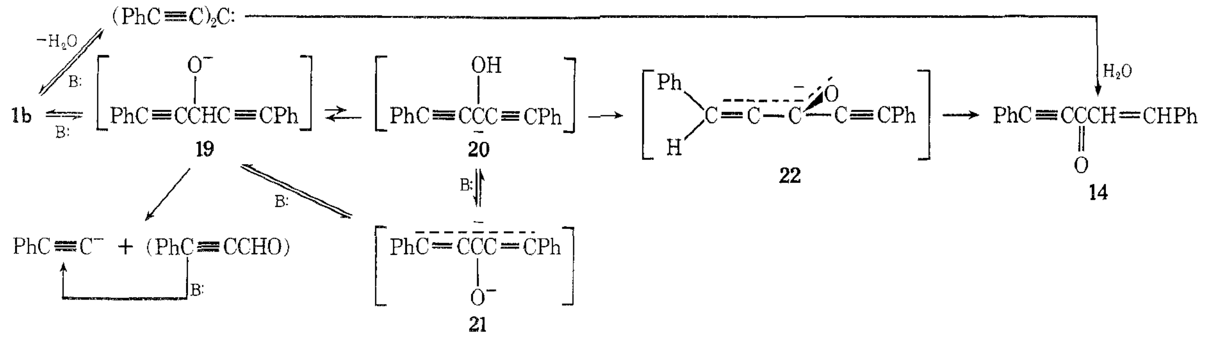
than triazole formation. Heated at reflux in triethylamine or in toluene in the presence of triethylamine for 24 hr, **1b** yields *trans*-**14** (>90%); heated at 50° in an aprotic solvent in the presence of base, **1b** yields *cis*- and *trans*-**14.** The cis and trans structural assignments of eq 11 are based on the observed nmr data.[20]

Finally, *cis*-**14** is formed under kinetic control and is gradually converted to *trans*-**14** (Table I). Moreover, the overall conversion of **1b** to **14** increases as the aprotic solvents become more polar, in the order benzene ~ dioxane < THF < DMF < DMSO. At this stage it becomes necessary to examine possible mechanisms in order to provide a rationale for our observations and the kinds of experiments to be described later.

Three possible pathways were considered, that is, *via* a carbene, a monocarbanion, and a dicarbanion (eq 17). A trapping experiment in which **1b** was treated with sodium hydride in the presence of an excess of olefin (cyclohexene, ethyl cinnamate, *trans*-stilbene) gave only starting material, **14,** phenylacetylene, and unreacted olefin. These results indicated that the carbene mechanism probably did not apply, although carbene mechanisms are known to operate under similar conditions in related propargylic systems.[21]



(17)

Incidentally, the phenylacetylene observed in eq 17 arises from the decomposition of **1b** under strongly basic conditions. This type of decomposition is simply the microscopic reverse of ethynylation, and hence the usual products are the parent alkynyl and carbonyl compounds.[22] In the case of **1b,** the related phenylpropiolaldehyde decomposes primarily to phenylacetylene under basic conditions.[23] Phenylacetylene did not interfere with the product analysis, since its concentration was usually less than 5% of the total residual product mixture.

Treatment of **1b** with sodium hydride in benzene followed by the addition of various substrates such as benzaldehyde, acetone, methyl iodide, benzyl chloride, tetramethylammonium iodide, ethyl cinnamate, ethyl bromoacetate, and acetyl chloride, gave, in every case except that of acetyl chloride, only **1b, 14,** and small amounts of phenylacetylene. The reaction with acetyl chloride, however, gave bis(phenylethynyl)methyl acetate (*ca.* 98%) along with small amounts of starting material, **14,** and phenylacetylene.

Reaction of **1b** with a threefold excess of sodium hydride liberated only 1 equiv of hydrogen gas. Quenching this reaction mixture with deuterium oxide led to *O*-deuterio-**1b,** which was identified by nmr. A quench with chlorotrimethylsilane gave **23** (97%) along with small amounts of phenylacetylene and another silylated product which was not identified.

$$(PhC{\equiv}C)_2CHOH \xrightarrow[\text{excess}]{NaH} \underset{\mathbf{19}}{(PhC{\equiv}C)_2CHO^-} \xrightarrow{Me_3SiCl} \underset{\mathbf{23}}{(PhC{\equiv}C)_2CHOSiMe_3} \quad (18)$$

Table I
Rearrangement of Diphenylethynylcarbinol (1b) in the Presence of Triethylamine at 60° to Give β-Styryl Phenylethynyl Ketone (14)

Solvent[a]	$[(C_2H_5)_3N]$, vol. %	Reaction time, hr	$PhCH{=}CHCOC{\equiv}CPh$ % trans[b]	% cis[b]
Benzene	4.8	10	*c*	2.5
Ethanol	4.8	10	1	3.5
Dioxane	4.8	10	~0	~0
THF	4.8	10	5	5
THF	8.5	10	29	19
DMF	4.8	5	21	54
DMF	4.8	10	34	57
DMSO	4.8	10	79	16
TEA	100	3.5	15	18
TEA	100	15	80	14
TEA	100	72	96	0

[a] THF, tetrahydrofuran; DMF, dimethylformamide; DMSO, dimethyl sulfoxide; TEA, triethylamine. [b] The values obtained by comparing the intensities of nmr for ethylenic hydrogens and the alcohol hydrogen. [c] The solvent peaks partially overlap the trans peak.

We also attempted to detect intermediates by nmr. Under typical rearrangement conditions, we added small amounts of sodium hydride to a solution of **1b** in benzene and recorded the chemical shift of the α proton ($R_2CHOH + R_2CHO^- + R_2COH^-$) after each portion reacted. The results were as follows (ν_{CH} in hertz, equivalents of NaH): 327.5, 0; 344, <0.5; 358, ~0.5; 368, >0.5; ν disappears, ~1.

Since the resonance of the α proton moves downfield as the alkoxide concentration increases, the resonance of the alkoxide proton (3) may simply be overlapped by the aromatic protons. When **1b** was treated with *n*-butyllithium in ether-hexane at −80°, the nmr spectrum of the reaction mixture showed a sharp resonance at 434 Hz superimposed on a broad, unresolved, presumably aromatic resonance. When **1b** was treated with dimsyl sodium in dimethyl sulfoxide at 25°, the resonance occurred at 424 Hz superimposed on a broad resonance. Thus, although we could not define the chemical shift of the α proton of **19** precisely, its direction was downfield relative to the α-proton resonance of the starting carbinol.

In passing, we note this relative downfield shift. The relative upfield shift of a proton at a carbanionic site ($>\bar{C}H$) is well known.[24a] The relative downfield shift of a proton β to the carbonionic center ($>CHC<^-$) is documented but less familiar.[24b] The analogy between the alkoxide series ($>CHO^-$) and this second carbanion is clear.

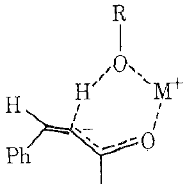
The preceding experiments indicated that the species which was present in highest concentration in the reaction mixture, or which was the most reactive, was **19.** Apparently no carbanionic or dianionic species **20–22** were detectable, although conditions appeared to be favorable for their formation and subsequent reaction.[25] Alternatively, one may speculate that, if **19–22** were intermediates, either

Table II
Reactions of 1,3-Diphenyl-2-propyn-1-ol (15) or Chalcone (16)

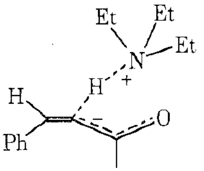
15 or 16 (g)	*p*-C_7H_7SH, (g)	Base (ml or g)	Solvent (ml)	Temp, °C	Time, hr	Product (yield, %)
15 (2.17)	1.29	$(C_2H_5)_3N$ (0.50)	DMF (20)	140	3	Oil[a]
15 (2.08)	1.24		DMSO (20)	140	20	**10** (3.5)
16 (3.01)	1.97		DMSO (20)	130	20	(*p*-$C_7H_7S)_2$ (16)[b]
15 (1.0)		$(C_2H_5)_3N$ (0.25)	DMSO (4)	140	10	**9**[c]
15 (3.0)		NaOH (0.50)	DMF (25)	25	3	Oligomer (17)[d]
15 (3.0)		NaN_3 (0.94)	DMF (30)	130	3	Oligomer (~10)[e]

[a] Mass spectrum shows a "parent" *m/e* 332 (no 330) consistent with **10**. [b] *p*-Tolyl disulfide, mp 46–48°. [c] Identified by mass spectral comparison. [d] Mp 254–255°. [e] Mp 188–189°.

the conversion rates exceeded the trapping rates by a factor of *ca.* 10^2 or proton transfers between them occurred within ionic aggregates. Certainly, there is evidence to support intramolecular proton transfer, at least in the product-forming step,[26] since the kinetically controlled product in DMF is *cis*-**14**. Secondly, 1,3-diphenylallyl anions possess significant rotational barriers.[27] Accordingly, species **24** depict proton transfers within bulky ionic clusters involving metallic alkoxide (RO^-M^+) and triethylamine. If in fact these selective proton transfers depict what happens, they are examples of Cram's conducted tour processes.[26] As for the slower cis to trans isomerization of **14**, this may or may not be base catalyzed; we did not investigate this point.



