equation[15] gave an activation energy of 36.1 ± 3.6 kcal/mol for this rearrangement. Calculation of the entropy of activation[16] using this activation energy gave -7.5 cal deg^{-1} mol^{-1}.

Discussion

McLean and Haynes[5] have previously reported $\Delta S^{\ddagger} = -10$ eu for the [1,5]-hydrogen rearrangement of 1-methylcyclopentadiene and a $\Delta S^{\ddagger} = -4$ eu for the hydrogen migration process in 1,2-dimethylcyclopentadiene, while Roth[6] reported $\Delta S^{\ddagger} = -12$ eu for 5*H*-perdeuteriocyclopentadiene. Although phenyl migrations have not been studied kinetically in the cyclopentadiene system, there should be similar $\Delta S^{\ddagger}$ values observed for phenyl migrations in this system as have been observed for hydrogen migrations. Studies performed on hydrogen and phenyl migrations in substituted indene systems[12] have shown the need for justifying $\Delta S^{\ddagger}$ values obtained for phenyl migrations which differ drastically from the $\Delta S^{\ddagger}$ values obtained for hydrogen migrations in similar systems. In the cyclopentadienol system no kinetic studies have been performed on either hydrogen or phenyl migrations; however, it is expected that the values of $\Delta S^{\ddagger}$ observed in this system for hydrogen and/or phenyl migrations should correspond with the $\Delta S^{\ddagger}$ values reported in both the cyclopentadiene and indene systems for hydrogen and/or phenyl migrations. Thus the values of $\Delta S^{\ddagger} = -7.5$ eu reported here for [1,5]-phenyl migration in 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol seems well within the region of $\Delta S^{\ddagger}$ values expected for rearrangements of hydrogen or phenyl in five-membered ring diene systems.[17]

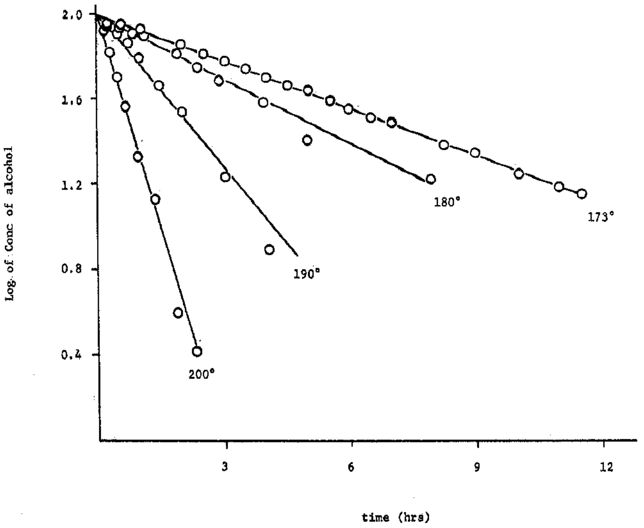


Figure 1.—Variation with time of the logarithm of the concentration of alcohol 1 at 173, 180, 190, and 200°.

The results reported here in isoamyl and diphenyl ether combined with our initial results in DMSO reported earlier[1] indicate that the observed phenyl migration is not solvent dependent. In addition, since previously reported results[1] indicate that this rearrangement proceeds without any ionic or radical character, it appears that the transition state for this phenyl shift is similar to the proposed transition state for sigmatropic hydrogen migrations[17,18] and that the phenyl rearranges *via* a true sigmatropic mechanism in 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol.

Registry No.—1, 2137-74-8; 2, 34759-47-2.

Acknowledgments.—We wish to extend our sincere appreciation to Dr. Harold McNair for allowing us the use of his glpc equipment, and to Mr. Benjamin Esquivel-Hernandez for his technical assistance. We also wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

---

(15) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1965, p 23.

(16) J. H. Bunnett in "Technique of Organic Chemistry," Vol. VIII, Part I, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience, New York, N. Y., 1961, p 201.

(17) K. W. Egger, *J. Amer. Chem. Soc.*, **89**, 3688 (1967).

