SYNTHESIS AND SPECTRAL PROPERTIES OF 1,4-AND 1,3-PENTADIYNES¹

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Abstract—"Skipped" (1,4-) diynes have been prepared by coupling alkynyl Grignard reagents with propargyl bromides. Treatment with base isomerizes the 1,4- to conjugated 1,3-diynes. Two alleged routes to 1,5-diphenyl-1,4-pentadiyne have now been shown to give 1,4-diphenylbutadiyne. Spectral properties, NMR, IR, UV, are given for both series. Shoolery's rule is found useful in predicting the chemical shift, τ (CH₂), for these and other kinds of acetylenic compounds. On the basis of their UV spectra, one can say that in the 1,4-diynes there is little, if any, conjugation "through" the internal methylene group, and what conjugation there is, is less than that in 1,3-diynes.

CONJUGATED polyacetylenes and related allenes are often found in nature; by contrast, drosiphila C, a polyacetylenic metabolite, is the only naturally occurring 1,4-diyne reported to date.² In view of the direction taken by interconversion 1,

 $RC = CCH_{1}C = CR' \rightarrow RC = CCH = C = CHR' \rightarrow RC = C - C = CCH_{1}R'$ (1)

which is accelerated by base, it is not surprising that the 1,4- or "skipped" diynes are uncommon. In this paper, we report on the synthesis and some properties of 1,4- and related 1,3-diynes (Tables 1-4).

Synthesis and chemical properties. Although the simplest member, 1,4-pentadiyne, seems to be unknown, the syntheses of a fair number of 1,4-diynes have been described.³⁻¹⁴ However, it is now apparent that in some of the older work, mixtures of isomers or impure materials were obtained.^{13.14} For apart from the problem of their

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L	TABLE 1. F	ROPERT	LES OF THE	DIYNES, RC	CCH, C CR'	AND R(C	Ц С Д	I,R'
		Time,		b.p.,	n _D (°C)	Analyses	, %C,H,	
1,4- and 1,3-Diynes	Method•	Ηr	Yield, %	(mm. Hg)	m.p.,	Calc.	Found	IR, $\nu \text{ cm}^{-1}$
				59-5°	1-4501	89-94	90-04	v(=CH) 3295(s), 642(s); v(C=C) 2120,
n-C,H,C=CCH,C=CH (I)°	<	-	50.5	(8)	(20·8°)	10-06	10-21	2230, 2290; v(CH) 2870(s), 2810,
				<i>1</i> 7°	1-4917	89-94	26-68	MC=C) 2260. 2175. 2140
n-C,H,(C=C),CH, (II) ⁶	B	ę	82	(5·3)	(21°)	10-06	10-05	»(C=CCH_) 2725, 2037
				66°	1-5713	94-25	94-55	•
C ₆ H ₆ C=CCH ₁ C=CH (III) ^c	۷	0.66	52	(0·25)	(20·7°)	5.75	5-67	w(≡CH) 3295(s), 649(s); w(C≡C) 2120,
				76°	1.6335 (22.7°)	94.25	94.47	2280; v(CH) 2890, 2800, 1316(s), 1253 v(C=C) 7747 7705 7164: v(C=CH)
C ₆ H ₆ (C≡C) ₅ CH ₄ (IV) ⁴	B	e	54	(0-2)	17.5-17.8°	5.75	5.81	2725, 2032; v(C,H,CH,) 1456(s), 729(s)
				120°	1-5464	61·16	91-44	v(C=C) 2280, 2240, 2220;
n-C,H,C=CCH,C=CC,H, (V)	4	0.66	52	(0-25)	(21-1°)	8·21	8.48	v(CH) 2870, 2807, 1315, 1253
				121–122°	1-5558	61·16	91-78	v(C==C) 2250, 2170, 2145
n-C _i H ₁ (C=C) ₁ CH ₁ C _i H ₅ (VI)	æ	72	2	(0-15)	(21°)	8·21	8.17	
-				168-170°		94:41	94-51	»(C=C) 2240, 2230; »(CH) 2880(s),
C,H,C=CCH,C=CC,H, (VII)	4	1	56	(0·2)	45-45-5°	5-59	5.73	2795, 1318(s), 1253
				151–153°		94:41	94·34	»(C=C) 2247, 2172
C ₆ H ₆ (C=C) ₁ CH ₁ C ₆ H ₆ (VIII)	C,D	7	57	(0-005)	3031°	(5.29)	5.88	v(C ₆ H ₆ CH ₄) 1453(s), 731(s)
				75°		93-46	93-30	v(=CH) 3294(s), 645(s); v(C=C) 2240,
4-CH,C,H,C=CCH,C=CH (IX)	×	-	42	(0.15)	22·5-22·8°	6-54	6-53	2124; v(CH) 2890(s), 2804, 1314(s),
								1253
						93-46	93-17	v(C==C) 2247, 2165, 2115;
4-CH ₃ C ₆ H ₄ (C=C) ₃ CH ₃ (X)	æ	24	8		68-8-69°	6-54	6.67	»(C=CCH_) 2727, 2037
			;	146-148°		93-87	94-51	»(C==C) 2235;
4-CH ₃ C ₆ H ₄ C=CCH ₃ C=CC ₆ H ₆ (XI)	A	24	જ	(0-025)		6.13	5.73	v(CH) 2880, 2800, 1316(s), 1256
				164-165°		93-87	94.19	»(C==C) 2240, 2160, 2135
4-CH ₅ C ₆ H ₄ (C=C) ₅ CH ₅ C ₆ H ₅ (XII)	۵			(0-1)	42-42·8°	6-13	6-03	v(C ₆ H ₆ CH ₈) 1450(s), 730(s)
^a Lit. ^{9.10} b.p. 77–77-5° (32mm); n_D^{20} 77° (3 mm) n_D^{30} 1-5745; v 3260, 2250, 2 isometrization of the corresponding 1.4.	^{as} 1.4499; 2120. ^d Lit divne: C	v 2260, • b.p. 81. countir	2150, 2190 3-89 (3 mm or reaction.	cm ⁻¹ . ^b Lit. ⁴) n _D ³⁰ 1·6305. Fo. 5: D. iso	b.p. 99–100° (3 • Preparation]	37 mm) $nMethods the 1 4-div$	^{b*} 1.491: are: A, c	5; v 2260, 2190, 2150 cm ⁻¹ . • Lit. ^{4,13} b.p. coupling reaction, eq. 2; B, base catalyzed remationshy on elumina. The construct
time for these methods is indicated.			0					1 viento graphi y a arainina. 1112 1 vacuou