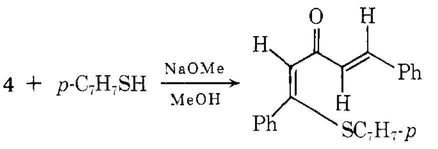
24a



24b

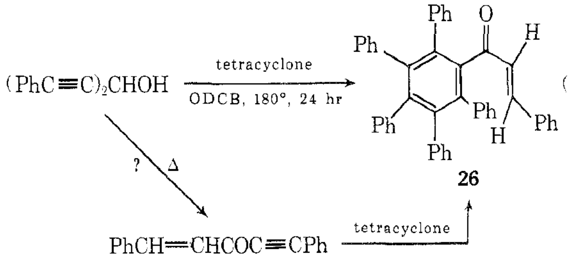
We did look into the scope of this rearrangement with other ethynyl alcohols. Although bis(*tert*-butylethynyl)methanol in triethylamine at 70° in 20 hr and **1a** in DMF at 135° in 18 hr do not isomerize, 1,3-diphenylpropynol (**15**) does isomerize in the presence of triethylamine at 140° in DMF (eq 13). *Strong bases such as azide and sodium hydroxide and possibly protic solvents*[17b] *convert* **15** *into different oligomers, according to the reaction conditions.* (As pointed out earlier, Lappin obtained cleavage products in eq 13 for several analogs of **15**.)[17b] Thus far, at least, the structural requirement for the ynol → enone rearrangement seems to be that the substituents on the ethynyl carbinol be electron-withdrawing groups, *e.g.*, Ph.

A number of other interesting conversions appear to depend on the rearrangement process. For example, **4** and *p*-toluenethiol in the presence of methanolic sodium methoxide at reflux yielded the single product, 1,5-diphenyl-2-(*p*-tolylthio)-1,4-pentadien-3-one (**25**). It was readily found that **4** was essentially saponified in 2–5 min in methanolic sodium methoxide. The nmr spectrum of the reaction mixture indicated the presence of **1b** and **14** but no ester. We were also able to make **25** from both **1b** and **14** under the same reaction conditions. Hence the sequence hydrolysis, isomerization, and addition is quite reasonable.



25 (19)

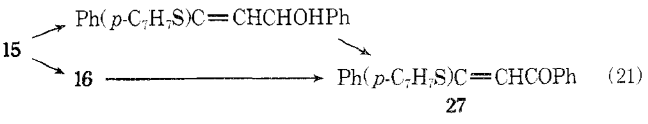
We have observed that at 180° in *o*-dichlorobenzene, both **1b** and **14** give the same Diels–Alder adduct with tetracyclone in the absence of added base.



26 (20).

Here we are inclined to believe that **1b** is first isomerized to **14**, presumably in a polar process, and **14** leads to the adduct.

In a reaction of p-toluenethiol with **15** *in a solution of* DMSO and triethylamine, we obtained 1,3-diphenyl-1-(*p*-tolythio)-prop-1-en-3-one (**27**) (eq 21). It appears that



$$\begin{tikzcd} & Ph(p\text{-}C_7H_7S)C{=}CHCHOHPh \arrow[dr] & \\ \mathbf{15} \arrow[ur] \arrow[r] & \mathbf{16} \arrow[r] & Ph(p\text{-}C_7H_7S)C{=}CHCOPh \ \mathbf{27} \end{tikzcd} \qquad (21)$$

amine is not essential in this curious synthesis but DMSO is. Replacement of DMSO by DMF as solvent in the reaction of **15** with *p*-toluenethiol in the presence of triethylamine does not give **27**. Clearly, overall rearrangement *and* oxidation–reduction has occurred; alternative routes to the product are given in eq 21. Now, DMSO can function as an oxidant, for we find that *p*-toluenethiol in an excess of DMSO yields di(*p*-tolyl) disulfide. It is thus possible that DMSO promotes oxidation on either or both branches of eq 21. Somewhat related examples in which thiyl radicals may be involved in oxidations have been reported, although redox processes involving interconversions of secondary alcohols and ketones seem most pertinent.[28] The results of several rearrangement conditions related to processes 13 and 21 are given in Table II.

To summarize this section, we note that the base-catalyzed *ynol → enone rearrangement* (eq 11–14) *does not* occur with alkyl ynols but appears to require at least a phenyl or extra ethynyl group to facilitate the formation of the anionic intermediates, *e.g.*, **19**. A number of strange-looking processes, eq 18–21, turn out to be straightforward once the basic rearrangement (eq 11, 13) is accepted.

Ultraviolet Spectra. The availability of a number of skipped diynes as well as adducts derived from **1** made a uv spectral study possible (Table III).[2-4] Here it was of special interest to see whether evidence for skipped conjugation could be found, that is, whether the central group was "chromolatory."[29]

Normally, λ_{max} for an alkyne is higher than λ_{max} for the corresponding alkene.[30] Thus, the data which are

Table III
Ultraviolet Spectra of Acetylenes and Their Polyarylated Derivatives, λ_{max} (Log ϵ_{max})[a]

R	$(RC{\equiv}C)_2CHOH$[c]	$(RC{\equiv}C)_3COH$[d]	$(RC{\equiv}C)_2C{=}O$[e]	$2\text{-}RPh_4C_6COC{\equiv}CR$[f]	$(2\text{-}RPh_4C_6)_2CO$[g]
CH_3	236 (1.95) 247 (1.95)	EA	236 (4.0) 247 (4.0)	233 sh (4.72) 280 sh (3.86)	
n-C_4H_9		EA	239 (4.08) 250 (4.08)	233 sh (4.66) 278 sh (3.94)	238 (4.84) 295 (4.08)
t-C_4H_9	239.5 (2.4) 251 (2.4)	EA	239 (4.15) 250 (4.15)	230 (4.63) 270 sh (3.87) 278 sh (3.77)	
C_6H_5	244 (4.53) 253 (4.56) 271 sh (3.33) 278 sh (3.03)	246 (4.73) 256 (4.73) 271 sh (3.79) 278 sh (3.48)	230 (4.3) 308 (4.36) 321 (4.36)	240 sh (4.72) 280 sh (4.32)	242 sh (4.85) 278 sh (4.32)

n-$BuC{\equiv}CCH_2C{\equiv}CCH_3$[b,h]	$(PhC{\equiv}C)_2CH_2$[b,i]	$PhCH{=}CHCOC{\equiv}CPh$[j]	$PhCH{=}CHCOC_6Ph_5$[k]
225 (2.71) 232.5 (2.66) 237 (2.68) 252 (2.48)	239 (4.95) 251 (5.05) 264 (3.23) 271.5 (3.12) 278.5 (2.96) 282 sh (2.55)	229.5 (4.22) 290 sh (4.24) 320 (4.40)	242 sh (4.51) 279 sh (4.17) 303 (4.21)

[a] EA = end absorption; sh = shoulder. The solvent was ethanol, unless otherwise noted. [b] Reference 2b. [c] Registry no.: R = t-C_4H_9, 50428-39-2. [d] Registry no.: R = C_6H_5, 50428-40-5. [e] Registry no.: R = n-C_4H_9, 18621-56-2; R = t-C_4H_9, 35845-67-1; R = C_6H_5, 15814-30-9. [f] Registry no.: R = CH_3, 50278-27-8; R = n-C_4H_9, 18627-92-4; R = t-C_4H_9, 50428-46-1; R = C_6H_5, 50278-28-9. [g] Registry no.: R = n-C_4H_9, 18627-95-7; R = C_6H_5, 18627-94-6. [h] Registry no., 50428-50-7. [i] Registry no., 6089-08-3. [j] Registry no., 16121-39-4. [k] Registry no., 50428-53-0.

given in Table III show that the 1,4-diynes are in our accessible range. On the other hand, 1,4-dienes, which include 1,3-dimethylenecyclobutane, two allene trimers,[31a] 1,4-cyclohexadiene [λ 270 nm (sh, log ϵ −0.5), 224 (sh, 1.5)],[31b] and 1,4-pentadiene [λ_{max} 181 nm (log ϵ 4.0)],[32] showed only end absorption, while the strained bicycloheptadiene showed several peaks of low intensity at λ_{max} 205 nm (log ϵ 3.32), 214 (3.17), 220 (2.94).[33] We shall return to this comparison shortly.