(18) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 114–132.

The Mechanism of the Base-Catalyzed Prototropic Propargylic Rearrangement in Vicinal Diamines[1]

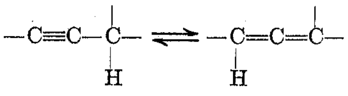
JOHN H. WOTIZ,* PAUL M. BARELSKI, AND DAVID F. KOSTER

Department of Chemistry and Biochemistry,
Southern Illinois University, Carbondale, Illinois 62901

Received May 23, 1972

The relative rates of rearrangement of 3-hexyne with a strong base in various amines were ascertained, and vicinal diamines, particularly ethylenediamine (EDA), were found to be the most effective solvents. A concerted mechanism involving the EDA anion and the propargyl group in a nine-membered ring transition state is suggested. Since, in the presence of EDA-d_4, the rate of deuterium incorporation into the rearranged products parallels closely the rate of rearrangement, an intramolecular hydrogen transfer is not likely the preferred reaction path.

The base-catalyzed propargylic rearrangement is well known and documented.[2] Jacobs[3] equilibrated the isomeric pentynes with alcoholic potassium hydroxide at 175°. The reaction mixture consisted of 1.3% 1-pentyne, 3.5% 1,2-pentadiene, and 95.2% 2-pentyne.



$$-C{\equiv}C-\overset{|}{\underset{\underset{\displaystyle H}{|}}{C}}- \rightleftharpoons -\underset{\underset{\displaystyle H}{|}}{C}{=}C{=}\overset{|}{C}-$$

---

(1) Abstracted in part from the Ph.D. Thesis of Paul M. Barelski, Southern Illinois University, 1972.

(2) J. H. Wotiz in "Chemistry of Acetylenes," H. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 7.

(3) T. L. Jacobs, R. Akawie, and R. G. Cooper, *J. Amer. Chem. Soc.*, **73**, 1273 (1951).

Table I

The Half-Time of Rearrangement of 3-Hexyne as a Function of the EDA-Sodium Amide Mixing Time

Mixing time, min	Half-time, min
0	12
5	11
15	9
30	0.5
60	0.5

Smadja[4] found equilibrium mixtures of heptynes and allenic heptadienes in alcoholic potassium hydroxide at 80–200°. However, the conjugated heptadienes were the major products when polar aprotic solvents (dimethyl sulfoxide, hexamethylphosphoric triamide, dimethylformamide, and dioxane) were used with potassium *tert*-butoxide.[4] The composition of the latter rearrangement mixtures represented the relative thermodynamic stabilities.

Wotiz[5] demonstrated that each of the isomeric normal C_6 acetylenes and allenes gave the same mixture when treated with sodium amide in ethylenediamine (EDA) at room temperature. The disproportionation time depended on the starting substrate and on the amounts of sodium amide used. Different quantities of sodium amide produced mixtures of different composition. No conjugated dienes, or other by-products, were observed.

Cram[6] proposed the "conducted tour" mechanism for the 1,3-intramolecular proton transfer in the isomerization of 1,3,3-triphenylpropyne to 1,3,3-triphenylallene. The intramolecularity ranged from 88% in dimethyl sulfoxide–methanol–triethylenediamine to 19% in methanol–potassium methoxide.

The purpose of the present investigation was to establish the mechanism of the base-catalyzed prototropic propargylic rearrangement of 3-hexyne in EDA.

Results and Discussion

Sodium amide or *n*-butyllithium (1.6 *M* in hexane) did not rearrange 3-hexyne within 72 hr at room temperature. Similarly, EDA alone did not rearrange 3-hexyne. However, the combination of such bases and EDA rapidly brought about rearrangement without by-products.

The relative rate of the 3-hexyne rearrangement was found to be a function of the time sodium amide and amine were allowed to interact prior to the addition of 3-hexyne. The rates were expressed as half-times, the time in which 50% of the starting 3-hexyne rearranged. Such values were secured by plotting experimental data, 3-hexyne (%) *vs.* reaction time (min). For EDA, the half-time decreased from 12 to 0.5 min (Table I) as the sodium amide and EDA interaction time increased. The lower limit was approached after 30 min of mixing time.

