

The ultraviolet spectrum possesses an absorption maximum in acetonitrile at 209  $m\mu$  ( $\epsilon$  26,200) with a shoulder at 247.5  $m\mu$  ( $\epsilon$  4,090). Significant infrared absorption bands are found at 3092(m), 2994(w), 2964(m), 2931(m), 2251(w), 1711(m), 1653(s), 1428(m-s) and 874(vs)  $cm^{-1}$  (KBr). The n.m.r. spectrum reproduced in Fig. 1c and determined in acetonitrile has peaks at  $\tau = 5.13$ , 5.24 and 6.45 with integrated areas of 1:1:2, respectively.

**Reaction of Tetramethylenecyclobutane (I) with N-Phenylmaleimide.**—A solution of I in ethanol (80 ml.) prepared from 1.0 g. of *trans,trans,trans*-1,2,3,4-tetrabromomethylcyclobutane (Va) was allowed to stand with 0.40 g. of N-phenylmaleimide at 4° for 2 days. The ethanol was then removed under vacuum and the residue after dilution with 4 ml. of benzene was chromatographed on acid-washed alumina. Two reaction products were isolated in approximately equal amounts. One compound (18 mg.) was eluted with the first 50 ml. of benzene and was shown to be the dimer VIII by comparison of its n.m.r. and infrared spectra with those of the authentic material. Unreacted N-phenylmaleimide was eluted with a solution of benzene-chloroform (20:1). The second product, a 1:1 Diels-Alder adduct of tetramethylenecyclobutane with N-phenylmaleimide, was eluted with 5:1 benzene-chloroform. When the reaction was conducted at 25° only the Diels-Alder adduct was isolated. The ultraviolet spectrum of this colorless, crystalline adduct X possesses an absorption maximum at 212.5  $m\mu$  ( $\epsilon$  37,800) and a shoulder at 248  $m\mu$  ( $\epsilon$  6,840). The n.m.r. spectrum observed in deuteriochloroform shows resonance peaks at  $\tau = 2.62$  (5), 5.30 (2), 5.41 (2), 6.68 (4) and 7.27 (2). Significant bands in the infrared spectrum (chloroform) are located at 3095(w), 2915(w), 2850(w), 1780(m), 1710(vs), 1749(m), 1610(m-w), 1430(m) and 865(m-s)  $cm^{-1}$  in addition to the characteristic phenyl absorption. An elemental analysis was not obtained on this adduct because of the difficulties associated with purifying and handling such an extremely oxygen-sensitive material.

**Preparation of Dihydropotetramethylenecyclobutane (XII).**—3,4-Dichloro-1,2,3,4-tetramethylcyclobutane (XI, 1.00 g., 5.6 mmoles) was dissolved in 15 ml. of *t*-butyl alcohol containing 1.7 g. (15 mmoles) of potassium *t*-butoxide and stirred under a nitrogen atmosphere at room temperature for 48 hr. The volatile product was then isolated by codistillation at 40° (0.02 mm.) into a Dry Ice-acetone trap and purification was achieved by preparative scale g.l.p.c. procedures using a silicone GE SF-96 column. The product possesses ultraviolet absorption maxima (isooctane) at 213 and 249  $m\mu$ . Minimum extinction coefficients (10,500 for  $\lambda_{max}$  213  $m\mu$  and 3530 for  $\lambda_{max}$  249  $m\mu$ ) were determined by assuming quantitative conversion of a weighed sample of XI to dihydropotetramethylenecyclobutane. The infrared spectrum determined in carbon tetrachloride shows significant peaks at 3089(m), 2970 (m), 2940(m), 2918(m), 2852(m-w), 1693(w), 1643(m-s), 1604(m), 1432(m), 1319 (m) and 852(vs)  $cm^{-1}$ . The mass spectrum of XII exhibits a parent mass, as

expected, at  $m/e$  106, almost as intense as the base peak at  $m/e$  91 which corresponds to loss of a methyl group. *t*-Butyl alcohol solutions of XII were employed for subsequent reaction studies because of the tendency of the pure hydrocarbon to oxidize.

