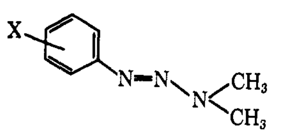
triazenes (**1**). These results establish that the rates of rotation around the N–N bond for these compounds are measurable by standard nmr methods and that the *exchange-averaging process obeys a linear free energy relationship.*



1

The proton spectra of **1** show a single methyl resonance at magnet temperature. Cooling the sample results first in a broadening of the methyl signal and then in formation of a widely separated doublet. The pertinent nmr and kinetic data are given in Table I.

Table I. Nmr Data[a,b] on the Rotation of **1**

X	T_c, °C	$\Delta\nu_0$, cps	$k(T_c)$, sec^{-1}	$\Delta F^{\neq}(T_c)$	$k(0°)$, sec^{-1}
p-CH$_3$	−33.9	19.2	42.6	12.1	533
H	−22.5	18.5	41.0	12.7	194
p-Cl	−11.3	20.2	44.8	13.3	81.9
m-CF$_3$	5.3	20.0	44.2	14.2	29.3
p-NO$_2$	35.1	20.2	44.8	15.7	5.3

[a] Spectra were taken in chloroform solution at a concentration of 14% (w/w) except for the p-nitro compound which was 7% (w/w). [b] A Varian A-60 equipped with a Varian variable-temperature probe was used to observe the chemical shift as a function of temperature. Temperatures were measured with an accuracy of ±0.8°. A given temperature could be held constant to ±0.1°. Spectra were calibrated by the side-band method, using a frequency counter to measure the side-band frequency. The method described by J. A. Pople, W. S. Schneider, and H. J. Bernstein ("High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 224) was used to calculate τ values. At each temperature no less than six determinations were made, with 15 determinations being made at the point of maximum separation. Arrhenius plots were made using no less than seven temperatures. All slopes gave a correlation coefficient of better than 0.99 when treated by the method of least squares.

Inspection of Table I shows that the $\Delta\nu_0$ values for the series of triazenes are all very similar, and therefore the rates at the coalescence temperature (T_c) are all nearly the same. However, T_c spans a range of almost 70°, progressively increasing in going from X = CH$_3$ to X = NO$_2$. It therefore would be expected that a comparison of rates at the same temperature for the series of triazenes would show a progressive rate decrease with increasing electron withdrawal by the substituent. This is also evident from a comparison of the $\Delta F^{\neq}$ values which progressively increase in going from p-CH$_3$ to p-NO$_2$.

In order to compare rates at the same temperature Arrhenius plots were determined for each compound, and from these data specific rate constants were calculated at both 25 and 0°. The values obtained at 0° are included in Table I. Figure 1 shows a Hammett plot of these data. An excellent linear relationship is observed at both 25 and 0° with a ρ value of −2.01 and −2.03, respectively. This is a gratifying result since a number of previous attempts to systematically correlate the electronic effects of substituents in a variety of nmr exchange processes, such as the rotational rates of amides,[6,7] nitrogen inversion rates,[8,9] and isomerization of iminocarbonates,[10] have not been successful. Inversion or rotational rates and barriers can be markedly affected by steric as well as electronic effects. Nonbonded interactions can destabilize the ground state and thereby lower the barrier[11–14] or these interactions can destabilize the transition state and increase the barrier.[15,16] There should be, however, no significant difference in nonbonded interactions between ground and transition states for the series of triazenes being reported here, and therefore the change in rate should be a function only of the electronic effect of the substituent.

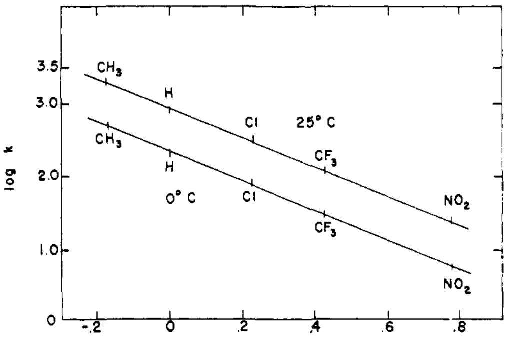


Figure 1. Plot of log k for the rotational rate of 1-aryl-3,3-dimethyltriazenes *vs*. Hammett substituent constants.