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synthesis, we find that 1,4-diynes deteriorate rapidly when exposed to air, even at room temperature. In our work, several lines of spectral evidence made structure assignments for 1,4- and related 1,3-diynes simple and unambiguous.

The cuprous chloride coupling in tetrahydrofuran (THF), has become a preferred route to the skipped diynes.^{3.6}

$$RC = CMgBr + BrCH_{3}C = CR' \xrightarrow{CuCl} RC = CCH_{3}C = CR'$$
(2)

The use of a strongly basic reagent, e.g. a sodium acetylide, has at best given low yields of the 1,4-diynes.^{6,18,15} Our own attempts to find an optimum yield of 1-phenyl-1,4-pentadiyne(III) are summarized in Table 6. The coupling goes rapidly in THF as compared with ether. Since the products are sensitive, the reaction time should not be prolonged. A list of the 1,4-diynes prepared in this way is given in Table 1. Spectral evidence supporting the structure assignments will be given later.

Some variations on the coupling reaction 2 have been used.^{4.5.7} R. Wielesek of this laboratory started with silver acetylides (R = phenyl or butyl) and propargyl chloride or bromide in several solvents. After one week at reflux, the 1,4-diyne (III)

$$RC = CAg + XCH_{s}C = CR' \rightarrow RC = CCH_{s}C = CR' + AgX$$
(2a)

was produced, but the yields in several preparations were variable and uncertain. The addition of aluminum chloride did not appear to be effective here. In another case, IR spectra indicated no more than a trace of the product, 1,5-diphenyl-1,4-pentadiyne (VII), produced in 2a. This essentially confirms the work of Gensler and Mahadevan who showed that a variety of metallic acetylides did not give any of the desired coupling product in reactions such as $2a.^6$

There is an interesting complication in the coupling process, Eq. 2. In 1928, Grignard and Lapayre treated phenylethynylmagnesium bromide with methylene iodide and obtained a compound, m.p. 89°, in 8% yield which they claimed to be 1,5-diphenyl-1,4-pentadiyne (VII).¹⁴ In 1962, Iwai and Hiraoka coupled phenyl-ethynylmagnesium bromide with phenylpropargyldiethylmethylammonium iodide and obtained a solid, m.p. 85–86°; they believed that their product was the same as that of the French workers for they repeated the coupling with methylene iodide and obtained a trace (<1%) of the same solid.¹⁶ Because this solid corresponded neither to our 1,4-diyne (VII), m.p. 45·5°, nor to our 1,3-diyne (VIII), m.p. 31° (see below), another possibility was sought. Since couplings of the type

$$RC = CMgX \xrightarrow{CuCl} (RC = C)_{a}$$
(3)
$$RC = CMgX + BrC = CR \xrightarrow{CuCl}$$

are well known,¹⁷ we prepared diphenylbutadiyne. A comparison of the elemental analysis, m.p. and UV spectrum of the compound with that prepared by Iwai and Hiraoka shows that they also obtained diphenylbutadiyne.

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One of the difficulties here turned out to be trivial, i.e. the elemental analyses for the diphenylbutadiyne or diphenylpentadiyne are fairly close. The real problem of course is in kind of coupling obtained, i.e. Eq. 1 vs Eq. 3. Thus, we attempted to prepare the 1,3-diyne(VIII) from 3-phenylpropynylmagnesium bromide and phenylbromoacetylene but could only isolate diphenylbutadiyne. Likewise, an attempt to produce VIII from phenylbutadiynylmagnesium bromide and benzyl bromide led to 1,2-diphenylethane (Eq. 4). Again, pretreatment at reflux of VII with ethylmagnesium

$$C_{6}H_{3}CH_{2}C = CMgBr + C_{6}H_{5}C = CBr \underbrace{CuCl}_{//\rightarrow} C_{6}H_{5}C = C)_{2}CH_{2}C_{6}H_{5} \qquad (4)$$

$$C_{6}H_{5}(C = C)_{2}MgBr + C_{6}H_{4}CH_{2}Br \underbrace{CuCl}_{//\rightarrow} C_{6}H_{5}(C = C)_{2}CH_{2}C_{6}H_{5} \qquad (4)$$

bromide followed by cuprous chloride and phenylbromoacetylene gave diphenylbutadiyne and not the hoped for triphenylethynylmethane. Incidentally, the coupling reaction which did give VIII is

$$C_{e}H_{6}(C = C)_{s}MgBr + 4-CH_{s}C_{e}H_{4}SO_{s}CH_{s}C_{e}H_{5} \rightarrow VIII$$
(5)

The earliest workers recognized that the methylene group in 1,4-diynes might be active.^{18.14} But just how available the hydrogen may be in polar and non-polar solvents is not yet clear. Although it now seems probable that they were testing 1,4-diphenylbutadiyne instead of 1,5-diphenyl-1,4-pentadiyne, Grignard and Lapayre reported that their compound consumed 1.84 equivs of ethylmagnesium bromide (Zerewitinoff reagent) in an ether-benzene solution at 70°.¹⁴ T. Y. Lai reported that 6,9-pentadecadiyne consumed 1.32 equivs of this reagent at 88°.¹⁸ However, Gensler and Cassella could not find active hydrogen in 1,4-nonadiyne with LAH or methylmagnesium bromide.⁹ After calibrating it against known acids, we found that with typical 1,4-diynes, our Zerewitinoff reagent in isoamyl ether at 100° evolved hydrogen, but no more than with tolan or diphenylbutadiyne. This suggests that Zerewitinoff test for labile hydrogen in 1,4-diynes may be an unreliable guide to their structure.