Recently it was found[7] that strong bases such as sodium amide or *n*-butyllithium react with EDA in the absence of air to yield the radical ion of pyrazine (I), which forms a gold-colored solution. However,

I

the presence of traces of air also produces an intense blue-colored product of unknown constitution.[7]

The rate of formation of the pyrazine radical ion and/or the blue-colored product seemed to parallel closely the enhancement in the rate of rearrangement of hexyne brought about by the product of the interaction of a strong base (*e.g.*, sodium amide) with EDA. The possibility that the propargylic rearrangement in EDA was brought about by I, and/or the blue-colored product, was eliminated when I and the blue compound, prepared directly from pyrazine,[8] failed to rearrange hexyne in EDA.

The rearrangement of hexyne was actually brought about by the salt of ethylenediamine (NaEDA), the first reaction product of sodium amide with EDA. This was demonstrated by measuring the rate of evolution of ammonia. Since sodium amide is only sparingly soluble in EDA, time was required before an effective concentration of NaEDA in EDA was formed.

$$H_2NCH_2CH_2NH_2 + NaNH_2 \longrightarrow Na^+EDA^- + NH_3$$

N-Lithoethylenediamine (LiEDA), which forms rapidly from *n*-butyllithium and EDA, was observed to rearrange hexyne as quickly as LiEDA prepared from lithium and EDA. However, the reaction product of sodium and EDA contained only small amounts of NaEDA and was not an effective rearrangement catalyst. This was in agreement with the earlier findings.[9]

In order to get an additional insight into the mechanism of the base-catalyzed rearrangement of 3-hexyne, the relative rates of rearrangement were also established in various amines and diamines (Table II). The "equilibrium" composition of the rearrangement products was always the same, irrespective of the amine used. With the molar ratio of 3-hexyne:sodium amide:amine of 18:1:18, the products consisted of 2-hexyne (80%), 3-hexyne (12%), 1-hexyne (4%), and 2,3-hexadiene (4%).

There was a definite rate enhancement in the presence of vicinal diamines of which EDA produced the fastest rearrangement. To show that this was due to more than the concentration factor involving twice as many amine groups and protons, the reaction with cyclohexylamine and 1,2-diaminocyclohexane was run with an equivalent amount of the amine function present. As the amount of cyclohexylamine was doubled, the half-time was almost halved. However, the half-time was still very high compared to the diamine (Table II). Similarly, 1-aminopropane gave no rearrangement after 100 hr, while 1,2- and 1,3-diaminopropane caused rearrangement of 3-hexyne with half-times of 3 and 15 min, respectively.

The half-times were found to increase with increased alkyl substitution on EDA. Steric crowding of the

---

[4] W. Smadja, *Ann. Chim. (Paris)*, **10**, 105 (1965).

[5] J. H. Wotiz, W. E. Billups, and D. T. Christian, *J. Org. Chem.*, **31**, 2069 (1966).

[6] D. J. Cram, F. Willey, H. P. Fischer, H. M. Relles, and D. A. Scott, *J. Amer. Chem. Soc.*, **88**, 2759 (1966); D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, Chapter V.

[7] J. H. Wotiz, R. D. Kloepfer, P. M. Barelski, C. C. Hinckley, and D. F. Koster, *J. Org. Chem.*, **37**, 1758 (1972).

[8] A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962).

[9] L. Reggel, S. Friedman, and I. Wender, *J. Org. Chem.*, **23**, 1136 (1958).