On the basis of negligible spectral changes between arylacetylenes and bis(arylethynyl)methanes and the large bathochromic shifts observed in the corresponding 1,3-diynes, we concluded previously that conjugation effects in the diethynylmethanes were small.[2b] Since 2,5-decadiyne[2b] (Table III) does indeed show a bathochromic shift relative to 1-butyne [λ_{max} 172 nm (log ϵ 3.65)] or 1-octyne [λ_{max} 1.85 nm (log ϵ 3.6), 225.5 (3.7)],[32,34] it appears that there is substantial conjugation in a 1,4-diyne, which is effectively overwhelmed in the aryl alkynes. The introduction of a hydroxyl group does not in general cause significant changes (Table III); the spectra of the bis(alkynyl)carbinols are much like those of the 1,4-alkadiynes, and the spectra of the bis- and tris(phenylethynyl)carbinols are still very similar to that of phenylacetylene.

By contrast, the trialkylethynylcarbinols appear to be anomalous in that their spectra show only the end absorption of simple alkynes (Table III).[30,32] This is all the more striking, since bicyclooctatriene has λ_{max} 208 nm (log ϵ 3.05) and 239 (2.48);[35] a bathochromic shift between divinyl- and diethynylmethane becomes hypsochromic between trivinyl- and triethynylmethane. It is the triethynylmethane, of course, which poses the problem in that the expected trend from mono- through diethynylmethane is broken.

Facile rationalizations may be hazardous here, since refined Pariser–Parr calculations have proved to be inadequate to reproduce observed spectral properties of bicycloheptadiene and bicyclooctatriene.[33]

The spectra of the diethynyl ketones have several interesting features (Table III). Despite the presence of cross-conjugation, λ_{max} of the triple bond chromophore is hardly affected relative to that in the bis(alkylethynyl)methanes or methanols, although the corresponding ϵ values are substantially increased. On the other hand, the low-intensity n → π* transition usually observed in the spectra of ketones, enones [$MeCH{=}CHCHO$, λ_{max} 321 nm (log ϵ 2.3)] and dienones [$(MeCH{=}CH)_2CO$, λ_{max} 336 nm (log ϵ 2.7)] was not in evidence.[30,36a] This may be rationalized as follows: the presence of a triple bond in a conjugated system does not appreciably alter λ_{max} but often decreases ϵ_{max} considerably;[30] the n → π* transition is symmetry forbidden and usually of low intensity (ϵ_{max} ~100); the cross-conjugation of the carbonyl chromophore between two double bonds can result in the total disappearance of the n → π* transition (possibly because the π system enforces planarity and inhibits the twisting needed to achieve a finite n → π* transition moment).[30,36a] The presence of an aryl group in **1b** restores normalcy in that more allowed transitions become available. Thus, the n → π* absorption, which is typical of aryl-substituted α,β-unsaturated carbonyl compounds, *e.g.*, *trans*-1,3-diphenyl-3-oxopentenyne (Table III) or bis(β-styryl) ketone [λ_{max} 330 nm (log ϵ 4.53)],[37] is now intense.

The absorption spectra of the Diels–Alder mono- and diadducts (Table III) may be regarded in part as those of polysubstituted benzenes and in part as ketones more or less related to acetophenone or benzophenone.[36b,38] Now, the single band (λ_{max} 251 nm) of biphenyl is comprised of the weak $^1B_{2u} \leftarrow {}^1A_{1g}$ (λ_{max} 262 nm) and the intense $^1B_{1u} \leftarrow {}^1A_{1g}$ (λ_{max} 208 nm) bands. The spectrum of hexaphenylbenzene, in which the outer phenyl groups are close (±10–25°) to perpendicular to the central ring, as in a paddlewheel,[39] clearly shows two intense peaks [λ_{max} 266 nm (log ϵ 4.54) and 247 (4.75)].[40] Evidently all of our adducts with the structural unit $2\text{-}RPh_4C_6\text{–}$ possess an analogous λ_{max} at *ca.* 278 and 235 nm. In somewhat simpler systems, *e.g.*, the triphenylbenzenes, spectral data indicate that steric interference may reduce conjugation and give rise to hypsochromic shifts: 1,3,5-, 1,2,4-, and 1,2,3-triphenylbenzenes have λ_{max} 252 nm (ϵ 58,000), 249 (33,000), and 239 (33,600), respectively.[41] However, the benzenoid bands of the series $2\text{-}RPh_4C_6COC{\equiv}CR$ appear to be relatively insensitive to changes in substituents (Table III); presumably the dominant effect is that of the four phenyl groups essentially locked almost perpendicular to the central ring.

Benzophenone has a weak n → π* band [λ_{max} 333 nm (log ϵ 2.2)], a strong π → π* band [λ_{max} 253 nm (log ϵ

Table IV
Infrared Carbonyl ν(CO) Bands of the Dialkynyl Ketones and Their Diels–Alder Adducts[a]

Ketone	ν, cm^{-1}	Ketone	ν, cm^{-1}
$(MeC{\equiv}C)_2CO$	1630[b]	$(t\text{-}BuC{\equiv}C)_2CO$	1605
$2\text{-}MePh_4C_6COC{\equiv}CMe$	1655	$2\text{-}t\text{-}BuPh_4C_6COC{\equiv}CBu\text{-}t$	1655
$(PhC{\equiv}C)_2CO$	1605	$(n\text{-}BuC{\equiv}C)_2CO$	1625[c]
$Ph_5C_6COC{\equiv}CPh$	1645	$2\text{-}n\text{-}BuPh_4C_6COC{\equiv}CBu\text{-}n$	1655
$(Ph_5C_6)_2CO$	1670	$(2\text{-}n\text{-}BuPh_4)_2CO$	1660

[a] In KBr pellets, unless otherwise noted. [b] In CCl_4. [c] Neat.

4.20)], and end absorption.[42] If anything, the n → π^* transition is slightly intensified with alkyl substitution in the benzophenones, as in 2,4,6,2′,4′,6′-hexakis(isopropyl)benzophenone [λ_{max} 336 nm (log ϵ 2.47)], although a minor reversal may be found in other series, *e.g.*, acetophenones or benzaldehydes.[36b] In general, however, strong deviation from coplanarity in the benzoyl moiety is reflected in a diminished intensity, *e.g.*, 2,2′-di-*tert*-butylbenzophenone [λ 330 nm (log ϵ 1.9)].[42] If, as we suppose, the carbonyl group is close to perpendicular to the ring in our adducts, the intensity should approach zero, which is observed (Table III). In these adducts, the phenylethynyl group does not elicit ("bring out") the n → π^* transition, although the β-styryl group in $Ph_5C_6COCH{=}CHPh$ does bring it in with high intensity (log ϵ 4.21), albeit at lower wavelength (λ 303 nm). This again indicates that the triple bond conjugates less efficiently than the double bond.[30]

There is independent evidence that supports our picture of a balance between steric hindrance and conjugation in the Diels–Alder adducts. Briefly, conjugation lowers the normal ir stretching frequency of a carbonyl band. Several series of molecules in Table IV illustrate the trend from "maximum" conjugation in the dialkynyl ketones through partial to "no" conjugation in the mono- and diadducts. For this group of compounds, the maximum $-\Delta\nu$ is 40 and 65 cm^{-1}, respectively, as one or both triple bonds flanking the carbonyl are converted to perphenylated rings (Table IV).