The negative slope found for the Hammett plot requires that during the rotational process the electron density at the nitrogen atom bonded to the aryl group decreases in going from ground to transition state. In addition, the relatively large magnitude of ρ suggests that there is a considerable difference in polarization of the ground state compared to the transition state. This is consistent with the view that restricted rotation is due to π overlap between the amino and azo nitrogens in the ground state which is lost when the dimethylamino group is rotated 90° out of the ArN=N plane. The observed change in rate, then, is attributed to the extent by which the substituents influence the difference in π delocalization energy between the ground and transition states,[14] and furthermore this energy difference is linearly related to the substituent.

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(7) C. W. Fryer, F. Conti, and C. Franconi, *Ric. Sci. Rend. Sez.*, [2] **A35**, 788 (1965).

(8) D. L. Griffith and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 4089 (1965).

(9) F. A. L. Anet, R. Trepka, and D. J. Cram, *ibid.*, **89**, 357 (1967).

(10) N. P. Marullo and E. H. Wagener, *ibid.*, **88**, 5034 (1966).

(11) A. T. Bottini and J. D. Roberts, *ibid.*, **80**, 5203 (1958).

(12) F. A. L. Anet and J. M. Osyany, *ibid.*, **89**, 352 (1967).

(13) S. J. Brois, *ibid.*, **89**, 4242 (1967).

(14) J. Sandstrom, *J. Phys. Chem.*, **71**, 2318 (1967).

(15) A. Mannschreck, *Tetrahedron Letters*, 1341 (1965).

(16) H. A. Staab and D. Lauer, *ibid.*, 4593 (1966).

(17) National Aeronautics and Space Administration Predoctoral Fellow.

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Received September 15, 1967

The Case of the Ersatz Aryne. A New Mechanism of Cine-Substitution

Sir:

One of the most characteristic features of the elimination–addition (benzyne) mechanism[1] of nucleophilic

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(1) J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, *J. Am. Chem. Soc.*, **78**, 601 (1956).

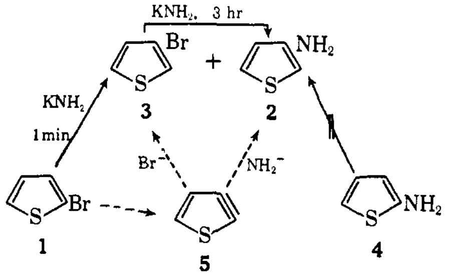
Table I. Reactions of 2-Bromothiophene (**1**) with Potassium Amide[a]

	Reactants, mmoles		Products, mmoles						
Run	KNH_2	**1**	**2**	**3**	*b*	*c*	*d*	*e*	*f*
A	600	100	59	5					
B[g]	0	100	0	0					
C[h]	600	100	14	38					
D	600[i]	100	1	48	4	Tr	Tr		Tr
E	200	100	19	38	1	Tr	Tr		
F[j]	600	100	50	7	1	Tr	Tr		
G[k]	600	100	19	10	11	1	Tr		
H[l]	600	100	3	2	15	4	3	1	1

[a] Unless otherwise noted all reactions were carried out in approximately 500 ml of liquid ammonia at −33° for 15 min. [b] 3,4-Dibromothiophene. [c] 2,3-Dibromothiophene. [d] 2,4-Dibromothiophene. [e] 2,3,4-Tribromothiophene. [f] Thiophene. [g] 96% recovery of **1**. [h] Sodium bromide added, 1 mole. [i] Sodium amide. [j] For 1 min; trace of **1** recovered. [k] −55°, 1 min. [l] −65°, 1 min.

aromatic substitution is the occurrence of cine-substitution.[2] In fact, although other mechanisms leading to this phenomenon are known,[3] it generally has been accepted that "if a strongly basic reagent is involved and if nitro-groups are absent, the occurrence of cine-substitution may reasonably be taken as evidence for the benzyne mechanism."[4] We wish to report an example of a reaction which fulfills the above criteria yet in all likelihood does not proceed *via* a benzyne mechanism.