TABLE II

3-HEXYNE REARRANGEMENTS[d]

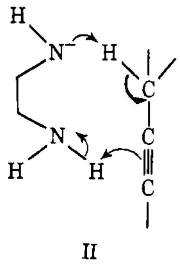
Amine	Base[a]	Half-time, min
Ethylenediamine	$NaNH_2$	0.5
Ethylenediamine	LiEDA	0.7
Ethylenediamine	Na and EDA reaction product	*c*
1-Aminopropane	$NaNH_2$	*c*
1,3-Diaminopropane	$NaNH_2$	15.0
1,6-Diaminohexane	$NaNH_2$	450.0
N,*N*′-Dimethylethylenediamine	$NaNH_2$	20.0
N,*N*-Dimethylethylenediamine	$NaNH_2$	12.0
N-Methylethylenediamine	$NaNH_2$	2.5
1-Methyl-1,2-diaminopropane	$NaNH_2$	44.0
1,2-Diaminocyclohexane, 36% *cis* and 64% *trans*	$NaNH_2$	9.3
Cyclohexylamine	$NaNH_2$	240.0
Cyclohexylamine	$NaNH_2$	145[b]
Trimethylethylenediamine	$NaNH_2$	540.0
Tetramethylethylenediamine	$NaNH_2$	2400.0
Aziridine	$NaNH_2$	4.5
Pyrrolidine	$NaNH_2$	63.0
Piperidine	$NaNH_2$	1500.0
Diethylamine	$NaNH_2$	*c*
Aniline	$NaNH_2$	*c*
Pyridine	$NaNH_2$	90.0
Tributylamine	$NaNH_2$	*c*

[a] $NaNH_2$ was stirred with the amine for 30 min before the addition of 3-hexyne. [b] Mole ratio: 3-hexyne, 18; $NaNH_2$, 1; amine, 36. [c] No arrangement after 100 hr. [d] Mole ratio: 3-hexyne, 18; base, 1; amine, 18.

active amine sites, as well as the decrease in the number of available protons, were likely reasons for the slower rearrangements in secondary and tertiary diamines. As the separation of the diamine function was increased, the half-times increased (Table II).

The reaction of sodium amide in diethyl- or diisopropylamine with 3-hexyne was too slow to observe even after 100 hr. In cyclic amines the half-time increased markedly as the ring size increased. Aniline and other aromatic amines failed as rearrangement solvents. The rate enhancement in pyridine over other tertiary amines may be due to its more effective solvating power.

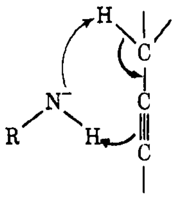
A mechanism is suggested that involves a concerted reaction with the diamine anion in a nine-membered ring transition state (II). Molecular models of II show



II

a favorable geometry. The linearity of the acetylene and allene preclude a ring size less than eight.[10]

A concerted mechanism with a monoamine anion involving a six-membered ring transition state (III) seems unlikely from examination of the models. However, this does not rule out a stepwise reaction of



III

base abstraction and proton recapture at the allenic position, or the conducted tour mechanism[6] by the base.

Valuable information concerning the mechanism of the proton transfer in the propargylic rearrangement was secured using deuterated EDA and *n*-butyllithium (BuLi). Starting with 3-hexyne these reagents produced rearranged products which contained deuterium. A mixture of EDA-d_4 (N–D) and 3-hexyne did not exchange deuterium and rearrangement was not noticed within 20 hr.

Since 1-hexyne does not appreciably rearrange within 12 hr[5] in the presence of EDA and strong base, it was treated with EDA-d_4 and BuLi to establish how much deuterium was exchanged without rearrangement. The terminal proton in 1-hexyne is relatively acidic and exchanges rapidly with solvent.[11] Mass spectroscopy was used in determining how many protons exchanged at the nonterminal position. The major peak of the 1-hexyne mass spectrum, recorded at 10 eV, was due to the hexynyl ion, $CH_3CH_2CH_2CH_2C{\equiv}C$, arising from the fragmentation of the terminal hydrogen (see also ref 12).