With other bases and particularly in protic solvents, 1,4-diynes do behave as carbon acids.⁹ In this work, we found that the isomerization given in Eq. 1 took place at room temperature and in ethanolic solutions of sodium ethoxide (ca. 0.1 M). In two cases, the conversion was also effected simply by chromatography on alumina. The resulting 1,3-diynes are given in Table 1.

The characteristic 1,4- to 1,3-diyne conversion of Eq. 1 is presumably one of the major problems in the attempted preparation of 1,4-diynes with sodium acetylides.^{13,15} In fact, Petrov and Molodova reported that the isomerization of III with base is violent,⁴ but this must simply be a matter of dilution.¹² Under the proper conditions, the prototropic shift can be followed kinetically. Using the spectrophotometric data of Gensler and Cassella for sodium ethoxide in alcohol-water (8:1) at ca. 25°,⁹ we calculate that the rate constant for formation of the allene from 1,4-nonadiyne is 0.661. mole⁻¹ min⁻¹ and the constant for formation of the 2,4-nonadiyne from the allene is $3.7 \times 10^{-2}1$. mole⁻¹ min⁻¹.

				TABLE 2	. PMR D	NO VIN	1,4-PENT	ADIYNES, R(CH CCH	Ç Ç	•			
R, R′		+	(a-CH ₁)		۲ (in	ternal-C	(H_1)		۲ ()	CH)			۴	
		Found	Calc.	Type	Found	Calc.	Type	J, c/s	Found	Type	J ₁₈ , c/s	Aryl	CH,	(CH 1)
n-C ₄ H, H	ε	7.87	7.86	X	6-91	68.9	e	J ₁₂ 2-8 J ₁₄ 2-4	7-96	F	2.81		8-93-9-3	8-38-8-93
С,Н,, Н	P(III)				6-68	6.68	D	J ₁₈ 2·73	7.82	Ţ	2.75	2-43-2-93		
n-C,H,, C,H,	ε	7.87	7-86	M	6.60	6.68	H	J ₁₄ 2·37				2-39-2-95	8.9 -9.3	8.4 -8.9
C,H, C,H,	(IIV)				6-50	6.47	s					2.5 -3-0		
4-CH ₃ C ₆ H ₄ , H	(XI)				69.9	6.68	۵	J ₁₃ 2.6	7-82	н	2.6	2.55-3.17	7-58-7-95	
4-CH ₁ C ₆ H ₁ , C ₆ H	(XI)				6-42	6-47	S					2.43–3.17	7-84	
 Chemical sh Calculated f Multiplet (N between the coup Ref. 4 gives 	ifts and J rom Shoc I), Quarte led hydrc the τ valu	values w blery's ruld it (Q), Trij bgen atom ues, 6·39,	sre obtai ss. plet (T), s s. 7·51 and	ned by a Singlet (S 2.42.	first orde	er analys (6). The	is. subscrip	ts to J are n	lot the po	sitions o	fattachme	ent but the	number of c	arbon atoms

			TABLE 3	. PMR DA	TA ON 1,3-	PENTADIYNE	s, RC C C		۶٬۵			1
R, R′		4	(C=CCH)	_		۲ ()	CH, C≡	CCH ₁)			+	
		Found	Calc.	Type [¢]	J ₁₆ c/s	Found	Calc. ^b	Type	J c/s	Aryl	CH,	(CH1)
n-C ₄ H, H	(II)	8.16	8·21	Т	1.18	7.71	7-74	X	J ₁₈ 6-2 J ₁₆ 1-2	 1	8-93-9-27	8-33-8-86
С,Н,, Н	• <u>(</u> 2)					8.21	8·21	S		2.47-2.93		
n-C,H,, C,H,	E	7.87	7.86	M		6.52	6-38	S		2.87	8-92-9-4	8-38-8-92
C,H,, C,H,	(IIII)					6.30	6.38	S		2.5 -3.1		
4-CH ₁ C ₁ H ₁ , H	Ś					8·06	8·21	s		2.58-3.08	7-70	
4-CH ₅ C ₆ H ₆ , C ₆ H ₆	(IIIX)					6-41	6.38	S		2.5 -3.3	6 <i>L</i> - <i>L</i>	
e Chemicel shif	te and I ve	do erem seul	tained hu a	first order	- analueie						4	

Chemical shifts and J values were obtained by a first order analysis.
Calculated from Shoolery's rules.
Multiplet (M), Triplet (T), Singlet (S).
In CCl₄.
Ref. 4 gives the τ values 7.9 and 2.43.

Divinylmethane and its analogs, e.g. fluorene, undergo condensation reactions.¹⁸

$$(C_{e}H_{s}C = C)_{s}CH_{s}$$
VII
or
$$+ 4 - (CH_{s})_{s}NC_{e}H_{s}NO \xrightarrow{N_{a}OC_{s}H_{s}}$$
(6)
VIII
$$4 - (CH_{s})_{s}NC_{e}H_{s}N = (C_{e}H_{s}CCCCCC_{e}H_{s})$$

At first glance it would appear that 1,4-diynes should also behave as "active" methylene compounds. Of the several condensation reactions we attempted with 1,4-diynes, only one gave an isolable product as in Eq. 6. In view of the lability of the 1,4-diynes, it is unlikely that the product with the branching at the middle carbon was produced, but until independent evidence becomes available, this possibility cannot be ruled out.

