

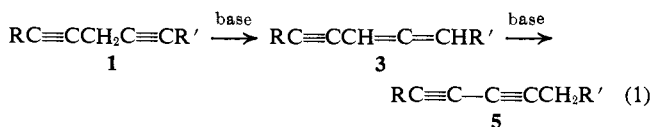
# On the Base-Catalyzed Isomerization and the Kinetic Acidity of 1,4-Diynes<sup>1</sup>

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**Abstract:** The kinetics of the ethoxide-catalyzed isomerization in ethanol of three skipped diynes, 1-phenyl-1,4-pentadiyne (**1a**), 1,5-diphenyl-1,4-pentadiyne (**1b**), and 1-phenyl-1,4-nonadiyne (**1c**), were determined. In each case, an allene was an intermediate, and a conjugated 1,3-diyne was the end product; with **1c**, kinetic evidence indicated that there were perhaps two allenic intermediates. The first step in the 1,4 to 1,3 isomerization is faster than the succeeding one(s). When the substituent in the 5 position changes, the rates follow the expected order  $C_6H_5 > H > n-C_4H_9$ ; at 26°, the values for these substituents, respectively, are 178, 86, and 1.0 for  $k_1$  and 158, 2.8, and 0.0015  $M^{-1} \text{min}^{-1}$  for  $k_2$ . For compound **1a**,  $\Delta H^\ddagger = 15.5 \text{ kcal/mole}$ ,  $\Delta S^\ddagger = -3.0 \text{ eu}$  (26°) for step 1, and  $\Delta H^\ddagger = 22.7 \text{ kcal/mole}$ ,  $\Delta S^\ddagger = 4.7 \text{ eu}$  (26°) for step 2. In a deuterated solvent, base-catalyzed exchange of the ethynyl proton of **1a** is somewhat faster than the isomerization; at the same time, it appears that the methylene protons are transferred to the solvent rather than intramolecularly to the terminal carbon. Although it is difficult to convert our kinetic acidities into pK values we would estimate the internal protons in **1a** to be less acid than the ethynyl proton. The acid-strengthening effect of the second ethynyl group on a methylene group is, in fact, quite remarkable. Two examples, benzylacetylene and 2-dihydropyranyl propargyl ether, are provided to show that, as substituted methanes, these are far weaker acids than the 1,4-diynes.

This work began on the premise that "skipped" diynes or diethynylmethanes (**1**) were active hydrogen compounds.<sup>2</sup> According to the Taft  $\sigma^*$  scale, ethynyl and carbomethoxy substituents have roughly the same electron-withdrawing power,<sup>3</sup> so that one might guess that they would bring carbon acids to about the same strength,  $pK \approx 14$  in water.<sup>4a</sup> If this were true, then a potentially interesting and useful family could be added to the recognized group of carbon acids. In this work, we have obtained estimates of the availability of the proton of **1** by following its base-catalyzed isomerization.



- a, R = C<sub>6</sub>H<sub>5</sub>; R' = H  
 b, R = R' = C<sub>6</sub>H<sub>5</sub>  
 c, R = n-C<sub>4</sub>H<sub>9</sub>; R' = C<sub>6</sub>H<sub>5</sub>

Process 1 is perhaps the most distinctive chemical property of 1,4-diynes. The preparation of the intermediate ethynylallenes in this way has not been fully exploited yet,<sup>5</sup> but the preparation of conjugated diynes is readily accessible. Typically, ethanolic ethoxide or chromatography on alumina can be used to effect the conversion of 1,4- to 1,3-diynes.<sup>2</sup> However, there are features about the availability of the proton of 1,4-diynes which are puzzling. It had been noted that Zerewitinoff determination on 6,9-pentadecadiyne indi-

cated active hydrogen.<sup>6</sup> Certainly, resonance stabilization of the anion **2** seems plausible.<sup>7</sup> The Zerewitinoff test, however, may not be reliable, for it has recently been shown to indicate active hydrogen where none is present.<sup>2</sup> In fact, the most successful preparation of 1,4-diynes involves coupling an ethynyl Grignard reagent with a propargyl halide, so that reaction between the internal methylene and the Grignard reagent is not significant.<sup>2</sup> There are also the observations that lithium aluminum hydride or methylmagnesium bromide do not react with 1,4-nonadiyne at ~25°. <sup>5</sup> These observations seem to be at odds with the facile base-catalyzed isomerization (1).

There is by now a substantial literature on analogous isomerizations in unsaturated series, C<sub>n</sub>H<sub>2n-2</sub>, C<sub>n</sub>H<sub>2n-4</sub>, C<sub>n</sub>H<sub>2n-6</sub>, which can involve alkynes.<sup>8-13</sup> A broad survey and an important contribution were made recently by Smadja: he concluded that on equilibration of the appropriate C<sub>7</sub> hydrocarbons, one obtained, in order of increasing stability, 1-heptyne ≤ 1,2-heptadiene < 3,4-heptadiene < 2,3-heptadiene ≪ 3-heptyne ≤ 2-heptyne ≪ 1,3-heptadiene < 2,4-heptadiene.<sup>8</sup> The preference for both "internal" and conjugated compounds was quite decisive.<sup>14</sup> These observations

(6) Y. L. Tchao, *Bull. Soc. Chim. France*, [4] **53**, 1537 (1933).

(7) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p 350.

(8) W. Smadja, *Ann. Chim. (Paris)*, **10**, 105 (1965). See also J. H. Wotiz, W. E. Billups, and D. T. Christian, *J. Org. Chem.*, **31**, 2069 (1966).

(9) H. Fischer, "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964: (a) Chapter 13; (b) Tables 3 and 6, Chapter 13.