Treatment of 2-bromothiophene (**1**) under typical benzyne producing conditions[1] (run A, Table I) gives predominantly 3-aminothiophene (**2**)[5] along with a small amount of 3-bromothiophene (**3**).[7] In the absence of amide ion (run B) no reaction occurs. The observed cine-amination is not due to normal substitution, either preceded by the rearrangement of 2- to 3-bromothiophene (**1** → **3**) or followed by rearrangement of 2- to 3-aminothiophene (**4** → **2**), since 3-bromothiophene undergoes (normal) substitution (**3** → **2**) almost 200 times more slowly than the 2 isomer (**1** → **2**), and 2-aminothiophene (**4**)[8] gives no detectable amount of the 3 isomer (**2**) under the reaction conditions (60% recovery).

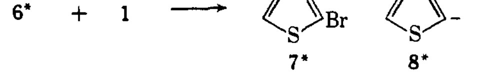


By all the commonly accepted criteria for the occurrence of an elimination–addition mechanism[4,9] the above experiments ought to be interpreted as an addition of amide ion to 2,3-dehydrothiophene (**5**)[10] in the direction expected[11] from the stability of the resulting anion. In apparent support of this conclusion, carrying out the amination in the presence of an excess of sodium bromide (run C) increased the yield of 3-bromothiophene (**3**) at the expense of 3-aminothiophene (**2**), as might be expected if both bromide ion and amide ion were competing for a common intermediate such as **5**.

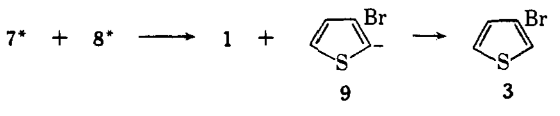
The inadequacy of this interpretation is revealed by the observations that: (i) addition of either sodium chloride or iodide to the reaction mixture does not lead to chloro- or iodothiophenes but once again, as in run C, to increased yields of 3-bromothiophene (**3**), and (ii) addition of *potassium* halides essentially has no influence on the product distribution of the original reaction (run A). These results suggest that the primary function of the sodium bromide in run C is not to compete with amide ion for the aryne **5** but to decrease the concentration of amide ion in solution by precipitating the relatively insoluble[12] sodium amide. This suggestion is substantiated by the fact that, when 2-bromothiophene (**1**) reacts with either sodium amide (run D) or with lower than usual concentrations of potassium amide (run E), 3-bromothiophene (**3**) becomes the major product.

Both this marked dependence of the product distribution on amide ion concentration and the apparent ability of bromide ion to compete with the much more nucleophilic amide ion and ammonia are inconsistent with the intermediacy of an aryne.[9,13] A reasonable alternative explanation for the above results involves transbromination *via* intermediate carbanions (reactions 1–3[14]) similar to that observed in related systems.[15–17] Evidence in favor of such a mechanism in-

(1)[14]



(2)[14]



(3)[14]

includes: (i) the typical[15–17] formation of di- and tribromothiophenes especially at lower reaction times and temperatures (runs E–H), presumably by transbrominations similar to reactions 1–3[14] (note the production of thiophene), and (ii) the conversion of some of these

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(2) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951).

(3) J. F. Bunnett and M. M. Rauhut, *J. Org. Chem.*, **21**, 944 (1956).

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(5) Isolated as the acetyl derivative.[6]

(6) E. Campaigne and P. A. Monroe, *J. Am. Chem. Soc.*, **76**, 2447 (1954).

(7) S. Gronowitz and T. Raznikiewicz, *Org. Syn.*, **44**, 10 (1964).

(8) H. D. Hartough, "Thiophene and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952, p 513.

(9) H. Heaney, *Chem. Rev.*, **61**, 81 (1961).

(10) G. Wittig and V. Wahl, *Angew. Chem.*, **73**, 492 (1961).

(11) J. D. Roberts, C. W. Vaughn, L. A. Carlsmith, and D. S. Semenow, *J. Am. Chem. Soc.*, **78**, 611 (1956).

(12) R. Juza, *Angew. Chem. Intern. Ed. Engl.*, **3**, 471 (1964).

(13) F. Scardiglia and J. D. Roberts, *Tetrahedron*, **3**, 197 (1958).

(14) A structure marked with an asterisk is merely an example of one of several equally possible intermediates including isomers and/or compounds containing additional bromine atoms.