PMR spectra. There have been a number of studies on the PMR spectra and coupling constants of acetylenic compounds.^{19–24} Petrov *et al.*, first recorded the spectra of III and IV and distinguished between isomeric 1,3- and 1,4-pentadiyne structures.⁴ Our PMR data in Tables 2 and 3 constitute a detailed survey of the chemical shifts and coupling constants of skipped diynes and their related isomers.

Generally speaking, the PMR chemical shifts, τ (C=CH), τ (CH₂), τ (CH₃), etc. fell in the expected ranges. It was of particular interest to see whether the internal methylene of the skipped diynes was unusual in any way; for example, how well did Shoolery's empirical additivity rule (Eq. 7) apply?²⁵ New effective shielding constants (σ_{eff}), alkylethynyl (1.44), arylethynyl (1.65), alkyl- or aryldiethynyl (1.56), were

$$\tau (CH_2XY) = 9.767 - \sigma(X) - \sigma(Y)$$
(7)

estimated from some of the diynes and then checked against the others. As can be seen in Tables 2 and 3, the differences between observed τ values and those calculated from Eq. 7 are quite small.

It was somewhat surprising that this approximate rule (Eq. 7) applied to the larger group of alkynes given in Table 5. Published²⁵ as well as new derived values of σ_{eff} are listed there. Although the observed range in $\tau(CH_2) = 5 \cdot 7 - 8 \cdot 3$ is broad, one can have some confidence in predicting $\tau(CH_2)$ for such acetylenes to ca. $0 \cdot 1 - 0 \cdot 2$ ppm and often better. The acetylenic ethers do show interesting non-additive behaviour which has already been pointed out.²³

Apart from the protons in the aryl and butyl groups which gave rise to complex multiplets, the splitting patterns were invaluable aids in the assignment of structure (Tables 2, 3). The terminal hydrogen in the pentadiynyl group ($HC \equiv C - CH_2 - C \equiv C -)$

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IN ETHANOL
1,3-DIYNES
1,4- AND
DATA OF
SPECTRAI
2
TABLE 4.

	R—C≡C—R	Amax	(log ɛ)	Amax	(log ɛ)	Amax	(log e)	Атах	(log ɛ)	λmax	(log £)	λmax	(log ɛ)	λ_{max}	(log ε)	Amax	(log ɛ)	λmax	(Jog E)
a n-Bu,	н													{		225-5	3.7	185	3.6
•	CH,C=CH											262ª	2.92			234ª	3-02		
II/	C≡CCH.											252	2.48	237	2.68	232-5	2.66	225	2-71
Ph,	н					281-5	2.55	277-5	2.79	270-5	2-88	263-5	2.84	246	4-20	235	4-24		
9	CH.													249	4.2	238	4:2		
III	CH, C CH					284s	2-48	278	2-86	271	3-02	264-5	2.97	248-5	4-31	237-5	4.30		
>	CH,C=CBu-1	c						279	2-93	272	3.02	265	3.05	249	4-36	238	4-37		
VII	CH, C=CPh					282	2.55	278-5	2-96	271-5	3·12	264	3-23	251	5.05	239	4-95		
υ υ	CH, Ph	326	2.57	305	2.66	279	2,90	272	3-02	267-5	3.04	2643	3-15	251	4-36	240	4-40	232	4:22
đ	CIICH							283-5	4-17	268	4-28	254-5	4-08	242	3.72	231	3.36	220	4-43
12	C≡CCH.							287	4-27	271	4-40	256	4-22	243	3-88	232.	3-40	221-5	4-81
III	C=CCH, Ph							288	4-29	272	4-38	258	4-19	245	3-84	233	3.54	223	4.66
q	C≡CPh	326-5	4.48	305-5	4-52	296-5	4-25	287	4-33	271	4.14	259	4-45	253-5	4-41	242	4.46	228	(4.5)
q	Ph			297	4-34	288	4-3 0	278	4-3	265	4-3 5								•
P-CH,C,H	н.			285∎	2·19	281	2-50	274	2.64	272	2.66	266	2.72	250	4·20	245	4·16	239	4.25
X	CH,C≡CH			286.5	3.14	281	3·17			270	3.33			252	4-32	247	4-25	241	4.32
XI	CH, C=CPh			286	2:46	282	2.68	278	2.82	275	2·88	271	2-98	254	4-47	250	4.42	243	4:42
×	C CCH			289	4-37	273	4-50			258	4.37	246	4·18	233	4.12	225	4.73	222	4.61
XII	C=CCH,Ph			292	4.39	275	4-51			260	4-38	247	4:20			226-5	4.76	223	4.60
VI n-Bu,	C≡CCH,Ph			288	3·10	272-2	3.27	264-2	3·11	257-5	3-32	244	3.27	241-8	3·27			233	3-23
e IIV data	is for 1-octype.	I N I	latt H	R Klev	Pue and	ر ۲	Price 1	Chem	Phue 1	7 466 (1040	Ref 1	7 ° T	Iacol	l pue se	Dani	ter I	0	2

- UV uata is for tructivity: J. K. Frisht, T. D. MEVERS and W. C. Frice, J. Chem. FNY: 1, 1, 00 (1957). Tech 11. - 1. L. Jacobs and D. Danker, J. Urg. Chem. 22, [1424 (1957). One other band is given, 2:87^a (4:80). ^d See also Ref. 17, ^e Ref. 9 gives 263 (1-4) for 95% ethanol. ⁷ Ref. 9 gives 252 (2:88), 237 (5:25), 232 (4:68), 224-5 (5:64) for 95% EtOH. ^a Shoulder.