(10) A. A. Petrov, *Usp. Khim.*, **29**, 1049 (1960).

(11) Some examples of base-promoted isomerization to or from naturally occurring alkynes are either cited or given in several places, e.g., (a) F. Bohmann, H. Bornowski, and C. Arndt, *Fortschr. Chem. Forsch.*, **4**, 138 (1962); (b) J. D. Bu'Lock, *Progr. Org. Chem.*, **6**, 86 (1964); (c) K. L. Mikolajczak, M. O. Bagby, and I. Wolff, *J. Am. Oil Chemists' Soc.*, **42**, 243 (1965).

(12) T. L. Jacobs, D. Danker, and S. Singer, *Tetrahedron*, **20**, 2177 (1964).

(13) J. H. Van Boom, P. P. Montijn, M. H. Berg, L. Brandsma, and J. F. Arens, *Rec. Trav. Chim.*, **84**, 813 (1964).

(14) The fact that alkali amides can convert 2-alkynes into 1-alkynes appears at first to be exceptional. However, here one is dealing with the

(1) This investigation was supported by Public Health Service Grant No. GM10020. Inquiries should be addressed to S. I. M.

(2) H. Taniguchi, I. M. Mathai, and S. I. Miller, *Tetrahedron*, **22**, 867 (1966). Key references to skipped diynes are included in this paper.

(3) M. Charton, *J. Org. Chem.*, **29**, 1222 (1964); J. Clark and D. D. Perrin, *Quart. Rev. (London)*, **18**, 295 (1964); G. B. Barlin and D. D. Perrin, *ibid.*, **20**, 75 (1966).

(4) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965: (a) p 10; (b) Chapter V; (c) D. J. Cram, F. Willey, H. P. Fischer, H. M. Relles, and D. J. Cram, *J. Am. Chem. Soc.*, **88**, 2759 (1966).

(5) W. J. Gensler and J. Casella, Jr., *ibid.*, **80**, 1376 (1958).

Table I. Rate Constants and Activation Parameters for the Isomerization of 1-Phenyl-1,4-pentadiyne in Ethanolic Sodium Ethoxide<sup>a,b</sup>

Temp, °C	Diyne, $M \times 10^4$	NaOC <sub>2</sub> H <sub>5</sub> , $M \times 10^3$	$k_1 \times 10^{-2}$ , $M^{-1} \text{min}^{-1}$	$k_2 \times 10^{-1}$ , $M^{-1} \text{min}^{-1}$
15.75 ± 0.05	0.2138	4.043	0.3762	0.06221
	0.1921	3.020	0.3078	0.06646
	0.2132	1.510	0.3220	0.06182
	0.2105	6.040	0.3490	0.06513
	0.1975	9.060	0.3651	0.06955
	$k_1/k_2 = 53$		Mean 0.34 ± 0.02	0.064 ± 0.002
17.7 ± 0.05	0.2025	4.034	0.4358	0.08956
	0.2050	6.051	0.4386	0.09093
	0.2080	3.025	0.3950	0.07944
	0.2120	8.068	0.4148	0.08913
	0.2052	2.017	0.4067	0.08736
	0.2052	3.631	0.4233	0.08560
	0.1971	5.043	0.3948	0.08735
	0.2032	2.622	0.4150	0.08101
	0.2111	5.648	0.4563	0.08824
	0.2012	4.034	0.3986	0.08825
	0.2050	4.639	0.4026	0.08476
	$k_1/k_2 = 48$		Mean 0.41 ± 0.02	0.086 ± 0.003
26.15 ± 0.05	0.1425	1.371	0.8176	0.3056
	0.1649	1.371	0.8424	0.2806
	1.6490	1.371	0.8512	0.2880
	0.1796	2.057	0.8682	0.2750
	1.796	2.057	0.8988	0.2778
	0.1765	1.645	0.9179	0.2751
	1.7650	1.645	0.9179	0.2879
	0.1976	1.041	0.8778	0.2553
	1.976	1.095	0.8545	0.2617
	0.1956	1.231	0.8691	0.3167
	1.956	1.231	0.8269	0.2751
	0.2098	0.7727	0.8620	0.2683
	2.098	0.7727	0.8074	0.2769
2.055	1.228	0.9185	0.2752	
	$k_1/k_2 = 31$		Mean 0.86 ± 0.03	0.28 ± 0.01
38.1 ± 0.1	0.2022	0.4386	2.510	0.9965
	0.2022	0.2924	2.447	1.089
	0.2095	0.3289	2.513	1.034
	0.2095	0.4239	2.486	1.125
	0.2012	0.3289	2.561	1.142
0.2180	0.3947	2.614	1.043	
	$k_1/k_2 = 24$		Mean 2.55 ± 0.04	1.08 ± 0.05
For step 1:	$E_{act} = 16.1 \text{ kcal/mole}$ $\Delta H^\ddagger = 15.5 \text{ kcal/mole}$ $\Delta S^\ddagger = -3.0 \text{ eu (26}^\circ)$		For step 2:	$E_{act} = 22.7 \text{ kcal/mole}$ $\Delta H^\ddagger = 22.1 \text{ kcal/mole}$ $\Delta S^\ddagger = 4.7 \text{ eu (26}^\circ)$

<sup>a</sup> For  $\lambda$  283 m $\mu$ , observed values are  $\epsilon_1 = 300 \pm 20$ ,  $\epsilon_5 = 11,750 \pm 50$ ; values computed in kinetic runs fall in the ranges:  $\epsilon_1 = 251-349$ ,  $\epsilon_5 = 18,425-18,988$ , and  $\epsilon_5 = 11,335-11,800$ . Average deviations are given for the temperatures,  $\epsilon$ 's, and the rate constants. <sup>b</sup> Mean  $k$  values were corrected for volume changes in solvent.