(15) S. Gronowitz, *Advan. Heterocyclic Chem.*, **1**, 75 (1963).

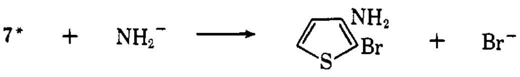
(16) J. F. Bunnett and C. E. Moyer, Jr., *J. Am. Chem. Soc.*, **85**, 1891 (1963).

(17) A. Vaitiekunas and F. F. Nord, *ibid.*, **75**, 1764 (1953).

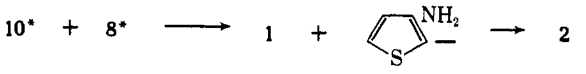
polybromothiophenes to 3-bromothiophene (**3**) under the conditions of run D.

A related and particulary significant observation is the rapid and complete reaction of each of the polybromothiophenes of Table I under the amination conditions of run A to produce 3-aminothiophene (**2**) in yields of up to 50%. Therefore not only the rearrangement (**1** → **3**) but also the cine-substitution (**1** → **2**) of 2-bromothiophene (**1**) may proceed by other than an elimination–addition mechanism. In fact, the exceptional stability of *o*-haloanions of five-membered heterocycles[18] and the recent reinterpretation[19] of the previous evidence[10,20] for the existence of five-membered hetarynes argue strongly against the intermediacy of arynes such as **5** in either of these reactions.[21]

A nonaryne mechanism for the cine-amination of 2-bromothiophene (**1**) which would account for all the data cited here and elsewhere[22] involves substitution of an activated[23] 3-bromine atom in one or several of the polybromothiophenes (**7***) present to give a 3-aminobromothiophene (**10***) (reaction 4[14]) which on subsequent transbromination (reaction 5[14]) would lead to the observed product, 3-aminothiophene (**2**). In support of this mechanism 2-bromo-4-aminothiophene can be



(4)[14]



(5)[14]

isolated in low yield from the reaction of 2-bromothiophene (**1**) with sodium amide and then converted to 3-aminothiophene (**2**) in 50% yield under conditions similar to run A.

Further details on this new mechanism as well as its applicability to other cases of cine-substitution *via* supposed aryne intermediates will be reported in subsequent publications.

Acknowledgment. This research was supported by the Robert A. Welch Foundation and the Texas Christian University Research Foundation.

[18] For a summary, including significant unpublished data, see R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press Inc., New York, N. Y., 1967, pp 290–291.

[19] Dissertations, University of Heidelberg, of V. Wahl (1962), H. Muller (1964), and M. Rings (1966); cited in ref 18, pp 291–292.

[20] G. Wittig, *Angew. Chem.*, 74, 479 (1962).

[21] Hoffmann (ref 18, p 293) concludes that "no unambiguous evidence is as yet available for the formation of dehydro derivatives of five-membered aromatic heterocycles."

[22] H. W. Adickes, Dissertation, Texas Christian University, 1968.

[23] Reference 15, p 69.

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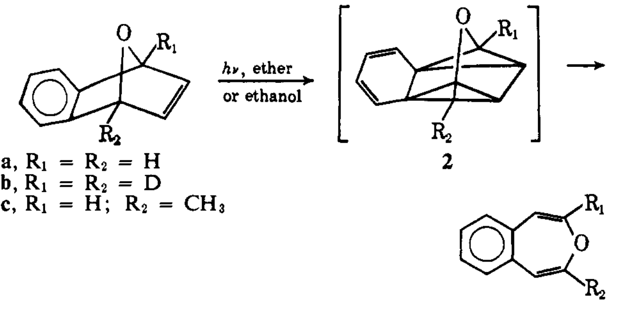
Received October 6, 1967

The Photorearrangement of 1,4-Epoxy-1,4-dihydronaphthalene to Benz[*f*]oxepin[1]

Sir:

The photoisomerization of norbornadienes and 7-oxanorbornadienes to quadricyclo[2.2.1.$0^{2,6}$.$0^{3,5}$]heptanes (quadricyclanes) and the corresponding 7-oxaquadricyclanes appears to be general.[2] These reactions are thought to proceed through an excited state which possesses interaction between the formally unconjugated double bonds.[2b] We report at this time an analogous reaction, the conversion of 1,4-epoxy-1,4-dihydronaphthalene to benz[*f*]oxepin **3** in a photoisomerization that apparently goes by way of intermediate **2**.