**Catalytic Reduction of Dihydropotetramethylenecyclobutane (XII).**—A *t*-butyl alcohol solution of XII was hydrogenated over palladium-on-charcoal catalyst at atmospheric pressure. The catalyst was then collected on a filter and the filtrate subsequently gas chromatographed on a silicone GE SF-96 preparative column. The infrared spectrum and g.l.p.c. retention time of the major product were shown to be identical to those obtained for an authentic sample of *cis,cis,cis*-1,2,3,4-tetramethylcyclobutane. Small amounts of isomeric hydrocarbons were also detected but not further characterized.

**Reaction of Dihydropotetramethylenecyclobutane (XII) with Tetracyanoethylene.**—To a *t*-butyl alcohol solution estimated to contain at least 32 mg. of dihydropotetramethylenecyclobutane (XII) was added to 140 mg. (1.1 mmoles) of tetracyanoethylene in 20 ml. of tetrahydrofuran. Immediately after addition of the tetracyanoethylene a cherry-red color developed which gradually faded as the reaction progressed. Stirring at room temperature was continued for 12 hr. The volatile solvents were then removed under reduced pressure at 35° and the residual orange solid was chromatographed on acid-washed alumina. The initial benzene fractions afforded 105 mg. of colorless crystals of the 1:1 adduct XIII. The ultraviolet spectrum of XIII determined in acetonitrile has a maximum at 227  $m\mu$  ( $\epsilon$  12,300) and the infrared spectrum (KBr) possesses significant absorption bands at 3090(w), 3031(m), 2980(m), 2958(m), 2922(m), 1692(m), 1629(s), 1432(s), 882(s) and 871(s)  $cm^{-1}$ . The n.m.r. spectrum is displayed in Fig. 1f and is consistent with the assigned structure.

*Anal.* Calcd. for  $C_{14}H_{10}N_4$ : C, 71.77; H, 4.32; N, 23.91; mol. wt., 234. Found: C, 71.62; H, 4.45; N, 23.84; mol. wt., 233 (ebullioscopic).

**Acknowledgment.**—The authors are indebted to the U. S. Army Research Office (Durham) and the Research Corporation, New York, N. Y., for mutual support of this work. We also wish to thank Miss R. Herberich and A. H. Struck of the Stamford Research Laboratories, American Cyanamid Co., Stamford, Conn., R. Jones, Esso Research and Engineering Co., Linden, N. J., as well as E. Schingh and H. Hoberecht of the Olin-Matheson Research Laboratories, New Haven, Conn., for mass spectral data. We also wish to thank N. F. Chamberlain and the n.m.r. group of the Humble Oil and Refining Co., Baytown, Tex., for the determination of certain n.m.r. spectra.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF FLORIDA, GAINESVILLE, FLA.]

## The Mechanism of the Base-Initiated Dehydrohalogenation and Rearrangement of 1,1-Diaryl-2-bromoethylenes in *t*-Butyl Alcohol<sup>1</sup>

BY W. M. JONES AND RALPH DAMICO<sup>2</sup>

RECEIVED DECEMBER 10, 1962

The reactions of the *cis* and *trans* isomers of 1-*p*-chlorophenyl-1-phenyl-2-bromoethylene and 1-*p*-methoxyphenyl-1-phenyl-2-bromoethylene with a large excess of potassium *t*-butoxide in *t*-butyl alcohol at 95.6°, 109.1° and 119.2° have been studied. The ultraviolet spectra of the resulting diarylacetylenes (and reactants, where necessary) were used to follow the rates. It was found that the *trans* substituents had only small effects on the reaction rates (at 95.6°, methoxy accelerated the rate by a factor of *ca.* 2.5 relative to its *cis* isomer, whereas the chlorine slows the rate to *ca.* 0.4 times the rate of its *cis* isomer) but caused rather large effects on the activation parameters. Furthermore, it was found that no bromostilbenes accumulate during the reaction of the unsubstituted 1,1-diphenyl-2-bromoethylene with potassium *t*-butoxide. From these observations and the similarity of the effect of the groups on activation parameters to such reactions as the Beckmann rearrangement and the rearrangement of triarylmethyl azides it has been suggested that the best representation for the mechanism of the rearrangement portion of this reaction is the migration of the aryl group to a transition state involving an electron-deficient phenyl ring with concomitant loss of the halide ion.