Table III shows that exchange occurred in the nonterminal position when 1-hexyne reacted with BuLi and EDA-d_4 for 5 min. The per cent of deuterium was calculated from the mass spectra assuming that the labeled and unlabeled species fragmented identically, and correcting the parent peaks for the P + 1 and P − 1 peaks.[13]

TABLE III

PER CENT OF DEUTERIUM IN 1-HEXYNYL IONS FROM THE MASS SPECTRA OF THE REARRANGEMENT MIXTURES FROM THE REACTION OF 1-HEXYNE WITH BuLi AND EDA-d_4

Sample time	% d_0	% d_1	% d_2	% Total D
5 min	36.7	63.3	0	6.9
18 hr	27.9	72.1	0	8.1

The positions of exchange in 1-hexyne were determined from the HA-100 nmr spectra. The data in Table IV shows that the more acidic acetylenic and

TABLE IV

POSITION OF PROTON EXCHANGE IN 1-HEXYNE

Position	Number of protons	Number of protons exchanged[a]
Acetylenic	1.0	0.7
Propargylic	2.0	0.4
Methylenes	4.0	0
Methyl	3.0	0

[a] After reacting with BuLi-EDA-d_4 for 5 min.

---

(10) W. R. Moore and H. R. Ward, *J. Amer. Chem. Soc.*, **85**, 86 (1963).

(11) J. Dale in "Chemistry of Acetylenes," Marcel Dekker, New York, N. Y., 1969, Chapter 1.

(12) G. J. Zwolinski (Director), American Petroleum Institute Research Project 44, mass spectral data, 1969, serial numbers 1811–1813.

(13) K. Biemann, "Mass Spectrometry: Organic Chemical Applications," McGraw-Hill, New York, N. Y., 1962.

TABLE V

RESULTS FROM THE REARRANGEMENT REACTION OF 3-HEXYNE WITH EDA-d_4 AND BuLi

Sample time, min	Per cent of labeled species (mass spectrum)							% D	Per cent of isomers (vpc)		
	d_0	d_1	d_2	d_3	d_4	d_5	d_6		2-Hexyne	2,3-Hexadiene	3-Hexyne
0.5	92.0	2.9	5.1					1.3	1.9	6.5	91.6
1	80.5	7.4	9.5	2.6				3.5	8.5	13.8	77.7
2	44.8	16.2	15.9	11.8	9.1	2.2		13.1	37.6	13.2	49.2
5	8.6	15.1	23.9	26.7	18.7	5.6	1.3	25.5	79.7	5.8	14.5

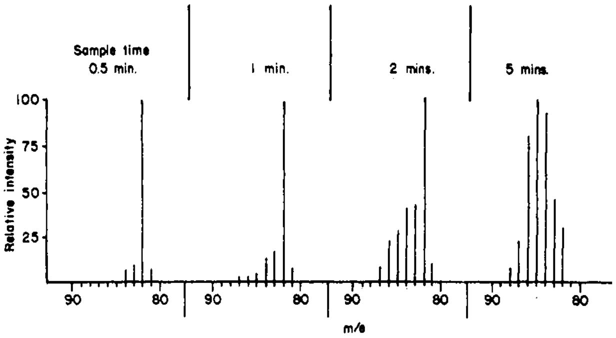


Figure 1.—Mass spectra from the reaction of 3-hexyne-EDA-d_4-BuLi.

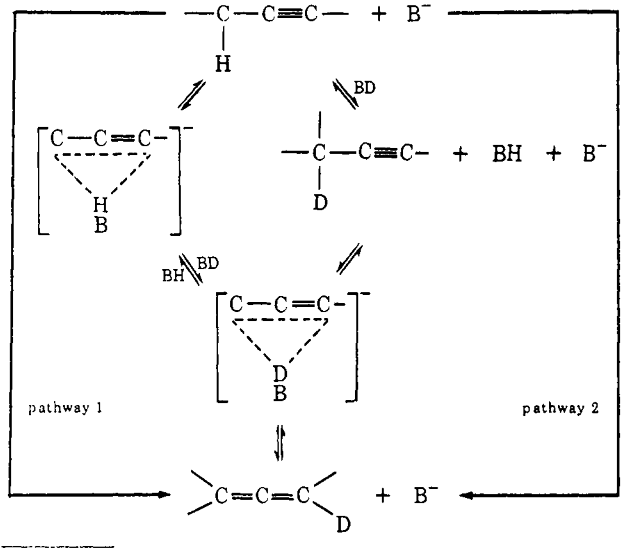
propargylic protons exchanged and 6.8% of deuterium (Table III) was incorporated at the propargylic positions. The lack of exchange in the methyl and methylene positions is in agreement with the findings of Shatenshtein,[14] who studied the exchange of hydrocarbons in deuterated potassium amide–amine systems.