Experimental Section

Infrared spectra were recorded on a Beckman IR-8 spectrophotometer. Solution spectra were measured in a matched set of 0.1-mm sodium chloride or calcium fluoride cells. Ultraviolet and visible spectra were recorded on either a Beckman DK-2 or DBG spectrophotometer. Proton magnetic resonance spectra were obtained on a Varian A-60 spectrometer and are reported in δ units (parts per million) relative to internal tetramethylsilane. The reported line frequencies are estimated to be accurate within 0.5 Hz; s, d, t, q, and m are used to designate singlet, doublet, triplet, quartet, and multiplet, respectively. Mass spectra were obtained on a Varian MAT CH-7 instrument at approximately 50 eV. All reported compounds were purified by standard techniques before the spectra were taken. All melting points were taken in glass capillary tubes on a Mel-Temp heated block instrument and are uncorrected. Microanalyses were performed by M-H-W Laboratories, Garden City, Mich.

Materials. Bis(1-propynyl)methanol (**1a**) was prepared from 1-propynylmagnesium bromide and ethyl formate[5c] with the modification that the course of the exchange reaction between ethylmagnesium bromide and propyne was monitored by nmr. The reaction was assumed to be complete when the ethylmagnesium bromide resonance [$\delta(CH_2) = -0.60$] became negligible and the propynylmagnesium bromide resonance [$\delta(CH_3) = 1.86$] reached maximum amplitude. **1a** had mp 102–103° (lit.[5c] mp 107°); ir (KBr) 3270, 2290, 2260, 2230 cm^{-1}; nmr ($CDCl_3$) δ 1.86 (d, 6 H, J = 2.2 Hz), 2.66 (d, 1 H, J = 6.8 Hz), 5.1 (m, 1 H, J = 6.8 Hz).

Bis(phenylethynyl)methanol (**1b**) was prepared from phenylethynylmagnesium bromide and ethyl formate.[3a] It had mp 84–86° (lit.[3a] mp 84–86°); ir (CCl_4) 3585, 2250, 1040, 1020, 1005 cm^{-1}; nmr ($CDCl_3$) δ 3.0 (s, 1 H), 5.5 (s, 1 H), 7.3 (m, 10 H).

1,3-Diphenylpropynol (15) was obtained from phenylethynylmagnesium bromide and benzaldehyde as a yellow oil (51%):[17b] bp 165° (3.0 mm) [lit.[17b] bp 168° (5 mm)]; nmr (CCl_4) δ 3.99 (s, 1 H), 5.52 (s, 1 H), 7.7 (m, 10 H); ir (CCl_4) 3360, 2210, 2180, 1600, 1592 cm^{-1}.

Bis(phenylethynyl)methyl *N*-Phenylcarbamate (2b). Phenyl isocyanate (4 ml, 0.037 mol), **1b** (4 g, 0.017 mol), and pyridine (1 ml) were dissolved in dry benzene (60 ml) and stirred for 18 hr at ~25°. This solution was then poured into cold, dilute acetic acid and extracted twice with ether. The extracts were washed with saturated sodium bicarbonate solution and then dried over sodium sulfate. Work-up gave 3.4 g of a white solid, mp 125–127°, from carbon tetrachloride. The analytical sample had mp 129–130°, from carbon tetrachloride or ligroin: ir (KBr) 3410 (NH), 2235 ($C{\equiv}C$), 1705 cm^{-1} ($C{=}O$); nmr ($CDCl_3$) δ 6.6 (s, 1 H), 6.9 (broad, 1 H), 7.3 (m, 15 H).

Anal. Calcd for $C_{24}H_{17}NO_2$: C, 82.08; H, 4.87. Found: C, 82.34; H, 5.11.

4-Benzyl-3-phenyl-5-phenylethynyl-4-oxazolin-2-one (3). A mixture of **2a** (1.0 g, 2.9 mmol) and sodium methoxide (0.76 g, 15 mmol) in absolute methanol (50 ml) was refluxed for 3 hr and then poured into ice water. The solution was extracted with ether (30-ml portions), and the extract was washed with saturated salt solution and dried with sodium sulfate. Removal of the ether left a red oil which was chromatographed on alumina. With ether–hexane (4:1, v/v) as the eluting solvent, the first fractions yielded a yellow oil which was rechromatographed on alumina with the same solvent. From one of the fractions we obtained white needles: mp 134–136°; ir (KBr) 2260 ($C{\equiv}C$), 1775 ($C{=}O$), 1620 cm^{-1} ($C{=}C$); nmr ($CDCl_3$) δ 4.58 (s, 2H), 7.1–7.6 (m, 15 H); mass spectrum m/e (rel abundance) 351 (P^+, 100), 322 (10), 274 (20), 215 (40), 91 (10).

Anal. Calcd for $C_{24}H_{17}NO_2$: C, 82.08; H, 4.87. Found: C, 82.28; H, 4.91.

Bis(1-propynyl)methyl *N*-Phenylcarbamate (2a). Phenyl isocyanate (2.2 ml, 0.06 mol), **1a** (1 g, 0.01 mol), and pyridine (1 ml) were dissolved in dry benzene and refluxed for 20 hr. The resulting solution was poured into 3% acetic acid at 0°, stirred, and extracted with ether. Work-up yielded 1.9 g of solid, which on recrystallization (ligroin or carbon tetrachloride) or sublimation at 80° (2 mm) gave a white solid: mp 84–86°; ir (KBr) 3410 (NH), 2260, 2290, 2320 ($C{\equiv}C$), 1705 cm^{-1} ($C{=}O$); nmr ($CDCl_3$) δ 1.8 (d, 6 H), 6.1 (m, 1 H), 7.02 (broad, 1 H), 7.35 (m, 5 H); mass spectrum m/e (rel abundance) 227 (P^+, 85), 182 (10), 91 (100).

Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.76. Found: C, 74.54; H, 5.65.

Methoxybis(1-propynyl)methane (6). Dipropynylcarbinol (0.5 g) in dry benzene was refluxed over an excess of freshly cut sodium metal for 2 hr. The unreacted sodium was then removed and an excess of methyl iodide was added. After standing at 25° for 5 days, the reaction mixture was filtered and the solvent was evaporated. The resulting yellow oil was chromatographed on silica gel with benzene–chloroform (1:1, v/v) as eluent. Three distinct bands appeared, of which the first eluted contained the desired methoxy compound as a yellow oil: nmr ($CDCl_3$) δ 1.85 (d, 6 H), 3.35 (s, 3 H), 4.81 (m, 1 H); mass spectrum m/e (rel abundance) 122 (P^+, 5), 91 (100), 65 (60), 47 (30), 39 (20).

Bis(phenylethynyl)methyl Acetate (4). Acetyl chloride (2 ml, 2.2 g, 28 mmol) was added dropwise to a solution of **1b** (2 g, 8.16 mmol) in dry benzene (40 ml) and dry pyridine (1 ml). This solution was refluxed for 12 hr and then poured onto crushed ice. Work-up, identical with that of the bromo ester (see below), yielded 2.1 g of cream-colored solid: mp 65–66°; ir (thin film) 2901 (CH_3), 2230 ($C{\equiv}C$), 1750 ($C{=}O$), 1220 cm^{-1} (CO); nmr ($CDCl_3$) δ 2.15 (s, 3 H), 6.66 (s, 1 H), 7.5 (m, 10 H).

Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 83.10; H, 5.18.

When **4** (0.27 g) and 3,4-xylidine (0.24 g) were refluxed in methanol, removal of the methanol gave a red oil which consisted of unreacted **4**, **1b**, and **14**. Prolonged reflux in methanol eventually yielded a small amount (~15%) of an adduct of 3,4-xylidine and **14**. This appeared to be a typical amine–alkyne adduct,[3] namely, *trans,trans*-$3,4\text{-}(Me)_2C_6H_3NHC(Ph){=}CHCOCH{=}CHPh$: ir ($CHCl_3$) 3400 (NH), 1610 ($C{=}O$), 1590, 1550 cm^{-1} ($C{=}C$); nmr ($CDCl_3$) δ 2.2 (s, 3 H), 2.1 (s, 3 H), 5.5 (s, 1 H).