The base-induced elimination of hydrogen halides from 1-halo-2,2-diphenylethylenes (the F.B.W. rearrangement) was first observed by Fritsch,<sup>3</sup> Buttenberg<sup>4</sup> and Wiechell.<sup>5</sup> Since the original investigations,

several studies have been made which have rather explicitly established certain aspects of the mechanism of this reaction. Thus, employing a combination of kinetics and deuterium isotope effects, Pritchard and Bothner-By<sup>6</sup> have shown that formation of diphenylacetylene from the reaction of 1,1-diphenyl-2-bromoethylene with potassium *t*-butoxide in *t*-butyl alcohol

(1) Based upon a thesis submitted by Ralph Damico in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Texaco Research Fellow, 1960-1961.

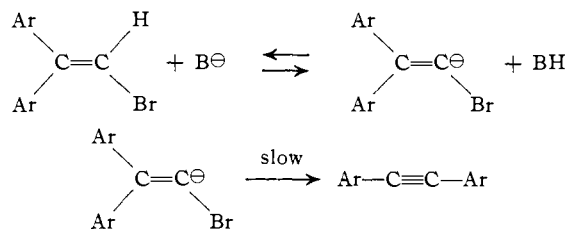
(3) P. Fritsch, *Ann.*, **279**, 319 (1894).

(4) W. P. Buttenberg, *ibid.*, **279**, 327 (1894).

(5) H. Wiechell, *ibid.*, **279**, 337 (1894).

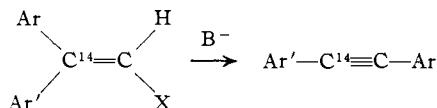
(6) J. G. Pritchard and A. A. Bothner-By, *J. Phys. Chem.*, **64**, 1271 (1960).

proceeds by a rapid acid-base pre-equilibrium involving formation of the vinyl carbanion followed by a slow rearrangement of the aryl group.<sup>7</sup>



$\text{B}^\ominus = t\text{-BuO}^\ominus$ ;  $\text{Ar} = \text{C}_6\text{H}_5^-$

Furthermore, by employing appropriately tagged carbon starting materials, both Bothner-By<sup>10</sup> and Curtin and his co-workers<sup>11</sup> have clearly demonstrated that the rearrangement is stereospecific, the aryl group which is originally *trans* to the halide being the one that migrates.



However, despite the fact that, at least in the reaction employing potassium *t*-butoxide in *t*-butyl alcohol, there is no doubt that the aryl group is migrating to the carbanion; there is no evidence to date regarding the more intricate details of this rearrangement.

To attempt to gain some insight into the rearrangement step of this reaction was the purpose of the research that we are reporting in this paper. The approach that was selected involved product analyses and a comparison of the migratory aptitudes of appropriately substituted phenyl rings.

### Results and Discussion

From the deuterium isotope experiments of Pritchard and Bothner-By<sup>6</sup> on the reaction of 1,1-diphenyl-2-bromoethylene with potassium *t*-butoxide in *t*-butyl alcohol, there can be little doubt but that, under these specific conditions, the reaction proceeds by an initial acid-base pre-equilibrium followed by a slow rearrangement of the aryl group. Furthermore, Bothner-By<sup>10</sup> has demonstrated the configurational stability of the anion at temperatures as high as 83°. Thus the reaction can be accurately pictured as initial formation of the anion followed by stereospecific migration of the phenyl. However, there are at least three different ways by which the aryl group could move to the anionic center.

The first mechanism, analogous to the Beckmann rearrangement,<sup>12</sup> involves displacement of the halide by the migrating aryl group.

(7) Curtin and Flynn<sup>8</sup> found that the same reaction, when effected with *n*-butyllithium in ethyl ether, apparently does not proceed by an initial rapid pre-equilibrium but, instead, either goes by a slow loss of a proton followed by rearrangement or, possibly, as has been suggested by Cristol and Bly,<sup>9</sup> by a reaction involving loss of a proton with concomitant rearrangement of the aryl group and loss of halide. Although it may, at first thought, appear contradictory to suggest that the stronger base, *n*-butyllithium, could change the mechanism of this reaction from a rapid pre-equilibrium to a reaction in which the first step is slow, these facts are readily explained when it is recognized that removal of the proton by *n*-butyllithium would be expected to be an essentially irreversible step.<sup>5</sup>

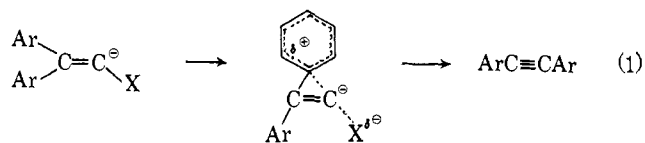
(8) D. Y. Curtin and E. W. Flynn, *J. Am. Chem. Soc.*, **81**, 4714 (1959).