In the rearrangement of 3-hexyne using BuLi and EDA-d_4, there was good correlation between the amount of rearrangement and the amount of deuterium incorporated into the rearranged mixture (Figure 1 and Table V). The amount of incorporated deuterium increased as the amount of 3-hexyne decreased. The per cent of d_0 species and the per cent of 3-hexyne may be within the limit of accuracy of the experiment.

It is likely that some deuterium exchange occurred independently of rearrangement in all the isomers, as shown with 1-hexyne. Thus, beside the pathway 1 in Scheme I, it is possible that some deuterium was incorporated through exchange followed by an intramolecular (conducted tour[6]) rearrangement, as in pathway 2.

SCHEME I

REARRANGEMENT AND DEUTERIUM INCORPORATION



On the basis of the relative amounts of deuterium incorporated in the 1-hexyne and 3-hexyne reactions (Tables III and IV), pathway 1 is more likely. Assuming the 6.9% deuterium incorporation in 1-hexyne without rearrangement to be general and applicable to 3-hexyne, there could be no more than twice that (13.8% deuterium) incorporated by exchange in 3-hexyne, which has twice as many propargylic protons. Table V shows that after 5 min 25.5% deuterium was incorporated during the 3-hexyne rearrangement.

The question of distinguishing between a concerted mechanism (II) and the intermolecular proton abstraction and proton (dueteron) recapture (pathway 1) cannot be answered at this time; most probably both occur in the EDA case.

Experimental Section

Vapor phase chromatograms were obtained using a Varian Aerograph Model 1860 chromatograph with a flame ionization detector, capillary splitter, and a Varian Aerograph Model 20 strip recorder with disc integrator.

All of the hexyne rearrangement mixtures were separated on a 200 ft × 0.01 in. (i.d.) stainless steel capillary column coated with (HHK) hexadecane, hexadecene, and k-cel (Perkin-Elmer).

The amines and diamines were analyzed on a 10 ft × 0.25 in. (o.d.) aluminum column packed with (DCKOH) 10% D.C. 710 silicone, 19% KOH on Chromosorb W.[15]

All mass spectra were obtained using a Consolidated Electrodynamics Corp. Model 21-104 mass spectrometer at both 10 and 70 eV. Nuclear magnetic resonance spectra were recorded on a HA-100 spectrometer.

Sodium amide (Robert's Chemicals, Inc.) was weighed into ampoules in the dry box (nitrogen atmosphere) and sealed.

n-Butyllithium (Foote Mineral Co.), 1.6 *M* in hydrocarbon solvent (hexane, pentane, benzene, and toluene), was always transferred in the drybox with a syringe.

Lithium wire and sodium (Matheson Coleman and Bell) were used as purchased, and were cut and weighed under benzene.

Ethylenediamine (Aldrich Chemical Co.), distilled (bp 116°) from sodium metal, was 99.9% pure (vpc).[7]

All of the other amines and diamines (Matheson Coleman and Bell or Aldrich Chemical Co.) were distilled from sodium prior to use.

Hexyne Rearrangements.—In the drybox, the amine was weighed into a 25-ml erlenmeyer flask containing a magnetic stirring bar. The base was added and the flask was capped with a rubber serum cap. Several of the vicinal primary or secondary diamines developed intensely colored solutions after a few minutes.[7] After this mixture stirred for 30 min outside the drybox, 3-hexyne was added with a syringe. The reaction was then stirred, sampled at intervals using a syringe to withdraw a portion through the rubber serum cap, and quenched with H_2O in an ice bath. The organic layer was separated, washed once each with 10% HCl and H_2O, and dried over sodium sulfate. In reactions run under vacuum samples of the volatile components were collected by vacuum transfer (precluding any 1-hexyne[5]). The mixtures were analyzed by vpc.