are in accord with the free energies of formation at 25° which are given for C<sub>4</sub> compounds in kcal/mole: 1-butyne, 48.3; 1,2-butadiene, 47.4; 2-butyne, 44.3; 1,3-butadiene, 36.0.<sup>15</sup>

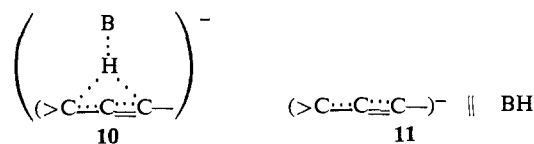
If one examines the literature on base-catalyzed reactions of enynes and diynes, the preference for internal and/or conjugated isomers in at least 20-30 examples is largely confirmed.<sup>9b,11</sup> If there is a choice between the cumulene **6** and the conjugated diyne **5**, the available evidence favors **5**.<sup>5</sup>

With regard to detailed mechanism, Cram, *et al.*, demonstrated that the base-catalyzed rearrangement of 1,3,3-triphenylpropyne to triphenylallene could involve an intramolecular proton shift, the so-called "conducted

equilibrium among the anions or the corresponding salts, and the stability preference may well be alkynide > alkadienide > alkenide > alkanide, perhaps for solubility reasons. See J. C. Craig and R. J. Young, *J. Chem. Soc., Org. Sect.*, 578 (1966).

(15) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953.

tour mechanism," to the extent of 22-88% depending on the base and the solvent: CH<sub>3</sub>OD, *t*-C<sub>4</sub>H<sub>9</sub>OD, or CH<sub>3</sub>OD-(CH<sub>3</sub>)<sub>2</sub>SO.<sup>4b,c</sup> Therefore, yne-allene interconversions may involve either the intimate (**10**) or the separated (**11**) ion pair intermediates, or both.



## Results and Discussion

**Isomerization of 1,4-Diynes.** The emphasis in this work is on the rates of isomerization of three 1,4-diynes in ethanolic sodium ethoxide (eq 1). Product studies have established the stoichiometry of the process.<sup>2</sup> The fact that an ethynylallene is an intermediate had already been determined by its isolation from 1,4-nona-diyne.<sup>5</sup> Although we did not prepare the pure allenes,

**Table II.** The Isomerization of 1,5-Diphenyl-1,4-pentadiyne at  $26.2 \pm 0.05^\circ$  in Ethanolic Sodium Ethoxide<sup>a</sup>

Diyne, $M \times 10^4$	$\text{NaOC}_2\text{H}_5$ , $M \times 10^3$	$k_1 \times 10^{-2}$ , $M^{-1} \text{ min}^{-1}$	$k_2 \times 10^{-2}$ , $M^{-1} \text{ min}^{-1}$
0.1882	0.4916	1.800	1.612
0.2258	0.4916	1.713	1.519
0.1870	0.3324	1.767	1.606
0.1870	0.6847	1.904	1.535
0.2150	1.127	1.769	1.541
0.2244	1.570	1.819	1.564
0.2244	0.6847	1.877	1.656
0.2141	0.5477	1.795	1.553
2.1410	0.4916	1.755	1.510
2.141	0.3408	1.683	1.489
1.152	0.8316	1.877	1.676
1.152	0.6847	1.782	1.706
2.250	0.8216	1.939	1.639
0.2002	0.1852	1.738	1.562
0.2325	1.232	1.805	1.441
0.2305	0.3423	1.796	1.563
0.2305	0.4108	1.782	1.539
0.2264	0.9885	1.755	1.660
0.2264	0.9216	1.725	1.656
0.2397	1.264	1.738	1.642
0.2397	1.005	1.701	1.553
$k_1/k_2 = 1.1$		Mean $1.78 \pm 0.05$ $1.58 \pm 0.06$	

<sup>a</sup> For  $\lambda$  280  $m\mu$ , observed values are  $\epsilon_1 = 630 \pm 30$ ,  $\epsilon_5 = 12,600 \pm 200$ ; values computed in kinetic runs fall in the ranges  $\epsilon_1 = 605\text{--}655$ ,  $\epsilon_3 = 29,158\text{--}30,048$ ,  $\epsilon_5 = 12,225\text{--}12,726$ . Average deviations are given for the temperature, rate constants, and  $\epsilon$  values.

we did stop the isomerization and obtain spectroscopic evidence for the formation of **3a** and **c**. Incidentally, the maximum concentration of **3** occurs at a time given by the relation<sup>16</sup>

$$t_{\max} = [\ln(k_2'/k_1')]/(k_2' - k_1') \quad (2)$$

where the rate constants are first order; in our isomerizations, these primed constants are pseudo first order.

The kinetics of process 1 was followed spectrophotometrically. Since the first and second steps had roughly comparable rates, it was convenient to use an

**Table III.** The Isomerization of 1-Phenyl-1,4-nonadiyne in Ethanolic Sodium Ethoxide at  $26.2 \pm 0.05^\circ$ 

Diyne, $M \times 10^4$	$\text{NaOC}_2\text{H}_5$ , $M$	$k_1$ , $M^{-1}$ $\text{ min}^{-1}$	$k_2 \times 10^3$ , $M^{-1} \text{ min}^{-1}$
0.6897	0.2164	1.015	1.539
0.8537	0.0725	1.030	1.684
0.9357	0.1443	0.9265	1.586
4.478	0.2463	1.019	1.610
4.657	0.4926	0.9271	1.540
0.9514	0.4926	1.030	1.555
0.9314	0.0550	1.015	1.569
9.061	0.5070	1.040	1.444
9.161	0.4050	0.8851 <sup>b</sup>	1.421
9.261	0.0507	1.056	1.568
0.9101	0.5070	1.067	1.457
4.551	0.0527	1.058	1.496
4.500	0.3042	0.8389 <sup>b</sup>	1.501 <sup>b</sup>
4.600	0.4800	0.9552	1.521
$k_1/k_2 = 65$		Mean $1.01 \pm 0.04$ $1.54 \pm 0.05$	