Compound	$\tau_{0H_{g}}$ (calc.)	$\tau_{CH_{g}}$ (obs.)	Ref.
HCC—CH ₁ —H	8·33	8.2	ь
HCCCH ₃ CH ₃	7.86	7.847	с
H ₃ CCC—CH ₃ —CH ₃	7·86	7.942	с
HCC-CH ₂ -C ₂ H ₇ -n	• 7·8 6	7.93	8
HCC-CH ₁ -CH ₁ CCH	7·86	7.63	8
HCCCH ₁ OH	5-97	5.74	b,d
HCC-CH ₄ -OR	5-97	5.82	d,e
HCC-CH ₁ -Cl	5·80	5.91	d
HCC-CH ₁ -Br	6·00	6-18	d
ClCH ₂ CCCH ₂ Cl	5.80	5.84	d
H—CH ₂ *—CC—CH ₂ —COOH	8.33,* 6.74	8·2,* (6·74)	f
H ₂ C—CH ₂ *—CC—CH ₂ —COOH	7.86,* 6.74	7.84,* 6.73	ſ
C ₆ H ₅ CH ₂ *CCCH ₂ COOH	6·50 ,* 6·74	6·49,* 6·73	f
C ₆ H ₅ -CC-CH ₂ -Br	5·79	6.00	d
C ₆ H ₅ CCCH ₃ C ₆ H ₅	6.29	6-33	d
HO-CH3-CC-CH3-OH	5-97	5.76	d,h
C ₆ H ₅ CCCH ₂ OH	5.76	5-41	d
HCCOCH ₁ H	6.46	6.16	8
HCCO-CH ₂ -CH ₂	5.99	5-94	8
HCCO-CH ₂ -C ₂ H ₅	5-99	(5-99)	8
HCCSCH ₃ CH ₃	7.27	(7·27)	8
C _t H _t CC—CH ₂ *—CH ₂ COOH	7·65,* 7·71	7.38, 7.38	d
C ₆ H ₉ CC—CH ₈ —OC ₈ H ₈	5-97	6 ∙01	i

TABLE 5. APPLICATION OF SHOOLERY'S ADDITIVITY RULE TO ALKYNES⁴

^a $\sigma_{1 \text{ eff}}$ were as follows: HC=C (1.44), alkyl (0.47), C_eH_s (1.832), alkylethynyl (1.44), arylethynyl (1.65), alkyl- or aryldiethynyl (1.56), COOH (1.59), Cl (2.53), Br (2.33), OR (2.36), RC=CO (3.29), RC=CS (2.03); figures are from Ref. 25 or are based on values in parenthesis. ^b Bhacca, Johnson and Shoolery, NMR

Spectra Catalog, Varian Associates, 1962. 'Ref. 21. 'This study. 'R / Ref. 22. 'Ref. 23. 'Run in EtOH. 'C₈H₆—cyclopentyl. S. H. Van Boom, P. P. Montigu, L. Brandsma, and J. F. Arens, *Rec. Trav. Chim.* 84, 31 (1965).

of I, III and IX appears as a triplet. The internal methylene appears as a doublet when flanked by ethynyl as in III and IX, a triplet when flanked by two propargyltype hydrogens as in V, or as a sextet when flanked by both groups as in I. As expected, isolated methyl or methylene groups of IV, VII, VIII, X, XI and XII appear as singlets.

Other long range couplings would be expected in these diynes (Tables 2, 3). For example, the internal methylene in I shows a pair of triplets involving coupling over three and four carbon atoms. In II, the terminal methyl band is cleanly split into three lines (J_{16}) and the α -CH₂ band is split into three quartets (J_{12}, J_{16}) . In V, the α -CH₂ band is split into three triplets (J_{12}, J_{14}) . The α -CH₂ multiplets in I and VI show a more complex pattern of overlapping bands which we did not attempt to resolve. Then, the benzylic—CH₂ band of VI, expected as a triplet (J_{16}) , appears as a singlet.

The long range coupling constants across one or more acetylenic bonds do fit into a coherent pattern. The fall off in the J values decreases sharply at first then more gradually as the number of interposed carbon atoms increases. Our J_{13} (values for I,

III, IX), J_{14} (values for I, V), and J_{16} (value for II) fall in reported ranges of ca. 2.6–3.6,¹⁹⁻²¹ 2.2–2.7,²⁰⁻²² and 1–1.3 c/s,²⁰ respectively.

UV spectra of the diynes. Our UV data on 1,3- and 1,4-diynes as well as on certain model compounds are collected in Table 4. Since most previous discussions^{17,26,27} are concerned either with simple alkynes or conjugated polyynes, we have arranged the data in Table 4 so as to focus attention on the skipped diynes and their near relatives. It has been suggested that there is less conjugation in 1,3-polyynes than in 1,3polyenes.²⁶ Our data indicate that the change from the conjugated 1,3- to the skipped 1,4-diynes leaves little yne-yne conjugation. For example, the insertion of methylene into diphenyldiacetylene either between the triple bonds as in VII or at the 4- position as in VIII leads to significant decreases both in the band wave length and extinction.