The purity of amide was determined by titration of the am-

---

[14] A. I. Shatenshtein, *Advan. Phys. Org. Chem.*, **1**, 178 (1963).

[15] E. D. Smith and R. D. Radford, *Anal. Chem.*, **33**, 1160 (1961).

monia liberated from the reaction with H_2O.[16] The amount of sodium amide, indicated in moles, was corrected for active amide present. The purity (55–64%) varied according to source and handling conditions. The equilibrium composition of the rearranged products was invariant to the amine or base used.

Reaction of Lithium and Sodium with EDA.—EDA (50 ml, 0.83 mol) and lithium wire (0.5 g, 0.07 mol) were allowed to react using the procedure described by Wender and coworkers.[9] The mixture immediately turned dark blue. It was refluxed and stirred for 30 min, after which the color discharged to cloudy white. On cooling, the condenser was replaced by a rubber stopper. Immediately, the solution turned light blue (different from the dissolved metal color) and on stirring, turned blue-purple.[7] Upon heating, the blue-purple color discharged and reappeared on cooling.

Sodium metal, when treated with EDA in a similar manner, gave a dark, viscous mixture. Numerous higher molecular weight amines were identified by vpc analysis.[7]

Preparation of Ethylenediamine-d_4 (94% N-D).—EDA (10 g, 0.17 mol) was stirred with D_2O (75 g, 3.7 mol) for 2 hr. The solution, cooled in a Dry Ice–acetone bath, was treated with sodium metal until the diamine layered out. The diamine (top layer) was separated in the same manner and was dried over sodium metal for 24 hr. Vacuum transfer gave 6.0 ml, nmr (CCl_4) δ 2.62 (s, 17, methylene), 0.99 (s, 1, NH).

Reaction of Sodium Amide with EDA.—EDA (78.3 mmol) was vacuum transferred into an evacuated flask containing sodium amide (5.7 mmol). The stirred mixture evolved ammonia (4.0 mmol), which was identified by ir and mass spectrometry. Quantitative data was obtained by using a volume calibrated vacuum manifold and a mercury manometer.

3-Hexyne and Pyrazine Radical Anion.[8]—The pyrazine radical anion was prepared by vacuum transferring 15 ml of 10^{-2} *M* pyrazine in THF to 0.015 mol of *n*-butyllithium.[7] 3-Hexyne was vacuum transferred and the mixture was stirred for 100 hr. No rearranged hexyne was found.

Reactions of Deuterated Ethylenediamine. A.—EDA-d_4 (2.0 ml, 28 mmol), BuLi (2.0 ml, 3.2 mmol), and 3-hexyne (2.0 ml, 18 mmol) were allowed to react. The reaction was sampled by vacuum transfer. The vpc and mass spectral results are found in Table V.

B.—EDA-d_4 (0.8 ml, 11 mmol), BuLi (1.0 ml, 1.6 mmol), and 1-hexyne (1.0 ml, 8.8 mmol) were mixed. A sample was vacuum transferred 5 min after thawing: nmr (CCl_4) δ 2.12 (m, 1.6, propargylic), 1.86 (t, 0.3, acetylenic), 1.47 (m, 4.0, methylene), 0.91 (m, 3.0, methyl); mass spectrum *m/e* (rel intensity) 81 (55.3), 82 (100), 83 (7.2). A second sample was taken after 18 hr, mass spectrum *m/e* (rel intensity) 81 (36.5), 82 (100), 83 (7.9). Neither sample showed any rearrangement (vpc).

C.—EDA-d_4 (0.5 ml, 7 mmol) and 3-hexyne (0.5 ml, 4 mmol) were stirred for 20 hr. The 3-hexyne did not rearrange (vpc) or incorporate any deuterium (mass spectrum).