<sup>a</sup> For  $\lambda$  287.5  $m\mu$ , observed values are  $\epsilon_1 = 156$ ; values computed in kinetic runs fall in the ranges  $\epsilon_1 = 100\text{--}154$ ,  $\epsilon_3 = 4200\text{--}4327$ ,  $\epsilon_5 = 1746\text{--}1800$ . Average deviations are given for the temperature,  $\epsilon$ 's, and rate constants. <sup>b</sup> This value is not included in the mean.

(16) A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," John Wiley and Sons, Inc., New York, N. Y., 1961, p 168.

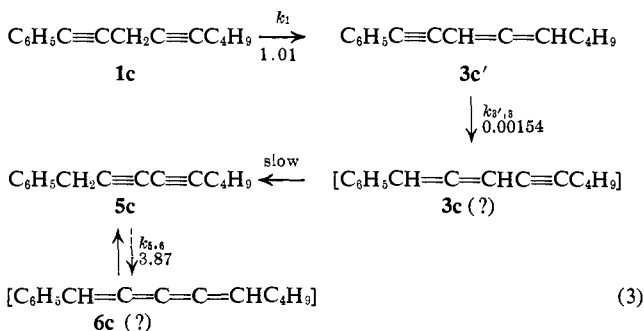
**Table IV.** The Ethoxide-Catalyzed Change in 1-Phenyl-2,4-nonadiyne at  $26.2^\circ$ 

Diyne, $M \times 10^4$	$\text{NaOC}_2\text{H}_5$ , $M \times 10^2$	$k$ , $M^{-1}$ $\text{ min}^{-1}$
0.5925	0.2035	3.660
0.5925	0.1017	3.511
0.5820	0.1113	4.061
0.5820	1.113	3.785
0.2910	1.113	4.116
0.2729	0.8907	3.901
2.279	0.8907	4.098
2.291	1.113	3.910
		Mean $3.87 \pm 0.18$

<sup>a</sup> For  $\lambda$  244.5  $m\mu$ .

excess of sodium ethoxide. The system could now be treated as two successive first-order reactions. With the aid of a computer and a suitable program, we obtained the extinction coefficients of the allenenes and two pseudo-first-order rate constants,  $k_1'$  and  $k_2'$ , for each run.<sup>17</sup> After dividing these by the concentration of sodium ethoxide, we obtained the second-order rate constants,  $k_1$  and  $k_2$ . Some of the kinetic data is given in Tables I–IV.

In working with system **1c**, it became clear that (1) required modification, as in sequence 3 ( $k$  values in  $M^{-1} \text{ min}^{-1}$ ). After the rapid initial formation of the



ethynyllallene **3c'**, the optical density at 287.5  $m\mu$  decreased, then increased; this we attribute to the formation of **3c** followed by its disappearance. Interruption of the reaction yielded mixtures which contained **1c**, **5c**, and allenenes, as determined by infrared and nmr spectroscopy. Apart from the systematic variations with time in the ultraviolet spectrum, we have no firm evidence for the presence or the structure of **6c**. We consider that the concentration of **6c** must be relatively low, since it does not show up in our spectral examination of partially isomerized **5c**. In any case, the rate constants for the first two steps of sequence 3 could be determined in the usual way. The change from **3c** to **5c** appeared to be slow, but could not be studied quantitatively because **5c** reacted further to **6c**.

When **5c** was subjected to the conditions of a kinetic run, a change in the optical density of the solution was observed. Kinetic studies on the process **5c** to **6c** gave reproducible  $A_\infty$  values and satisfactory rate constants (Table IV). The ultraviolet spectrum, however, remained unchanged on acidification so that free carbanions did not contribute to the spectrum. Now, **5c** is prepared by the base-catalyzed isomerization

(17) K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, pp 567–569. This program was modified for us by Mr. E. Stedronsky.

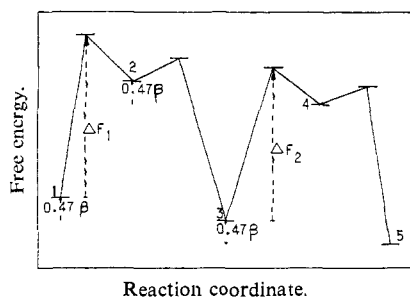
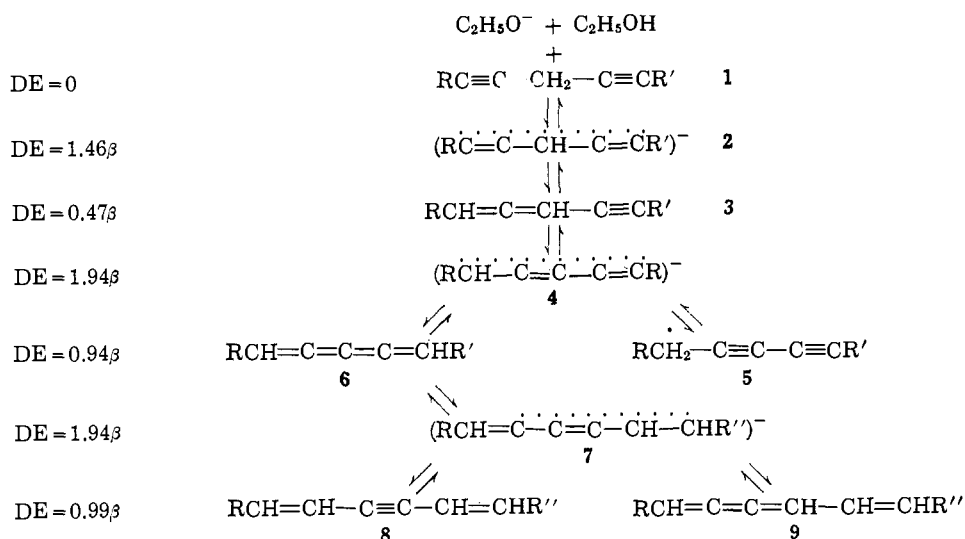