1a, $R_1 = R_2 = H$
b, $R_1 = R_2 = D$
c, $R_1 = H$; $R_2 = CH_3$

2

3a, $R_1 = R_2 = H$
b, $R_1 = R_2 = D$
c, $R_1 = H$; $R_2 = CH_3$

Irradiation[3] of 1% solution of **1a**[4] in ether or absolute ethanol for 48 hr gave benz[*f*]oxepin **3a** in 4% yield or 6% in sealed, degassed tubes. The structure of **3a** was established by comparison of its melting point and infrared, ultraviolet, and nuclear magnetic resonance spectra with those reported by Dimroth, *et al.*[5] When the reaction was attempted in the presence of sensitizers,[6] no **3a** was formed. A small amount of a dimer was formed along with a large amount of other high molecular weight material. This suggests two conclusions. (1) The oxepin is formed from an excited singlet state of **1a**. (2) Direct excitation of **1a** does not lead to any significant yield of triplets.

In order to elucidate the mechanism of the transformation to benz[*f*]oxepin, **1b**[4] and **1c**[7] were synthesized and photoisomerized.

Figure 1 presents the vinyl regions of the nmr spectra for compounds **3a–c**.[8] It is expected that benz[*f*]oxepins are separated from their arene oxide valence tautomer by a relatively high energy barrier and that the nmr spectra are due only to the oxepin forms. If this is true, the anomalous shifts observed in the spectrum of

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[1] Mechanisms of Photochemical Reactions in Solution. LI. Part L: L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, in press.

[2] (a) S. J. Cristol and R. L. Snell, *J. Am. Chem. Soc.*, **80**, 1950 (1958); (b) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961); (c) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961); (d) H. G. Richey, Jr., and N. C. Buckley, *ibid.*, **85**, 3057 (1963); (e) P. R. Story and S. R. Fahrenholtz, *ibid.*, **86**, 1270 (1964); (f) P. G. Gassman, D. H. Ave, and D. S. Patton, *ibid.*, **86**, 4211 (1964); (g) D. M. Lemal, R. A. Lovald, and R. W. Harrington, *Tetrahedron Letters*, 2779 (1965); (h) H. Tanick, Y. Hata, Y. Matsui, and J. Tanaka, *J. Org. Chem.*, **30**, 2259 (1965); (i) H. Prinzbach, M. Arguelles, and E. Druckrey, *Angew. Chem. Intern. Ed. Engl.*, **5**, 1039 (1966); (j) E. Pazo, L. Cortés, J. Mantecón, C. Rivas, and G. de Pinto, *Tetrahedron Letters*, 2415 (1967); (k) H. Prinzbach, reported at the International Symposium on Photochemistry, Enschede, July 1967.

[3] A low-pressure Hg resonance lamp was used. About 90% of its intensity is at 2537 Å.

[4] E. Wolthuis, *J. Org. Chem.*, **26**, 2215 (1961). Our material was prepared *via* benzyne generated from anthranilic acid by a variation of the method of L. Freidman and F. M. Logullo, *J. Am. Chem. Soc.*, **85**, 1549 (1963).

[5] K. Dimroth, G. Pohl, and H. Follmann, *Ber.*, **99**, 634 (1966).

[6] Acetophenone, benzophenone, and acetone were tried as sensitizers.

[7] Furan-2,5-d_2 and benzyne gave **1c** in 70% yield. Furan-2,5-d_2 was prepared by metalation of furan with a threefold excess of *n*-BuLi in refluxing ether for 4 hr, followed by quenching with D_2O. The material was shown by nmr to be 80% dideuterated.

[8] Suitable carbon and hydrogen analyses were obtained for this compound (mp 44–45°). The nmr showed three regions: aromatic protons at τ 2.8–3.7, vinyl protons at τ 4.1–5.0, and methyl protons at τ 8.30 in the ratio 4:3:3. The infrared spectrum had strong peaks in the 1650 and 1050-cm^{-1} regions.