Registry No.—3-Hexyne, 928-49-4; EDA, 107-15-3; 1-hexyne, 693-02-7; EDA-d_4, 37164-19-5; BuLi, 109-72-8.

---

[16] D. A. Skoog and D. M. West, "Analytical Chemistry," Holt, Rinehart, and Winston, New York, N. Y., 1965, p 308.

Electrophilic Bromination of Aromatic Conjugated Olefins. II. The Mechanism of the Dual-Path Additions in Stilbene Bromination. Evidence from Multiple Substituent Effects for Carbonium Ion Intermediates[1]

JACQUES-EMILE DUBOIS* AND MARIE-FRANÇOISE RUASSE

Laboratoire de Chimie Organique Physique de l'Université de Paris VII, associé au C. N. R. S., 75 Paris 5°, France

Received July 21, 1972

Kinetic data for the bromination of disubstituted stilbenes, $XC_6H_4C_xH{=}C_yHC_6H_4Y$, in methanol are interpreted in terms of the dual-path addition mechanism in which two pathways (with rate constants k_x and k_y, respectively), leading to discrete carbonium ions, C_x^+ and C_y^+, are involved. The nonlinear free energy relationship corresponding to this scheme is $\log (k/k_0) = \log [(k_x + k_y)/k_0] = \log [10^{\rho_\alpha\sigma_X^+ + \rho_\beta\sigma_Y} + 10^{\rho_\alpha\sigma_Y^+ + \rho_\beta\sigma_X}]$, where ρ_α and ρ_β are the reaction constants for aryl substituents α and β to the charged center, respectively. Values of ρ_α (-5.07) and ρ_β (-1.40) are obtained by simplification of the above equation using sets of compounds for which k_x or k_y can be neglected. These values are found to be applicable, in a reactivity range of six powers of ten, to compounds for which k_x and k_y are of comparable magnitude. However, substituent effects are only approximately additive; *i.e.*, substituents do not act wholly independently, and agreement between calculated and experimental reactivities is occasionally unsatisfactory. Nevertheless, it is possible to exclude any significant contribution from a bromonium ion pathway for this reaction. The bromination of the same stilbenes in carbon tetrachloride, where intermediates are bromonium-ion-like, reveals a dramatically different situation, there being an additive linear free-energy relationship, $\log (k/k_0) = \rho\Sigma\sigma$, which shows that in this solvent the structures of the transition states are symmetrical, whereas, in methanol, the transition states are carbonium-ion-like.

For electrophilic additions involving carbonium ion intermediates, a dual-path mechanism is postulated since the attacking electrophile can, in principle, choose for σ bonding either one of the two olefinic carbon atoms in the rate-determining step. The feasibility of this mechanism has been evaluated by studying the monosubstituted trans stilbenes, $XC_6H_4C_xH{=}C_yHC_6H_5$, whose bromination is assumed to lead to two discrete intermediates, the carbonium ions C_x^+ and C_y^+ (1 and 2; Y = H), by competitive pathways, referred to as the C_x and C_y paths. The kinetic data have been interpreted in terms of a nonlinear free-energy relationship derived from this mechanism by application of the Hammett equation to each pathway. Circumstantial evidence for the validity of this scheme is provided by the agreement between the regioselectivity of attack by methanol and the calculated relative importance of each pathway. However, the assumption regarding the structures of the intermediates cannot be verified beyond doubt. Only for the C_x path can it be stated with certainty that the intermediate is a carbonium ion; the effect of the substituent X in this path is expressed by ρ_α, whose value is closely related to those obtained for reactions with benzylic cationic intermediates. For the intermediate of the C_y path, the value of ρ_β requires only that the

---

[1] M. F. Ruasse and J. E. Dubois, *J. Org. Chem.*, **37**, 1770 (1972). Also regarded as Part XXXV of the series "Reactivity of Unsaturated Compounds: Bromination." Part XXXIV: J. E. Dubois, J. Guillo, and X. Q. Huynh, *J. Chim. Phys.*, in press.