Figure 1. Partially schematic energy diagram for the isomerization of 1,4-diyne. See Scheme I for the species and delocalization energies involved. The species are numbered as in Scheme I.

of **1c**. Furthermore, though the action of base promotes a visible change in **5c**, there is little if any effective change in **5c**, as far as infrared and pmr tests of the isolated product could determine. All of this suggests that the quantities of **6c** that are formed from **5c** cannot be large. Our identification of **6c** in Scheme I must be considered speculative.

#### Scheme I



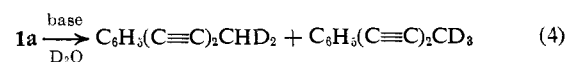
A few remarks on the experimental problems are in order. Since the 1,4-diyne deteriorate on storage, we were concerned that optical densities in our kinetic runs should reflect changes associated only with process 1, and no other. Furthermore, we did not have the extinction coefficients of the allenes, although we did have them for the skipped and conjugated diyne. For this reason, considerable effort was put into some systems to establish reproducibility. Then, concentrations of both base and diyne were varied sufficiently to establish the kinetic order; here, the spectrophotometric technique we used imposed some obvious practical limitations. For system 1a, we also obtained the activation parameters (Table I).

A minimum Scheme I for the isomerization of a five-carbon diyne involves five, and perhaps six, species, **1-6**. If the ends of the chain differ, *i.e.*,  $R \neq R'$ , the number of possibilities increases. Again, if  $R' = R''CH_2$ , interesting extensions to longer chains become possible as in **7**, **8**, and **9**. We have also included delocalization energies (DE) in Scheme I, which derive from simple Hückel molecular orbital theory: anion **4** is assumed to consist of two  $\pi$ -electron systems, 1,3-buta-

diene and a pentadienyl anion; **8** and **9** consist of 1,3,5-hexatriene and (isolated) ethylene.<sup>18</sup> This overall scheme provides a description of our isomerizations; it is supported by the equilibrium studies on simpler systems, *e.g.*, those mentioned above for  $C_7$  alkynes and alkadienes.

A free-energy *vs.* reaction coordinate diagram (Figure 1) gives a better representation of the gross changes involved in our systems. In general, the energy drops from **1** to **3** to **5**; under our kinetic (15–40°) or preparative conditions (~80°),<sup>2</sup> the conversions of **1** and **3** are complete. Since  $k_1 > k_2$ , we have measured the free energies of activation,  $\Delta F_1 < \Delta F_2$ , in Figure 1; it will be recognized that this order could easily be reversed by changing the temperature, especially for **1b** and **3b**. The anions, which are all indicated as "open," *e.g.*, **11**, may be partners in intimate ion pairs, *e.g.*, **10**. In such systems, specific solvent effects are also known to be important, *e.g.*, in determining product ratios.<sup>4</sup> For these reasons, we emphasize that the free energies of some of the species in Figure 1 could change appreciably with substituent, solvent, temperature, base, etc.

Under the conditions of our kinetic study, *i.e.*, ethanolic ethoxide, we believe that discrete carbanions are involved in isomerization. For, by carrying out the isomerization of **1a** under less "polar" conditions, *i.e.*, with potassium *t*-butoxide-deuterium oxide solution in an excess of diethylene glycol dimethyl ether, we found that the methylene protons were lost to the solvent.



Thus, the intramolecular proton transfer ("conducted tour") found for the isomerization of 1,1,3-triphenylpropyne by tripropylamine in *t*-butyl alcohol<sup>4b,c</sup> was not applicable under our conditions.

Substituent effects on the isomerization of  $RC\equiv CCH_2-C\equiv CR'$  follow predictable trends. The most electron-withdrawing group, phenyl in **1b**, is associated with the highest rate. Thus, the relative rates for the 1,4-diyne ( $R = C_6H_5$ ) follow the order in  $R'$  of  $C_6H_5 > H > n-C_4H_9$ , 178:86:1.0 for  $k_1$ , and 158:2.8:0.0015 for  $k_2$ .

(18) A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 2.

When  $R = H$  and  $R' = C_4H_9$ , we estimate relative rates of  $k_1 \simeq 0.7$  and  $k_2 \simeq 0.004$  for an alcohol-water (8:1) solvent.<sup>2,5</sup>

It is also possible to make a rough comparison of the skipped diyne (**1a**) with a skipped enyne, methyl *cis*-9-octadecen-12-ynoate, obtained from a seed oil.<sup>11c</sup> If we estimate the half-lives at several temperatures from qualitative curves given for the latter compound in potassium hydroxide-ethylene glycol at 75–121°, we obtain  $E_a = \sim 26$ , which is much higher than  $E_a = 16$  kcal/mole for **1a**. This agrees, of course, with the fact that a triple bond is more electronegative than a double bond, and thus more effective in increasing the availability of the internal protons.<sup>3</sup>

**Acidity of 1,4-Diynes.** At this stage we are still uncertain about the acidity of a skipped diyne. We do know that it is probably far more acidic than a propargylic methylene group, for we did test this qualitatively. Thus, benzylacetylene and 2-dihydropyranyl propargyl ether exchange their ethynyl protons with a basic deuterated medium, but do not appear to isomerize readily. The propargyl ether was treated with potassium hydroxide and deuterium oxide in ethylene glycol-dimethyl ether at 180° for 20 hr without apparent isomerization or deuteration of the propargylic methylene. Literature data on alkylethyne<sup>8</sup> can be used to demonstrate the marked difference in acidity that is effected in going from ethynylmethane to diethynylmethane.