Bis(1-propynyl)methyl *m*-Bromobenzoate (5). To 0.3 g of sodium hydride dispersion (50% in oil, washed with pentane prior to use) under dry benzene (5 ml) in a nitrogen atmosphere was added **1a** (0.5 g, 5 mmol). After all the sodium hydride had reacted, the reaction mixture was cooled to 0° and a solution of *m*-bromobenzoyl chloride (1.1 g, 5 mmol) in dry benzene (2 ml) was added dropwise. The resulting suspension was stirred for 30 min at 25° and then poured into ice water. Work-up gave a yellow oil which was then chromatographed on silica gel with ligroin–benzene (2:1, v/v) as the eluent. This yielded white crystals: mp 88–90° from ligroin; ir (CCl_4) 2265 ($C\equiv C$), 1735 ($C{=}O$), 1250 cm^{-1} (CO); nmr ($CDCl_3$) δ 1.85 (d, 6 H), 6.25 (m, 1 H), 7.1–8.3 (m, 4 H).

Anal. Calcd for $C_{14}H_{11}BrO_2$: C, 57.91; H, 3.78. Found: C, 57.78; H, 3.43.

4-Bromo-2,5-heptadiyne (7a) and 2-Bromo-2,3-heptadien-5-yne (8a). A mixture of **1a** (2 g, 20 mmol) and phosphorus tribromide (2 g, 7.5 mmol) in absolute ether (20 ml) was stirred at 0° for 2 hr and then treated with saturated aqueous sodium bicarbonate (100 ml) at 0° for 15 min. The ether layer was separated and the bicarbonate solution was extracted with ether (2 × 20 ml). The combined extract was dried over magnesium sulfate and evaporated to yield a bright yellow semisolid which was unstable at 25° but stable at −78°. This material consisted of *ca.* 98% **7a** and *ca.* 2% **8a** based on ir and nmr analyses. In a second synthesis, a mixture of **1a**, phosphorus tribromide, and dry pyridine (1 equiv) in absolute ether was refluxed for 18 hr and then poured onto ice. Work-up yielded a yellow semisolid which was shown by combined ir and nmr analyses to contain a 1:1 ratio of **7a** and **8a**. **7a** had ir (CCl_4) 2320, 2270, 2255 ($C\equiv C$), 630 cm^{-1} (CBr) and no OH absorption; nmr ($CDCl_3$) δ 1.88 (d, 6 H, J = 2.0 Hz), 5.17 (m, 1 H, J = 2.0 Hz); mass spectrum *m/e* (rel abundance) 172 (P^+, 20), 170 (2), 92 (40), 91 (100), 90 (35), 89 (50), 65 (80), 39 (50). **8a** had ir (CCl_4) 2320, 2270, 2255 ($C\equiv C$), 1945 ($C{=}C{=}C$), 630 cm^{-1} (CBr); nmr ($CDCl_3$) δ 1.8, 5.5 (m).

2,5-Heptadiyne (9). To 1 equiv of aqueous chromium(II) sulfate[43] in a flask sealed under nitrogen with a serum stopper was injected 1 g of **7a** in 10 ml of peroxide-free tetrahydrofuran. The blue color of chromium(II) was immediately discharged and the reaction mixture warmed up. The reaction mixture was stirred for 5 min, saturated with ammonium chloride, and extracted with ether. This extract was washed with water, dried over sodium sulfate, and distilled under nitrogen. The residue (*ca.* 0.5 ml) was cooled to −78° and left at 0.6 mm for 15 min. The remaining oil, which appeared to be mainly the desired heptadiyne (*ca.* 95%), discolored on standing at 25°, although it appeared to be stable indefinitely at −78°. It had ir (CCl_4) 2240 ($C\equiv C$), 1318 cm^{-1} ($C\equiv CCH_2C\equiv C$); nmr ($CDCl_3$) δ 1.75 (t, 6 H, J = 2.6 Hz), 3.06 (m, 2 H, J = 2.6 Hz); mass spectrum *m/e* (rel abundance) 92 (P^+, 40), 91 (100), 65 (72), 47 (35), 39 (20).

The ethynyl-allenic (9:1) bromide mixture (**7a** + **8a**) was treated with an excess of magnesium metal in absolute ether. This reaction mixture was stirred at 25° for 24 hr and then poured into cold, saturated ammonium chloride solution. Standard work-up yielded an oil which consisted of unreacted bromides, **9**, and 2,3-heptadien-5-yne, as determined by ir and nmr.

3-Bromo-1,5-diphenyl-1,4-pentadiyne (7b). A solution of **1b** (6 g, 26 mmol) and phosphorus tribromide (3 g, 11 mmol) in absolute ether (100 ml) was stirred at 0° for 6 hr, and then treated with saturated aqueous sodium bicarbonate solution at 0° for 15 min. The ether layer was separated and the bicarbonate solution was extracted with ether (2 × 20 ml). The combined extract was dried over magnesium sulfate, evaporated under reduced pressure to *ca.* 30 ml, and treated with ligroin (100 ml), and the resulting solution was heated gently to drive off the remaining ether. When the resulting solution was cooled rapidly to −78° and the vessel was scratched vigorously, a solid precipitated. Two recrystallizations from hexane yielded a lemon-yellow solid, mp 48–49°, which could be stored for several weeks at −78°, but which was unstable at 25°, turning into a red tar in *ca.* 8–12 hr. The solid had ir (CCl_4) 2300, 2260, 2240 ($C\equiv C$), 630 cm^{-1} (CBr), and no OH bands; nmr ($CDCl_3$) δ 5.8 (s, 1 H), 7.3 (m, 10 H); mass spectrum *m/e* (rel abundance) 296 (10), 294 (P^+, 10), 216 (80), 215 (100), 213 (75), 189 (20).

When **7b** in THF was treated with an excess of chromium(II) sulfate in THF–water under nitrogen, the blue color of chromium(II) was immediately discharged. Extraction of the mixture with ether followed by removal of the ether gave a red oil which crystallized upon addition of methanol to give a yellow solid, mp 90–115°. Tlc on silica (chloroform) showed one major and two minor components. Column chromatography on silica gel or on a column of silver nitrate on silica gel also failed to separate the components. The ir spectrum of this solid showed only typical aromatic absorptions. The nmr spectrum showed an aromatic multiplet at δ 7.2 along with a doublet at δ 6.1 and a singlet at δ 4.3. Mass spectral data indicated a molecular weight of 430, with a base peak at *m/e* 215; 1,1,2,2-tetrakis(phenylethynyl)ethane would have P^+ 430.

When **7b** (1.5 g) was treated with magnesium metal (0.12 g) in absolute ether under nitrogen and stirred at 25° for 1 hr, a yellow precipitate appeared. Stirring was continued for 1 hr and the mixture was quenched with saturated ammonium chloride solution. Work-up yielded a yellow solid identical in all respects with that obtained from chromium(II) reduction.

Tetrakis(1-propynyl)ethylene Glycol (10). To a cooled solution of propynylmagnesium bromide in ether (1 *M*, prepared from ethylmagnesium bromide and propyne) was added an ethereal solution of freshly distilled diethyl oxalate (36.5 g, 0.25 mol). After the addition was completed, the reaction mixture was warmed to 25°, stirred overnight, refluxed for 2 hr, and finally poured into cold, saturated ammonium chloride solution. Extraction with ether followed by work-up gave a yellow-white solid (25 g, 50%), mp 153–154° dec (lit.[12a] mp 150–154° dec), from ligroin–benzene: ir ($CHCl_3$) 3540 (OH), 2240 ($C\equiv C$), 1135 cm^{-1} (CO); nmr ($CDCl_3$) δ 1.92 (s, 12 H), 3.07 (s, 2 H). A solution of this glycol in toluene was refluxed for 18 hr. Removal of the solvent left a red oil, whose ir spectrum had bands at 2240, 1650, 1640, 1605, and 970 cm^{-1}. This oil was worked up to yield dipropynyl ketone, mp 75–77° (lit.[5c] mp 78–80°), on sublimation. The ir bands at 1650, 1605, and 970 cm^{-1} indicate the presence of hept-2-en-5-yn-4-one (**12**) [lit.[44] ir (neat) 1650, 1600, and 960 cm^{-1}] in the crude product.

4,4,5,5-Tetrakis(1-propynyl)-1,3-dioxolan-2-one (13). A solution of **10** (1.06 g) and 1,1′-carbonyldiimidazole (0.66 g) in toluene (50 ml) was refluxed for 30 min. The reaction mixture was cooled to 25° and washed several times with water. After the toluene layer was dried with sodium sulfate, the solvent was removed to give a brown-tan solid. Two recrystallizations from benzene–ligroin (Norit) gave white crystals, mp 166–168°, in 80% yield: ir ($CHCl_3$) 2260 ($C\equiv C$), 1815 ($C{=}O$), 1160, 1000 cm^{-1} (CO); nmr ($CDCl_3$) δ 1.93 (s, 12 H).

Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 75.29; H, 4.94.

Isomerization of Bis(phenylethynyl)methanol (1b) to 1,5-Diphenylpent-1-en-4-yn-3-one (14). A solution of **1b** (1.92 g, 8.27 mmol) and sodium acetate (0.75 g) in DMF (20 ml) was warmed to 50° for 3.5 hr and then worked up to give *trans*-**14** (0.35 g, 18%) as a white solid, mp 69° (lit.[37] mp 69–70°), from petroleum ether: nmr ($CDCl_3$) δ 6.8 (d, 1 H, J = 16.1 Hz), 7.5 (m, 10 H) 7.9 (d, 1 H, J = 16.1 Hz); ir (CCl_4) 2225 ($C\equiv C$), 1660, 1650, ($C{=}O$), 1580 ($C{=}C$), 980 cm^{-1} (trans $C{=}C$). Alternatively, a solution of **1b** (1 g, 4.25 mmol) in anhydrous triethylamine (40 ml) was refluxed for 24 hr. The solvent was then removed (Rotovap) and the oil was taken up in hot ligroin. Upon cooling, this solution deposited a yellow solid (0.8 g, 85%) of *trans*-**14**, mp 67–68°.

The stereochemical preference of the rearrangement was checked as follows. A solution of **1b** (1.00 g, 4.31 mmol) and triethylamine (0.20 ml) in DMF (10 ml) was charged into an ampoule and sealed. The ampoule was heated at 50° for 5 hr, opened, and analyzed by nmr. The products, *ca.* 29% *cis*-**14**, *ca.* 12% *trans*-**14**, and unchanged **1b** could be estimated from the peak areas of ethylenic and tertiary carbon hydrogens. The accuracy of these and similar analyses (Table I) was reduced at lower concentrations of the solution when the solvent peak (DMF) interfered. The solution was evaporated under vacuum at 50° to leave a yellow oil, which was chromatographed on silica gel. Carbon tetrachloride, as the first developing solvent, gave *cis*-**14** (0.24 g, 24%); dichloromethane–carbon tetrachloride (3:7) as the next solvent gave *trans*-**14** (0.045 g, 4.5%); finally, dichloromethane as the solvent gave the unchanged reactant (0.36 g, 36%). *cis*-**14** had nmr (acetone) δ 6.40 (d, J = 12.3 Hz, 1 H), 6.28 (d, J = 12.3 Hz, 1 H), 7.80–7.35 (m, 10 H); ir (neat) 2220 ($C\equiv C$), 1650, 1630 ($C{=}O$), 1570 ($C{=}C$), 693 cm^{-1} (cis $C{=}C$); mass spectrum *m/e* 232 (P^+), 231, 203,202, 169, 168, 104, 76.

1-(2,4-Dinitrophenyl)-3-(β-styryl)-5-phenylpyrazole. To a boiling solution of 2,4-dinitrophenylhydrazine (0.25 g) in acidified ethanol (20 ml) was added a solution of **14** (0.3 g) in ethanol (10 ml). The solid (0.89 g), which formed immediately, was recrystallized from acetic acid to yield orange-red needles: mp 232–234°; ir ($CHCl_3$) 1620 ($C{=}C$, $C{=}N$), 980 cm^{-1} (trans $C{=}C$).

Anal. Calcd for $C_{23}H_{16}N_4O_4$: C, 66.98; H, 3.91. Found: C, 67.32; H, 3.88.

Trapping Experiments during the Conversion 1b → 14. Compound **1b** (0.5 g, 2 equiv) in dry benzene was added to sodium hydride (0.3 g, 50% dispersion in oil, prewashed with pentane) under benzene in a nitrogen atmosphere. After being stirred at 25° for 10 min or until gas evolution ceased, the reaction mixture was treated in different ways.

1. When excess absolute ethanol was added and the mixture was worked up, the resulting oil consisted of **1b** and **14** (2:1) plus a trace of phenylacetylene, according to an nmr analysis.

2. When the reaction mixture was quenched with D_2O and filtered through sodium sulfate, evaporation of the solvent gave an oily solid consisting of **1b** (90%) and **14** (10%). Subsequent experiments showed that deuterated **1b** exchanges upon contact with the sodium sulfate used here.

3. When the reaction mixture was quenched with excess chlorotrimethylsilane at 0° and the reaction mixture was stirred for 30 min at 25°, evaporation of the solvent gave an oil consisting of 95% **23**, 1% unreacted **1b**, and 4% **14** by ir and nmr analysis. Attempts to purify **23** were unsuccessful; $(PhC{\equiv}C)_2CHOSi(CH_3)_3$ had nmr ($CDCl_3$) δ 7.3 (m, 10 H), 5.72 (s, 1 H), 0.3 (s, 9 H); ir (CCl_4) 2230 ($C{\equiv}C$), 1250, 950 ($SiCH_3$), 1085 cm^{-1} ($OSiCH_3$).

4. When the reaction mixture was quenched with acetyl chloride, a red solution and a white precipitate formed. The solid was filtered off and the solvent was removed to give a red oil, which consisted of bis(phenylethynyl)methyl acetate (98%), **14** (1%), and a trace of phenylacetylene.

5. When the reaction mixture was quenched with other substrates such as benzaldehyde, acetone, iodomethane, benzyl chloride, tetramethylammonium iodide, ethyl cinnamate, and ethyl bromoacetate and stirred for 30 min at 25°, work-up generally yielded unreacted **1b** and **14** in varying proportions as well as 1–5% phenylacetylene.

In experiments in which possible carbene intermediates were sought, we modified the standard procedure slightly: sodium hydride (1 equiv) was suspended either in dry cyclohexene (10 ml) or in a solution of *trans*-stilbene in ether or in ethyl cinnamate in benzene, and **1b** (0.5 g) was added at 0°. After work-up, only **1b**, **14** and unreacted alkene could be detected and isolated.

Other Observations Relevant to 1b → 14. When **1b** was treated with 1 equiv of *n*-butyllithium in ether–hexane at −78°, the nmr spectrum of this solution showed that the α-CH resonance of **1a** (δ 5.5) had disappeared. Here OH resonance (δ 3.0) was obscured by the solvent and could not be traced. When **1b** was treated with sodium hydride (1 or 2 equiv) in dry benzene, only 1 equiv of hydrogen gas was evolved, within experimental error. The nmr spectrum of the resulting deep-red solution showed that both the α-CH (328 Hz, δ 5.5) and the OH resonances (129 Hz, δ 2.19) of **1b** had disappeared and a new resonance at 416 Hz (δ 6.93) had appeared. This resonance is attributed to the α-CH of $(PhC{\equiv}C)_2CHO^-$ (**19**).

1-(Pentaphenylphenyl)-3-phenylprop-2-en-1-one (26). Tetracyclone (11 g, 0.03 mol) and **1b** (7 g, 0.03 mol) were refluxed in *o*-dichlorobenzene under nitrogen for 24 hr. The resulting solution was cooled at −78° for 1 hr and filtered. The retained brown solid was washed with acetone until the washings became colorless. Recrystallization from methylene chloride–acetone gave 4 g of cream-colored solid, mp 335–336°. Alternatively, **14** and tetracyclone (1:1) were refluxed in xylene for 3 days. At 25°, a white solid crystallized out. One recrystallization from methylene chloride–acetone gave a white solid: mp 335–336° (sealed tube); ir (KBr) 1640 (C=O), 1620 cm^{-1} (C=C); nmr ($CDCl_3$) δ 6.33 (d, 1 H, J = 16 Hz), 6.8–7.25 (m, 31 H); mass spectrum m/e (rel abundance) 588 (P^+, 100), 487 (20).

Anal. Calcd for $C_{45}H_{32}O$: C, 91.8; H, 5.48. Found: C, 92.08; H, 5.67.