Now, the UV data on skipped divnes raise the further question of conjugation "through" a methylene group in the excitation process.²⁷⁻²⁹ Previous reports on series of the type $C_6H_6(CH_2)_nY$ showed that if there was conjugation with n = 0, there could still be appreciable conjugation with n = 1.27-29 It was suggested that this effect followed the order $CN < CH = CH < COOH < CONH_2 \sim CO$. Examination of Table 4 shows that the spectral characteristics of III, V, and VII are similar to those of phenylethyne or 1-phenylpropyne and the spectral characteristics of IX and XI are similar to those of p-tolylethyne. Where the extinction of the diyne is enhanced as in VII or IX, this might be attributed to a doubling of the part structure. There is an "extra" effect, however, which is most prominent in the region ca. 230-260 mµ. Compare 1,5-diphenyl-1,4-pentadiyne (VII) (at $\lambda = 251$, 293 m μ) with 1-phenylpropyne and phenylethyne, or 1-p-tolyl-5-phenyl-1,4-pentadiyne (XI) ($\lambda = 254, 250,$ 243 m μ) with p-tolylethyne and 1-phenylpropyne. Here, bathochromic shifts of 2.5-5 mµ and small increments in the extinction coefficients show up over and above the sum of the "part" spectra. These increments may be taken as qualitative indications of conjugation in the skipped divides during the optical excitation process.

IR spectra of diynes. Space limitations preclude more than a brief description of the IR spectra (Table 1). Only recently, Gensler et al.⁸ and Petrov et al.,⁴ have noted that 1,4-diynes have a strong band at ca. 1315 cm⁻¹. This band is also prominent in the 1,4-diynes of this study. By its position we would suppose it to be a methylene wagging vibration.³⁰ (Where the 1,3-diynes have a band in this region e.g. 1303 cm⁻¹ in II, 1323 cm⁻¹ in IV, and 1338 cm⁻¹ in VIII, it tends to be of weak to medium intensity.) Three other weak to medium intensity bands i.e. at $2880 \pm 10, 2800 \pm 10$ and 1253 ± 5 cm⁻¹ appear to be characteristic of 1,4-diynes.

As a group, the 1,3-diynes do not have outstandingly characteristic bands. However, the group $CH_3(C \equiv C)_2$ —appears to give rise to two weak bands at ca. 2725 and ca. 2035 cm⁻¹; the group $C_6H_5CH_2(C \equiv C)_2$ —appears to give rise to two strong peaks at 1453 and 730 cm⁻¹. Whether these bands are useful for identification is another matter. For example, Gensler *et al.*, suggests that the skipped diynes have a weak

²⁶ H. Krauch, J. Chem. Phys. 28, 898 (1958); S. F. Mason, Quart. Rev. 15, 344 (1961).

²⁷ A. E. Gillam and E. S. Stern, *Electronic Absorption Spectroscopy*, Chap. 6. Arnold, London (1957).

²⁸ E. A. Braude, J. Chem. Soc. 1902 (1949).

²⁹ P. Ramart-Lucas, *Traité de Chimie Organique* (Edited by V. Grignard) Vol. II; p. 59. Masson et Cie., Paris (1936).

²⁰ R. N. Jones and C. Sandorfy, *Technique of Organic Chemistry* (Edited by W. West) Vol. IX; Chap. IV. Interscience, New York, N.Y. (1956).

band at ca. 2035 cm^{-1} ; in our determinations this was extremely weak or absent. In any case, some of the conjugated divides have absorptions in this region.

Mass spectra. In view of the confusion of 1,4-diphenylbutadiyne with 1,5-diphenyl-1,4-pentadiyne,^{14.16} we were concerned with the structures of VII and VIII. Mass spectrometric analysis proved to be helpful. We give below the relative abundances of a few of the masses. The parent peak of VII (MW 216), the most abundant peak, was scaled to 100. All other peaks from VII were relatively small: the largest of these at m/e 190 had a relative intensity of 5 while the $C_7H_7^+$ peak (m/e 91) had a value of 0·3. The parent peak of VIII had a relative intensity of 41 compared to that of $C_7H_7^+$; other prominent peaks for $C_5H_4^+$, $C_7H_8^+$ and $C_{10}H_8^+$ had intensities of 24, 22 and 10, respectively.



Several mass spectra of III and IV had to be taken before satisfactory results were obtained, since there was evidence that these compounds absorbed oxygen and decomposed in the heated inlet.

EXPERIMENTAL

Starting compounds such as phenylacetylene, 1-hexyne, ethoxyethyne and propargyl bromide were distilled and kept in stoppered bottles in the dark until they were used. Other compounds, phenylpropargyl alcohol,^{\$1} phenylpropargyl bromide,^{1a} benzyltosylate,^{\$2} *p*-tolylacetylene,^{\$3} phenylbutadiyne,^{\$4} 1,4-diphenylbutadiyne,^{17, \$5} 1,3-diphenylpropare,^{\$4} were prepared by known methods.

NMR spectra were obtained on neat liquids or CCl₄ solutions on a Varian A-60 spectrophotometer; tetramethylsilane served as an internal reference. IR spectra were run neat or in CCl₄ on Perkin-Elmer Model 137 or Beckman IR-8 spectrophotometers. UV spectra were run in EtOH solution on Beckman DK-1 and Cary Model 11 spectrophotometers. M.ps were taken in a heated metal block and are uncorrected. Microanalyses were run by Micro Tech Laboratory, Skokie, Illinois.

Preparation of 1,4-diynes. Literature methods for the preparation of this class of compounds were modified. One detailed example will be given to illustrate the method. In some cases, variations from this "standard" were employed, e.g. 1-3 g CuCl, different mixing rates of the reagents, etc., but these are not considered important. On exposure to air, particularly at room temp, these compounds discolor immediately. Therefore, they were distilled and stored in dry ice in a N₁ atmosphere. When pure, these compounds are colorless liquids or white solids.

Besides elemental analysis, spectroscopic criteria of purity were helpful. Usually, the PMR spectra were sufficiently diagnostic of a structure: these provided the characteristic chemical shifts, band splitting patterns, coupling constants as well as proton counts. Although VII and VIII had different line patterns in the aryl proton region, their PMR spectra were otherwise closely alike. Therefore, in this as well as in other cases, the IR spectra allowed unambiguous structural assignments.