Base-catalyzed deuterium exchange on **1a** indicates that the terminal ethynyl proton exchanges somewhat more rapidly than **1a** isomerizes. If a parallel between proton abstraction ( $k$ ) and acidity ( $K$ ) holds in this instance, we can make two divergent estimates:<sup>4a</sup> the  $pK$  of **1** falls in the range  $pK = 17$ – $21$  of the phenylethyne,<sup>19</sup> or it falls in the range  $pK = 5$ – $13$  of the Pearson and Dillon series of pseudo acids with nitro, cyano, carbonyl, etc., substituents.<sup>4a</sup> The hazards of forcing disparate acids into a Brønsted relation is rather well illustrated here.

Lacking a better model, we are inclined to use the ethynyl hydrogen as a basis for comparison. Therefore, we judge that the  $pK \leq 21$  for the internal methylene of skipped diynes.<sup>4a,19</sup> Clearly, further work is needed to "calibrate" our kinetic acidities on an unambiguous  $pK$  scale.

## Experimental Section

**Materials.** The methods of preparation of the diynes (**1** and **5**) and their properties have been reported in detail previously.<sup>2</sup> On exposure to air and on standing, the diynes discolor. Therefore, **1a** and **c** were distilled before use under reduced pressure and stored in an atmosphere of nitrogen in stoppered containers in Dry Ice. Diyne **1b** was recrystallized from ethanol and stored under nitrogen in a stoppered bottle in the refrigerator.

Fresh sodium ethoxide solutions were prepared as needed from absolute ethanol and sodium. Aliquots of the stock solution were standardized against a known hydrochloric acid solution to the methyl red end point. At the first sign of darkening, these solutions were discarded. Volk deuterium oxide (99.8%) was used in exchange experiments.

**Kinetics.** For a given run, a volumetric flask was flushed with nitrogen and weighed. A known volume of the 1,4-diyne was quickly added to the flask, and the flask was weighed again. Absolute ethanol was then added to give a solution of known concentration. The solutions were then brought to the reaction tempera-

ture in thermostated water baths. Because of small variations from run to run, the extinction coefficient of the diyne was determined on a Beckman DK2 spectrophotometer. Appropriate volumes of the diyne and sodium ethoxide solution were then mixed rapidly in a cell and placed in the thermostated compartment of the spectrophotometer; a record of optical density,  $A$ , vs. time ( $t$ ) at a given wavelength was obtained.

Our reaction sequence usually involved two steps. Since the integrated rate expressions for process 1 are known,<sup>16,17</sup> we could use as input data for a computer program both the estimated  $\epsilon_3$ , pseudo-first-order rate constants ( $k_1'$  and  $k_2'$ ), and the more precise  $\epsilon_1$  and  $\epsilon_2$  to obtain fits to observed  $t$  and  $A$  values. In the first trial, up to 500 iterations with 10% changes in the input parameters were tried for best fit; in a second run, iterations with 1% changes were tried. Output data consisted of:  $\epsilon_1$ ,  $\epsilon_2$ ,  $\epsilon_3$ ,  $k_1'$ , and  $k_2'$ ; the running concentrations of **1**, **3**, and **5**; observed and calculated values of  $A$ ; and the average deviation in  $A$ . For the final set of results, these average deviations were almost all within experimental error. The pseudo-first-order rate constants were converted to  $k_1$  and  $k_2$  (Tables I–III). The mean value at any temperature was corrected for ethanol expansion or contraction, as required.

**Miscellaneous Results.** A number of experiments provided useful reference data. A benzylacetylene-phenylallene (~1:1) sample (1 ml), deuterium oxide (1 ml), sodium methoxide (0.1 g), and DMF (5 ml) were kept at ~25° for 3 days. Infrared spectra indicated that the ethynyl proton ( $\nu_{C=CH}$  3292  $cm^{-1}$ ) was replaced by deuterium ( $\nu_{C=CD}$  2598  $cm^{-1}$ ), but that the benzylic or allenyl protons were unaffected. Similar results were obtained with 2-dihydropyranyl propargyl ether ( $\nu_{C=CH}$  3280,  $\nu_{C=C}$  2108,  $\nu_{C=CD}$  2580,  $\nu_{C=C}$  1970  $cm^{-1}$ ); here, the most forcing conditions used were 47 hr at 125° or 20 hr at 180° on a sample mixture containing the ether (5 ml), potassium hydroxide (~0.2 g), deuterium oxide (5 ml), and ethylene glycol-dimethyl ether (10 ml).

Proton magnetic resonance (pmr) shifts of  $\tau$  3.87 (triplet,  $J = 7$  cps) and  $\tau$  4.98 (doublet,  $J = 7$  cps) in phenylallene, as well as  $\tau$  3.36 reported for triphenylallene,<sup>4c</sup> were useful standards for identification.