(9) S. J. Cristol and R. S. Bly, Jr., *ibid.*, **83**, 4027 (1961).

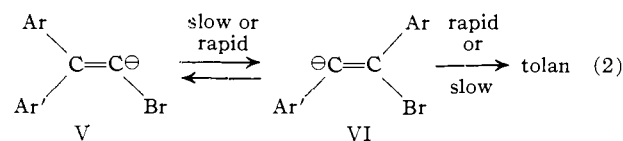
(10) A. A. Bothner-By, *ibid.*, **77**, 3293 (1955).

(11) D. Y. Curtin, E. W. Flynn and R. F. Nystrom, *ibid.*, **80**, 4599 (1958); D. Y. Curtin, E. W. Flynn, R. F. Nystrom and W. H. Richardson, *Chem. Ind. (London)*, 1453 (1957).

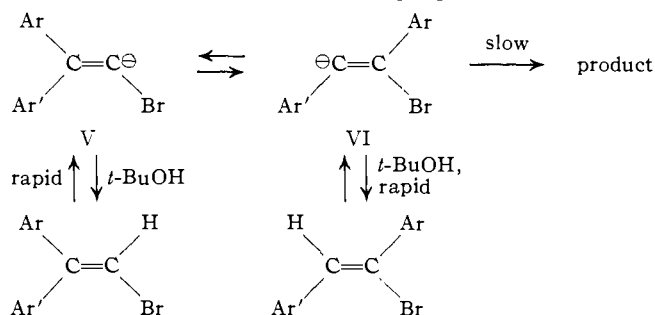
(12) Cf. L. G. Donaruma and W. Z. Heldt, *Org. Reactions*, **11**, 1 (1960). E. Pearson and E. D. Watts, *J. Org. Chem.*, **20**, 494 (1955); R. Huisgen, J. Witte, H. Walz and W. Jira, *Ann.*, **604**, 191 (1951), and references cited in these papers.



The second and third mechanisms, which find their analogy in the recently demonstrated carbanion rearrangements of aryl groups,<sup>13,14</sup> are pictured in eq. 2, one mechanism involving a rapid equilibrium between anions V and VI followed by a slow loss of the halide ion and the other involving a slow migration of the aryl group followed by a rapid loss of the halide ion from anion VI.



The mechanism involving rapid migration of the aryl group to give anion VI followed by slow loss of halide became a rather unlikely candidate for this rearrangement as a result of the following considerations. It is known that the first formed anion (V) is in equilibrium with its conjugate acid<sup>6</sup> (the starting material). This being the case, then it would certainly be expected that if anion VI is in equilibrium with V it should also be in equilibrium with its conjugate acid (either *cis*- or *trans*-bromostilbene). Now, keeping in mind the fact



that the mechanism under consideration is the one in which the anion (or even its conjugate acid) is losing halide ion in the slow step, then it follows that either or both of the monobromostilbenes should accumulate in the reaction mixture. A reaction of 1,1-diphenyl-2-bromoethylene with potassium *t*-butoxide in *t*-butyl alcohol was therefore allowed to proceed to partial completion and the crude reaction mixture was analyzed for both *cis*- and *trans*-monobromostilbenes. Employing both gas chromatography and infrared, it was found that the reaction mixture resulting from the partial reaction consisted only of starting material and diphenylacetylene with no detectable trace of either of the bromostilbenes being present. These observations tend to exclude as being operative mechanism 2 with a rapid rearrangement of the aryl group followed by a slow loss of the halide ion.

A distinction between the concerted displacement of the halide ion by the migrating aryl group (mechanism 1) and a slow rearrangement of the aryl group into the center of high electron density to give the intermediate anion (mechanism 2) followed by a rapid loss of the halide could not be as easily effected. However, in view of the fact that mechanism 1 should involve a net electron deficiency on the migrating group in the rate-determining transition state, whereas mechanism 2 should lead to a transition state in which the migrating

(13) (a) H. E. Zimmerman and F. J. Smentowski, *J. Am. Chem. Soc.*, **79**, 5455 (1957); (b) H. E. Zimmerman and A. Zweig, *ibid.*, **83**, 1196 (1961).