- ²¹ H. H. Guest, J. Amer. Chem. Soc. 47, 860 (1925).
- ²² H. Gilman and N. J. Beaber, J. Amer. Chem. Soc. 47, 518 (1925).
- ** L. I. Smith and H. H. Hoehn, J. Amer. Chem. Soc. 63, 1175 (1941).
- ²⁴ M. Nakagawa, J. Chem. Soc. Japan 72, 561 (1951); Chem. Abstr. 45, 7081 (1951).
- ³⁵ J. F. Arens, Advances in Organic Chemistry (Edited by R. A. Raphael, E. C. Taylor and H. Wynberg) Vol. II. Interscience, New York, N.Y. (1960).
- ³⁴ A. Eglington and M. C. Whiting, J. Chem. Soc. 3052 (1953).

1-Phenyl-1,4-pentadiyne (III). A 500 ml three neck flask, fitted with a stirrer, dropping funnel and reflux condenser (surmounted by a drying tube) was flushed with N₃. Here, EtMgBr was prepared from Mg (8 g, 0.33 mole) in 100 ml solvent (dry ether or dry THF) and EtBr (43.6 g, 0.4 mole). Phenylacetylene (40.9 g, 0.4 mole) was added to the flask over a period of ca. 0.5 hr, just fast enough to keep the solution at reflux; then the solution was heated for 1 hr. The catalyst, CuCl (1 g) and/or THF (5 ml), was added and the mixture was stirred another hr. Propargyl bromide (31.5 g, 0.265 mole) in 50 ml solvent was now added to the refluxing solution and the mixture was heated (Table 6 for conditions). The product mixture was poured into 500 ml ice-water and worked up conventionally, that is, by acidification (25 ml conc. H₃SO₄) ether extraction, neutralization (NaHCO₃aq), washing, drying (MgSO₄), and vacuum distillation. The "best" conditions for this preparation are given in the last column of Table 6.

Solvent	EE	EE,	EE	THF	THF	THF
Catalyst HC=CCH ₂ Br ^o Reflux ^d % Reaction ^e Yield, g Yield, % ¹	THF 4 hr 48 hr 62 2.4 7	CuCl 8 hr 55·5 hr 90 15·9 47	CuCl + THF 4 hr 48 hr 52 7.2 21	none 4 hr 15 hr 95 2·4 7	CuCl 4 hr 15 hr 100 5.5 16	CuCl 0·33 hr 0·33 hr 95 17·4 52
, , ,						

TABLE 6. PREPARATION OF 1-PHENYL-1,4-PENTADIYNE (III)

^a EE, ethyl ether; THF. ^b This preparation was on double the scale. ^a The time taken for addition of propargyl bromide. ^a The reflux time for the coupling reaction. ^b The percent of unreacted Grignard reagent was determined: an aliquot (1 ml) of the solution was quenched with standard HCl and back-titrated with standard base. ¹ The yield of fractionated product is based on the propargyl bromide.

Attempted synthesis of 1-ethoxy-1,4-diynes. The procedures for 1-ethoxy-1, 4-pentadiyne and 1-ethoxy-5-phenyl-1,4-pentadiyne were similar to those for the preparation of III. The product fractions obtained by vacuum distillation appeared to be impure for their IR spectra contained strong carbonyl bands at ca. 1720 cm^{-1} as well as a weak band at ca. 2200 cm^{-1} ; at the same time, the characteristic IR and PMR bands of the internal methylene group was either weak or absent. We assumed, therefore, that in our final work-up of the 1-ethoxy-1,4-diynes, hydration had occurred:³⁴

$$(R = H, C_{\mathfrak{s}}H_{\mathfrak{s}}) RC = CCH_{\mathfrak{s}}C = COC_{\mathfrak{s}}H_{\mathfrak{s}} \xrightarrow{H^+, H_{\mathfrak{s}}O} RC = CCH_{\mathfrak{s}}CH_{\mathfrak{s}}COOC_{\mathfrak{s}}H_{\mathfrak{s}}$$
(8)

This assumption was confirmed as follows.

The residues were treated with alcoholic NaOH and the solutions were worked up to give the free acids. Only a few mg of impure pent-4-ynoic acid was available: it had m.p. 49–52° (lit.³⁶ 56–57°), and ν_{max}^{KBr} 3280 (C=CH), 2110 (C=C), 1710 (C=O), and a broad absorption 3500–2500 (H-bond) cm⁻¹. 5-Phenylpent-4-ynoic acid differed from the isomeric 3-ynoic and 2-ynoic acids.³³ It had m.p. 99·5-100·5° (from Skelly B), $\nu_{max}^{CCl_4}$ 3525 (OH), 2205 (C=C), 1730 (C=O) cm⁻¹, a broad absorption 3400–2400 (H-bond) cm⁻¹, and τ –1·94 (OH), 2·56 (CeH₅), 7·38 (CH₃) ppm. (Found: C, 75·58; H, 5·72. Calc. for C₁₁H₁₀O₅: C, 75·84; H, 5·79%.)

Identification of the 1,5-diphenylpentadiynes VII, VIII. Grignard and Lapayre and Iwai and Hiraoka reported the preparation of VII.^{14,14} Since we suspected that their compound was really diphenylbutadiyne, we prepared it by a known method:^{17,87} m.p. 93° (lit.¹⁷86–87°). (Found: C, 95·07; H, 5·32. Calc. for C₁₆H₁₀; C, 94·76; H, 5·24%.) UV data are given in Table 4. The compound claimed to be VII had m.p. 89° and 85–86°.^{14,16} (Found: C, 93·5, 94·46; H, 5·4, 5·11; we found: C, 94·51; H, 5·73. Calc. for C₁₇H₁₈: C, 94·41; H, 5·59%.) Furthermore, the nine peaks reported in the UV for the reported compound¹⁶ correspond very closely (both λ and ε) to nine out of the ten we found for 1,4-diphenylbutadiyne. These differ substantially from the pentadiynes VII and VIII. In addition, we could easily distinguish diphenylbutadiyne from VII and VIII by PMR spectra as well as by a proton count.