**Isomerization of 1-Phenyl-1,4-pentadiene (1a).** The kinetics of isomerization of **1a** posed no serious difficulties;  $\epsilon_1$  and  $\epsilon_2$  were available for the pure compounds. A fair estimate of  $\epsilon_3$  could be obtained when **3a** appeared to go through its maximum concentration, because the first step, **1a**  $\rightarrow$  **3a**, was fast compared with the second step, **3a**  $\rightarrow$  **5a**. Preliminary estimates of  $k_1'$  and  $k_2'$  were obtained from initial and final slopes of a plot of  $\log(A_\infty - A_t)$  vs.  $t$ . After the computations of  $k_1$  and  $k_2$ , as described above, conventional Arrhenius plots gave activation energies for the two steps of compound **1a** (Table I). Activation parameters were also calculated from the standard expression

$$k = (kT/h)e^{-\Delta H^\ddagger/RT}e^{\Delta S^\ddagger/R} \quad (5)$$

In order to identify the allene (**1c**), the isomerization in ethanolic ethoxide was allowed to proceed only part way. The reaction mixture was cooled below  $-70^\circ$ , treated with an excess of solid carbon dioxide, and then diluted with water. The mixture was extracted with ether, the extract was dried with magnesium sulfate, and the ether was evaporated under nitrogen. An infrared spectrum of the residue indicated allenic bands,  $\nu_{C=C}$  1935 and  $\nu_{C=CH_2}$  850  $cm^{-1}$ .<sup>20</sup> The pmr spectrum had a peak at  $\tau$  5.0 (doublet,  $J = 7$  cps) for the terminal hydrogen. The internal protons are part of an  $AB_2$  system in which the line intensity and couplings are those expected for  $J/(\nu_A - \nu_B) \simeq 0.19$ ;<sup>21</sup> a quartet is found consisting of lines at  $ca. \pm 7$  and  $\pm 0.7$  cps centered at  $\tau$  4.4.

The ionization of the ethynyl proton, as well as the isomerization, were studied as follows. A mixture of **1a** (4 g, 0.027 mole), deuterium oxide (4 g, 0.2 mole), anhydrous sodium carbonate (1.5 g, 0.014 mole), and anhydrous ethylene glycol-dimethyl ether (30 ml, distilled from sodium) was agitated for 48 hr. The mixture was extracted with hexane; the extract was dried with magnesium sulfate and filtered, and the solvent evaporated under nitrogen. The infrared spectrum of the residue had the bands  $\nu_{CH}$  3310 and  $\nu_{CD}$  2600  $cm^{-1}$  of about equal intensity, while the characteristic internal methylene frequency,  $\nu_{CH_2}$  1313  $cm^{-1}$ , of **1a** was essentially unchanged; weak allenic carbon-hydrogen bands at 1935 and 850  $cm^{-1}$  were in evidence. The pmr spectrum confirmed the presence of the allene. Purification of the residue by vacuum distillation (62°, 0.15 mm) appeared to give chiefly **1a** and **1a** deuterated at the ethynyl carbon. A proton count of the pmr spectrum for

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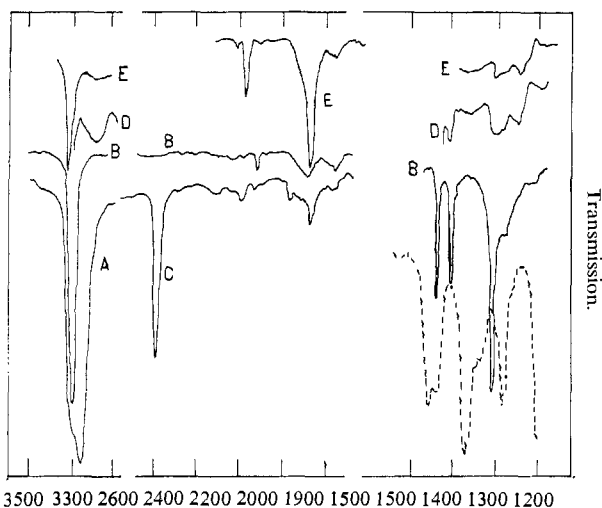


Figure 2. Portions of the infrared spectrum of  $C_6H_5C\equiv C-CH_2-C\equiv CH$  (**1a**) under various conditions. Note the shifts in the vertical scale of transmission. The dotted line is a part of the triethylamine (liquid film) spectrum. A, compound **1a** in ethylene glycol-dimethyl ether; the ethynyl proton is hydrogen bonded; B, pure **1a** (liquid film); C, partially isomerized **1a** (liquid film) after treatment with sodium carbonate and deuterium oxide in ethylene glycol-dimethyl ether for 24 hr at *ca.* 25°; the bands,  $\nu_{C-H}$ ,  $\nu_{C=C-C=C}$ , and  $\nu_{C=C=C}$  have appeared; D, triethylamine and **1a** after 8 min at 65°; the intensity of  $\nu_{CH_2}$  of **1a** appears to be diminished, and a hydrogen bonding band at 3180  $cm^{-1}$  has appeared; E, triethylamine and **1a** after 28 hr at 65°;  $\nu_{CH_2}$  and  $\nu_{C=C}$  of **1a** have essentially disappeared, and  $\nu_{C=C-C=C}$  and  $\nu_{C=C=C}$  have appeared. The spectra of D and E were taken on liquids run against a reference sample of triethylamine.

phenyl, methylene, and terminal protons indicated 5:2:0.76, or the incorporation of  $\sim 0.24$  deuterium atom in the terminal position. Under the reaction conditions of this experiment, it appears that the rate of terminal proton exchange is comparable to, and possibly slightly higher than, the rate of isomerization. In passing, we note that in ethylene glycol-dimethyl ether, **1a** has a broad band at 3240  $cm^{-1}$ , presumably for the hydrogen bond  $\equiv C-H \cdots O <$  (Figure 2).

In a second exchange experiment of the type just described, we used triethylamine instead of sodium carbonate. Again, deuterium exchange at the terminal carbon and allene formation were established from infrared spectra of the products.