1,5-Diphenyl-2-(*p*-tolylthio)-1,4-pentadien-3-one (25). To a solution of bis(phenylethynyl)methyl acetate (02.7 g, 1 mmol) and *p*-toluenethiol (0.12 g, 1 mmol) in absolute methanol (20 ml) was added a saturated solution of sodium methoxide in methanol (5 ml). After 10 min at *ca.* 65° and cooling to 25°, the reaction mixture deposited a yellow precipitate. In a second approach, a solution of **1b** (0.23 g, 1 mmol) and *p*-toluenethiol (0.12 g, 1 mmol) in absolute methanol was treated and worked up essentially as above to give the same solid. In a third approach, the same solid dropped out on mixing a saturated solution of methanolic sodium methoxide, a solution of **14** (0.23 g, 1 mmol), and *p*-toluenethiol (0.12 g, 1 mmol) in methanol. All of the solid products were recrystallized from methanol to give yellow needles: mp 169–171°; ir ($CHCl_3$) 1665, 1650 (C=O, cis and trans), 1590 cm^{-1} (C=C); nmr ($CDCl_3$) δ 2.17 (s, 3 H), 6.9 (d, 1 H, J = 16 Hz), 6.92 (s, 1 H), 7.75 (d, 1 H, J = 16 Hz), 7.0–7.6 (m, 14 H); mass spectrum m/e (rel abundance) 356 (P^+, 30), 279 (20), 249 (30), 225 (35), 181 (100), 131 (50), 103 (10), 91 (5).

Anal. Calcd for $C_{24}H_{20}OS$: C, 80.86; H, 5.65. Found: C, 81.13; H, 5.32.

Isomerization of 1,3-Diphenyl-2-propyn-1-ol (15) to Phenyl β-Styryl Ketone (16). An ampoule (25 ml) containing **15** (2 g, 9.18 mmol), triethylamine (0.4 ml), and DMSO (10 ml) was flushed with nitrogen, sealed, and heated at 140° for 10 hr. Work-up gave a brown oil which contained essentially **15** and **16** (*ca.* 10%), according to mass spectral analysis. To separate **16** the oil was dissolved in DMF (10 ml) and treated with phenyl isocyanate (1.19 g, 10 mmol) and stannous chloride (0.050 g). This mixture was heated at 100° for 2 hr, treated with methanol (2 ml), heated at 100° for another 1 hr, cooled, and poured into water (10 ml). Work-up afforded **16** (0.044 g, 2.2%): mp 54–56° (lit.[45] mp 57–58°); nmr ($CDCl_3$) δ 8.10–7.75 (m); ir (CCl_4) 1668, 1647, 1450 cm^{-1}.

The results of a number of other similar experiments are given in Table II. We describe the last two entries in some detail. The product solution from the sodium hydroxide reaction was poured into cold water (40 ml) and extracted three times with ether (*ca.* 100 ml). The ether extract was washed with water. Removal of half the ether (50 ml) gave a white solid, which was filtered off. The solid was reprecipitated from ether (yield 0.51 g, 17%). The structure of this material is unknown: mp 254–255°; nmr ($CDCl_3$) δ 6.7–7.7 (m, *ca.* 35 H), 5.44 (d, J = 2.4 Hz, 1 H, -OH), 4.0–4.74 (m, 4 H), 2.25–2.6 (m, 2 H); ir (Nujol) 3480 (OH), 1670 (C=O), 1640 (C=O or C=C), 1259, 1222, 1070, 1005, 977, 702 cm^{-1}; mass spectrum P^+ *ca.* 670.

The product solution from the azide reaction was extracted with ether and dried to yield a white solid. This was purified by several reprecipitations with cyclohexane or ether (0.3 g, 10%). The molecular weight of the product corresponds to that of a dimer but the structure is unknown: mp 188–191°; nmr ($CDCl_3$) δ 7.90–7.25 (m, 22 H), 5.32 (d, J = 2.6 Hz, 1 H), 4.83 (d, J = 2.6 Hz, 1 H); ir ($CHCl_3$) 3030, 1680, 1658, 1597, 1495, 1450 cm^{-1}.

1,3-Diphenyl-1-(*p*-tolylthio)-prop-1-en-3-one (27). A solution of *p*-toluenethiol (1.24 g, 10 mmol), **15** (2.07 g, 10 mmol), and triethylamine (0.5 ml) in DMSO (20 ml) was heated at 140° for 20 hr, cooled, poured into cold water (20 ml), and extracted three times with ether. The ether extract was then washed with water to remove DMSO and triethylamine. Removal of ether left **27**, a yellow solid from CCl_4–$CHCl_3$ (1:1) (0.680 g, 21%): mp 179–181°; nmr ($CDCl_3$) δ 8.25–7.95 (m, 2 H), 7.60–6.75 (m, 13 H), 2.18 (s, 3 H); ir ($CHCl_3$) 1635, 1600, 1580, 1530 cm^{-1}.

Anal. Calcd for $C_{22}H_{18}OS$: C, 79.97; H, 5.49; S, 9.70. Found: C, 80.06; H, 5.36; S, 9.60.

Registry No.—**1a**, 50428-54-1; **1b**, 15814-32-1; **2a**, 50428-56-3; **2b**, 50428-88-1; **3**, 50428-89-2; **4**, 50428-57-4; **5**, 50428-58-5; **6**, 50428-59-6; **7a**, 50428-60-9; **7b**, 27871-98-3; **8a**, 50428-62-1; **9**, 50428-63-2; **10**, 50428-64-3; **13**, 50428-65-4; *trans*-**14**, 37845-36-6; *cis*-**14**, 50428-67-6; **14** adduct, 50428-68-7; **15**, 1817-49-8; **16**, 94-41-7; **25**, 50428-71-2; **26**, 50428-53-0; **27**, 50428-73-4; 1-(2,4-dinitrophenyl)-3-(β-styryl)-5-phenylpyrazole, 50428-74-5.

References and Notes

(1) Abstracted from the Ph.D. Theses of K. G. M., May 1973, and Y. T., May 1972, Illinois Institute of Technology.

(2) I. M. Mathai, H. Taniguchi, and S. I. Miller, *J. Amer. Chem. Soc.*, **89**, 115 (1967); H. Taniguchi, I. M. Mathai, and S. I. Miller, *Tetrahedron*, **22**, 867 (1966).

(3) (a) T. Metler, A. Uchida, and S. I. Miller, *Tetrahedron*, **24**, 4285 (1968); (b) K. G. Migliorese and S. I. Miller, *J. Org. Chem.*, **39**, 843 (1974).

(4) C. K. Tseng, K. G. Migliorese, and S. I. Miller, *Tetrahedron*, in press.

(5) (a) A. W. Johnson, "The Chemistry of Acetylenic Compounds," Vol. I, Edward Arnold Co., London, 1946, p 135 ff; (b) E. R. H. Jones, L. Skattebøl, and M. C. Whiting, *J. Chem. Soc.*, 4795 (1956); (c) J. Chauvelier, *Ann. Chim. (Paris)*, **3** (12), 393 (1948).

(6) C. K. Liang, *Bull. Soc. Chim. Fr.*, 33 (1933); (b) *ibid.*, 41 (1933).

(7) (a) R. D. Dillard, D. R. Cassady, and N. R. Easton, *J. Med. Chem.*, **10**, 1180 (1967); (b) R. D. Dillard, G. Poore, D. R. Cassady, and N. R. Easton, *ibid.*, **10**, 40 (1967); (c) N. R. Easton, D. R. Cassady, and R. D. Dillard, *J. Org. Chem.*, **27**, 2927 (1962); (d) K. Sisido, K. Hukuoka, M. Tuda, and H. Nozaki, *ibid.*, **27**, 2663 (1962); (e) S. L. Shapiro, V. Bandurco, and L. Freedman, *ibid.*, **26**, 3710 (1961).

(8) (a) S. Swaminathan and K. V. Narayanan, *Chem. Rev.*, **71**, 429 (1971). (b) I. Iwai and Y. Okajima, *Yakugaku Zasshi*, **79**, 1284 (1959); *Chem. Abstr.*, **54**, 4474 (1960).

(9) Y. Hori, K. Noda, S. Kobayashi, and H. Taniguichi, *Tetrahedron Lett.*, 3563 (1969).

(10) J. H. Wotiz in, "Chemistry of Acetylenes," H. G. Viehe. Ed., Marcel Dekker, New York, N. Y., 1969, pp 365–424.

(11) J. R. Hanson and E. Premuzic, *Angew. Chem., Int. Ed. Engl.*, **7**, 247 (1968).

(12) (a) G. I. Iotsitch, G. N. Tokarski, and A. I. Chibaef, *Bull. Soc. Chim. Fr.*, 1324 (1911); *J. Russ. Phys. Chem. Soc.*, **42**, 1493

(1910); (b) F. J. Wilson and W. M. Hyslop, *J. Chem. Soc.*, 1556 (1924).