³⁷ H. K. Black and B. C. L. Weedon, J. Chem. Soc. 1785 (1953).

1,3-Diynes by isomerization. Two methods were used for the preparation of the conjugated diynes. In the first, a 1,4-diyne was isomerized; the second method involved a direct synthesis by coupling. Our most typical approach is illustrated by the preparation of 1-phenyl-1,3-pentadiyne. 1-Phenyl-1,4-pentadiyne (14 g, 0·1 mole) and KOH (5·6 g, 0·1 mole) in EtOH were kept under N₂ at ca. 0° for 3 hr, after which the solution was allowed to reach room temp. This solution was acidified and extracted with benzene; the extract was washed, dried and evaporated to leave a viscous reddish oil. Chromatography over alumina yielded a yellow liquid (7·6 g), which on recrystallization from EtOH gave white crystals, m.p. $17\cdot5-17\cdot8^{\circ}$.

A simpler method of isomerizing the 1,4- to the 1,3-diynes was found later. In the course of purifying 1-p-tolyl-5-phenyl-1,4-pentadiyne (4.6 g) by elution chromatography over alumina, 1-p-tolyl-4-benzylbutadiyne (2.8 g), emerged in the benzene eluate. Recrystallization from EtOH produced white crystals, m.p. 42-42.8°.

1-Phenyl-4-benzylbutadiyne (VIII). An ethyl Grignard reagent was prepared from bromoethane (12 g, 0·11 mole) and Mg (2·43 g, 0·1 mole) in ethyl ether (100 ml). Phenyldiacetylene (11·35 g, 0·09 mole) in ether (100 ml) was added to the Grignard reagent at a rate which sustained reflux, i.e. over a period of ca. 1 hr; the solution was stirred at reflux for 1 hr more. Benzyl tosylate (53 g, 0·2 mole) in ether (300 ml) was then added to the Grignard solution and left overnight. The ether solution was treated with dilute acid, then washed and dried. After evaporation of the solvent, the residue was fractionally distilled under N_a. The middle fraction (10·9 g), b.p. 145–153° (0·005 mm), crystallized from EtOH to give pale yellow crystals, m.p. $30-31^\circ$.

p-Nitrosodimethylaniline with VII or VIII. 1,5-Diphenyl-1,4-pentadiyne (2:16 g, 0:01 mole) and p-nitrosodimethylaniline (1:8 g, 0:01 mole) in ethyl ether (70 ml) were mixed with ethanolic (15 ml) EtONa (0:01 mole). The mixture was left in a refrigerator for 24 hr, then filtered to separate a yellow solid. Evaporation of the solution followed by chromatography over alumina gave more yellow solid which on recrystallization from benzene and elemental analysis, turned out to be p,p'-bis-dimethyl-aminoazoxybenzene, m.p. 242:5-244° (lit.³⁶ m.p. 238°). The other eluted product recrystallized from EtOH, was red and had m.p. 138:7-139°, $\lambda_{0:M_{0}}^{\circ M_{0}} \cap m\mu(\varepsilon)$: 259(1:2 × 10^s), 465(4:7 × 10^s), $v_{c=c}$ 2210, 2135 cm⁻¹. The same red and yellow solids were prepared from 1-phenyl-4-benzylbutadiyne (0:005 mole) and p-nitrosodimethylaniline in ethanolic ethoxide. The red product could arise from condensation at the 3-carbon of the pentadiyne, but we believe condensation at 1-carbon is more probable. (Found: C, 86:08; H, 5:74; N, 8:21. Calc. for C₁₈H₁₈ON: C, 86:18; H, 5:79; N, 8:04%).

Active hydrogen determination. A conventional Zerewitinoff method, i.e. MeMgI in isoamyl ether distilled from Na, was used. The results for several diynes as well as three "standards" are given in Table 7. It may be that the Zerewitinoff reagent decomposed at the reflux temp and thereby evolved some gaseous product(s). This would account for the active hydrogen found in inactive compounds.

Compound	Weight, g	Conditions	Number of active hydrogens found
C,H,COOH	0.0568	25°	1.18
C₅H₅C≡=CH	0.0746	reflux, 1 hr	0.77
CH ₂ (COOC ₂ H ₅) ₂	0.0662	25°	1.0
(C ₄ H ₅ C==C) ₂ CH ₃	0.0823	reflux, 1 hr	0.45
C ₆ H ₄ (C=C) ₂ CH ₂ C ₆ H ₅	0.115	reflux, 1 hr	0.28
p-C₁H₁C≔CCH₃C≔CC₅H₅	0.0837	reflux, 1 hr	0-28
(C _t H _t C=C) ₁	0.0833	reflux, 1 hr	0.24
C ₆ H ₈ C=CC ₆ H ₅	0.0231	reflux, 1 hr	0.3

TABLE 7. ZEREWITINOFF DETERMINATIONS

Acknowledgment—We wish to thank Mr. R. A. Wielesek for exploratory work in connection with the coupling in Eq. 2a, Mr. M. Baldwin for taking the mass spectra on the AEI-MS 9 instrument at University College, London, and the Air Reduction Company for several propargyl derivatives; Dr. S. H. Marcus helped us in the early stages with the PMR work.

³⁹ P. Ehrlich and F. Sachs, Ber. Disch. Chem. bes. 32, 2341 (1899); E. Bergmann, J. Chem. Soc. 1628 (1937).