The third experiment shed further light on the mechanism. Freshly distilled diyne **1a** (2 g, 0.013 mole) was added to a flask which had been flushed with nitrogen and which contained 2 ml of 0.011 *M* potassium *t*-butoxide in deuterium oxide and ethylene glycol-dimethyl ether (10 ml). The flask was stoppered and put on a shaker for 48 hr. The product was worked up in the usual way. An infrared spectrum of the product indicated that the product was mostly 1-phenyl-1,3-pentadiyne-5- $d_2$ . A broad but weak allenic absorption at  $\sim 1910$ , the absence of  $\nu_{CH_2}$  bands at 1450 and 650  $cm^{-1}$ , and a relatively weak aliphatic  $\nu_{CH}$  2915- $cm^{-1}$  band were noted. The crude residue was distilled under nitrogen and a proton count taken on the pmr spectrum of the product. Instead of the phenyl to methyl proton ratio of 5:3, the observed value was 5:0.86. The pure 1-phenyl-1,3-pentadiyne (**5a**) does not exchange protons for deuterons and is recoverable under these conditions. These results suggest that the protons on the internal methylene of **1a** go into the general proton pool of the solvent before the terminal carbon is protonated.

Some exploratory work on the possibility of following the triethylamine-promoted isomerization of **1a** in dimethylformamide (DMF) by an infrared method brought out another facet of the system. The 1,4-diyne (**1a**) bands (3310 and 1313  $cm^{-1}$ ) disappeared; the allene (**3a**) bands (1935 and 850  $cm^{-1}$ ) appeared and disappeared; and a 1,3-diyne (**5a**) band (2190  $cm^{-1}$ ) appeared (Figure 2). In addition, there was a broad absorption in **1a** at  $\sim 3180$   $cm^{-1}$ , which we have also found in phenylacetylene ( $\sim 3180$   $cm^{-1}$ ), and may be ascribed to hydrogen bonding of the type  $\equiv C-H \cdots N(C_2H_5)_3$ . This band appears to have no parallel or analog in the internal methylene of **1a**, in the allene **3a**, or in the diyne **5a**.

At first glance, one might be inclined to use the obvious hydrogen bonding to the ethynyl hydrogen and its apparent absence to the internal methylene of **1a** as a criterion of relative acidity. Unfortunately, the carbon-hydrogen stretching frequency for the internal methylene is sufficiently weak so that even a large effect on it might not be evident. The characteristic wagging frequency for this internal methylene,  $\nu_{CH_2}$  1313  $cm^{-1}$ , appears to decrease in intensity markedly on mixing **1a** and triethylamine, while the ethynyl proton frequency,  $\nu_{C-H}$  3310  $cm^{-1}$ , seems to disappear much more slowly.

**Isomerization of 1,5-Diphenyl-1,4-pentadiyne (1b).** Since the two steps of the isomerization, **1b**  $\rightarrow$  **3b**  $\rightarrow$  **5b**, had comparable rates,  $\epsilon_3$  was estimated as follows. Plots of  $\log(A_\infty - A)$  vs.  $t$  were made, and the linear portions at large  $t$  were extrapolated back to small  $t$ . Runs in which the initial concentration of diyne was the same but the ethoxide was different came to a common point (approximately). This gave a value for  $\log(A_\infty - A_3)$ . Since  $A_\infty$  could be measured,  $\epsilon_3$  could be obtained from  $A_3$ . The slopes of these plots at large  $t$  give us estimates of  $k_2'$ . This and  $t_{max}$ , the time at which the concentration of **3b** was a maximum, allowed us to estimate  $k'$  from eq 2. These  $k'$  values served as input data in the computer calculation.

**Isomerization of 1-Phenyl-1,4-nonadiyne (1c).** As pointed out earlier, sequence 3 appeared appropriate for **1c**. The rate constants of the first and second steps ( $k_1$  and  $k_{2,3}$ ) are sufficiently different so that they could be evaluated as described for **1a**. It should be noted that here the second step has been tentatively assigned to the interconversion of two ethynylallenes; several more steps bring us to the "final" product, the conjugated diyne **5c**. Unlike the other conjugated diynes, **5c** appears to react in basic solution. By following the change in the ultraviolet spectrum at 244.5  $m\mu$ , we were able to obtain a rate constant. Upon acidification with acetic acid, the ultraviolet spectrum of the solution remained unchanged. Since **5c** may be obtained from **1c** in basic solution under preparative conditions, we ascribe the gradual change in the ultraviolet spectrum of **5c** to the production of a compound—not a carbanion—in low concentration and with a large  $\epsilon$ ; very tentatively, this has been given as **6c** in sequence 3. The spectral changes in  $\epsilon$  for **5c** at four wavelengths ( $m\mu$ ) are: 288.5 (4186  $\rightarrow$  4219), 272 (5333  $\rightarrow$  5265), 257.5 (3781  $\rightarrow$  5333), and 244.5 (2059  $\rightarrow$  6244).

When the ethoxide-promoted isomerization in ethanol of **1c** was interrupted, and the solution worked up as described for **1a**, we could demonstrate the presence of the allene **3c**. The product had allenic infrared bands at 1945 and 870  $cm^{-1}$ . The pmr evidence was tentative rather than definitive. In addition to peaks of **1c** and **5c**, peaks in the allenic region were weak and could only be detected at high gain. One of the products had what appeared to be a doublet at  $\tau$  3.8 ( $J = 7$  cps) and a multiplet ( $\tau \sim 4.5-4.8$ ); these resonances could in part be assigned to **3c'**. The product of another experiment lacked the  $\tau$  3.8 peak, and had a different multiplet ( $\tau$  4.45-4.73) which could in part be assigned to **3c**.

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