(13) A. Viola, J. H. MacMillan, R. J. Proverb, and B. L. Yates, *J. Amer. Chem. Soc.*, **93**, 6967 (1971); J. Chuche and N. Manisse, *C. R. Acad. Sci., Ser. C*, **267**, 78 (1968).

(14) E. J. Corey and R. A. E. Winter, *J. Amer. Chem. Soc.*, **85**, 2677 (1963).

(15) P. S. Wharton, G. A. Hiegel, and S. Ramaswami, *J. Org. Chem.*, **29**, 2441 (1964).

(16) R. J. Bushby, *Quart. Rev., Chem. Soc.*, **24**, 585 (1970).

(17) (a) R. Raphael and A. Nineham, *J. Chem. Soc.*, 119 (1949); (b) G. L. Lappin, *J. Org. Chem.*, **16**, 419 (1951).

(18) E. A. El'perina, B. P. Gusev, and V. F. Kucherov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2215, (1965); *Chem. Abstr.*, **64**, 11077 (1965).

(19) Y. Tanaka, S. Velen, and S. I. Miller, *Tetrahedron*, **29**, 3271 (1973).

(20) P. Laszlo and P. R. Schleyer, *Bull. Soc. Chim. Fr.*, **87** (1964); S. Castellano and J. S. Waugh, *J. Chem. Phys.*, **34**, 295 (1962).

(21) W. J. le Noble, Y. Tatsukami, and H. F. Morris, *J. Amer. Chem. Soc.*, **92**, 5681 (1970).

(22) H. Meister, *Chem. Ber.*, **98**, 2862 (1965).

(23) J. Hine and G. Koser, *J. Org. Chem.*, **36**, 1348 (1971).

(24) (a) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, p 262 ff; (b) K. Takahashi, M. Takaki, and R. Asami, *J. Phys. Chem.*, **75**, 1062 (1971).

(25) Y. Leroux and R. Mantione, *Tetrahedron Lett.*, 592 (1971).

(26) J. M. Figuera, J. M. Gamboa, and J. Santos, *J. Chem. Soc., Perkin Trans. 2*, 1435 (1972); D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, pp 175–191; D. H. Hunter and D. J. Cram, *J. Amer. Chem. Soc.*, **86**, 5478 (1964).

(27) J. W. Burley and R. N. Young, *J. Chem. Soc., Perkin Trans. 2*, 1843 (1972); K. Bowden and R. S. Cook, *ibid.*, 1407 (1972).

(28) (a) T. J. Wallace, H. Pobiner, J. E. Hofmann, and A. Schriesheim, *J. Chem. Soc.*, 1271 (1965); (b) R. M. Kellog, *Methods Free Radical Chem.*, **2**, 1 (1969); (c) S. G. Cohen, S. Orman, and D. A. Laufer, *J. Amer. Chem. Soc.*, **84**, 3905 (1962).

(29) E. A. Braude, *J. Chem. Soc.*, 1902 (1949).

(30) E. S. Stern and C. J. Timmons, "Electronic Absorption Spectroscopy in Organic Chemistry," 3rd ed, Edward Arnold, London, 1970, Chapters 4 and 5.

(31) (a) B. Weinstein and A. H. Fenseleau, *J. Chem. Soc. C*, 368 (1967); (b) L. W. Pickett and E. Sheffield, *J. Amer. Chem. Soc.*, **68**, 216 (1946).

(32) L. C. Jones, Jr., and L. W. Taylor, *Anal. Chem.*, **27**, 228 (1955).

(33) C. F. Wilcox, Jr., S. Winstein, and W. G. McMillan, *J. Amer. Chem. Soc.*, **82**, 5450 (1960).

(34) J. R. Platt, H. B. Klevens, and W. C. Price, *J. Chem. Phys.*, **17**, 466 (1949).

(35) H. E. Zimmerman and R. M. Paufler, *J. Amer. Chem. Soc.*, **82**, 1514 (1960).

(36) (a) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, Chapters 5 and 10; (b) Chapter 15.

(37) J. G. Dinwoodie, H. M. White, and W. J. Day, *J. Org. Chem.*, **27**, 327 (1962).

(38) H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press, New York, N. Y., 1967, Chapters 12 and 21.

(39) J. C. J. Bart, *Acta Crystallogr., Sect. B*, **24**, 1277 (1968).

(40) M. A. Ogliaruso and E. I. Becker, *J. Org. Chem.*, **30**, 3354 (1965).

(41) D. Buza and W. Polaczkowa, *Tetrahedron*, **21**, 3409 (1965).

(42) R. F. Rekker and W. T. Nauta, *Recl. Trav. Chim. Pays-Bas*, **80**, 765, 747 (1961).

(43) J. Lingane and R. Pecsok, *Anal. Chem.*, **20**, 425 (1948).

(44) G. N. Bondarev and A. A. Petrov., *Zh. Org. Khim.*, **2**, 782 (1966).

(45) E. P. Kohler, H. M. Chadwell, H. T. Clarke, and R. P. Leavitt, *Org. Syn.*, **2**, 1 (1922).

Reactions Involving Electron Transfer. V. Reduction of Nonconjugated Acetylenes[1a]

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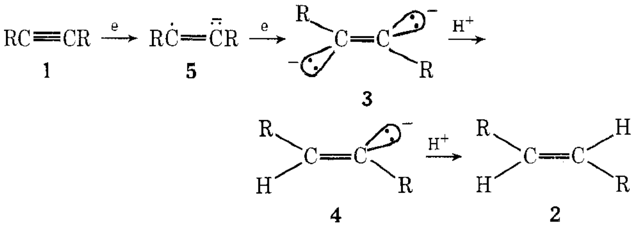
The reduction of 3-hexyne (**9**) and of 1-hexyne (**7**) with solutions of sodium in hexamethylphosphoramide (HMP)–tetrahydrofuran (THF) mixtures has been studied. In the absence of an added proton donor, the internal acetylene was reduced to mixtures of the 2-hexenes **28** and **29** and the 3-hexenes **24** and **25**. However, in the presence of a proton donor, *t*-BuOH, only the 3-hexenes were produced. At low temperature (−33°) in the presence of excess Na and *t*-BuOH, >95% of the olefin product was the trans isomer **24**. At higher temperatures (0 or 25°) or employing an inverse addition procedure to limit the Na concentration, mixtures containing 80–90% trans olefin **24** and 10–20% cis olefin **25** were obtained. Comparable mixtures (77–82% **24** and 18–23% **25**) were formed when 3-chloro-*cis*-3-hexene was reduced under various conditions with solutions of Na and *t*-BuOH in HMP–THF. These results are compared with reductions effected by solutions of Na in liquid NH_3 and the reaction pathways operative in these reductions are discussed.

A well-established synthetic route to trans symmetrically disubstituted olefins **2** involves the reduction of disubstituted acetylenes **1** with solutions of alkali metals (particularly sodium) in liquid ammonia[2,3] or with solutions of lithium in low molecular weight amines.[3a,b] It has been suggested[2c,d] that the stereochemistry of this reduction process is attributable to the addition of two electrons to the linear acetylene **1** to form a nonlinear dianion that adopts the trans geometry indicated in structure **3** to minimize electrostatic repulsion between the two unshared electron pairs. The successive addition of two protons at rates more rapid than the relatively slow rate of inversion of the vinyl anion **4**[4] would then account for the formation of the trans olefin **2** containing much less cis isomer than would be expected in an equilibrium mixture.

Scheme I



However, this process (Scheme I), involving two successive electron transfers to the acetylene **1** to form the intermediate radical anion **5** and the dianion **3**, is difficult to reconcile with polarographic studies of the electrochemical reduction of acetylenes. Although acetylenes conjugated with a carbonyl group[5] or with one or two aryl groups[6] can be reduced electrochemically to the radical anion **5** in aprotic media (typically DMF or DME with n-$Bu_4N^+X^-$ as a supporting electrolyte) at relatively negative potentials (−2.0 to −2.9 V *vs.* sce), the formation of a free dianion **3** is uncertain[6a,b] even in these cases where delocalization of negative change is possible. This uncertainty arises both because at the very negative potentials required to reduce the anion radical **5** to the dianion **3**, competing reduction of the supporting electrolyte (n-$Bu_4N^+X^-$) becomes substantial (at −2.9 to −3.0 V *vs.* sce) and because the possible abstraction of either a hy-