(14) E. Grovenstein and L. P. Williams, *ibid.*, **83**, 412, 2537 (1961).

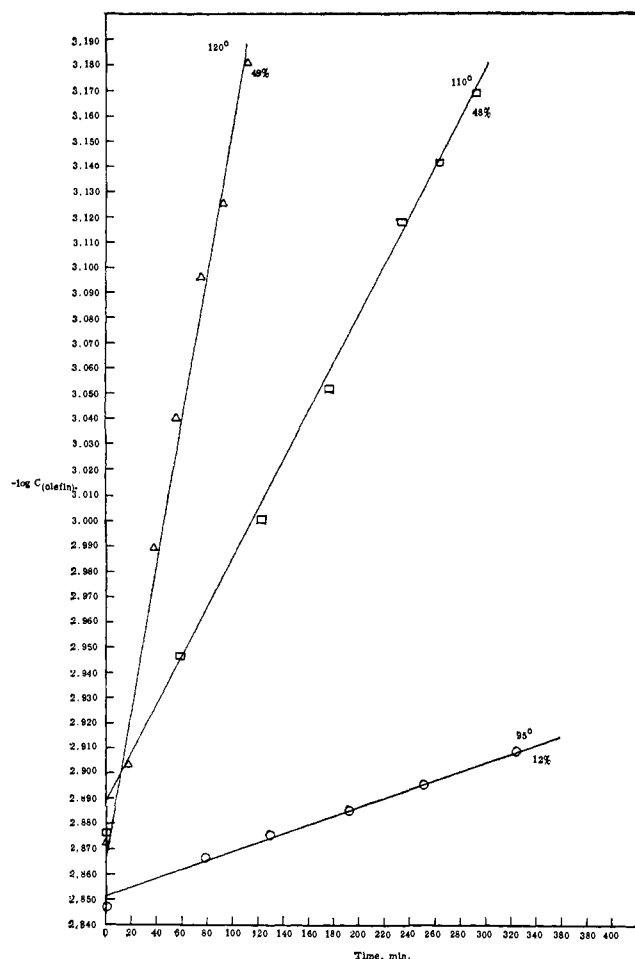
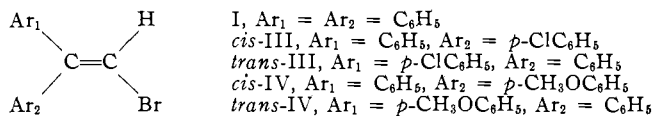


Fig. 1.—The rate of dehydrobromination of *trans*-1-*p*-chlorophenyl-2-bromoethylene with potassium *t*-butoxide in *t*-butyl alcohol.

group has become electron rich, we felt that an examination of the relative migratory aptitudes of appropriately substituted aryl groups might prove enlightening.

The *cis* and *trans* isomers of 1-*p*-methoxyphenyl-1-phenyl-2-bromoethylene (*cis*- and *trans*-IV) and 1-*p*-chlorophenyl-1-phenyl-2-bromoethylene (*cis*- and *trans*-III) were prepared for kinetic studies.



The *cis-trans* isomer pairs were selected for study in order to maintain the acidity of the vinyl hydrogen as nearly constant as possible.<sup>15</sup> This was necessary since the reaction mechanism involves an acid-base equilibrium preceding the migration of the aryl group.

The geometrical configurations of the two *p*-chlorophenylethylenes have been conclusively determined.<sup>16</sup> However, although both of the isomeric *p*-methoxy compounds have been reported and geometrical structures assigned, these assignments were based solely on the melting points of the two isomers.<sup>17</sup> For this reason, dipole moments of the two *p*-methoxy compounds were measured. It was found that the higher

(15) The n.m.r. spectra of the various olefins lend strength to the assumption that the acidity of the hydrogen is not appreciably affected by the stereochemistry of the olefin. It was found that the position of the vinyl hydrogen was shifted by *p*-substitution on one of the phenyl rings but was unaffected by the stereochemistry of the olefin. Details are given in the Experimental section.

(16) E. Bergmann, L. Engel and H. Meyer, *Ber.*, **65B**, 446 (1932).

(17) R. Stoermer and M. Simon, *ibid.*, **37**, 4167 (1904).

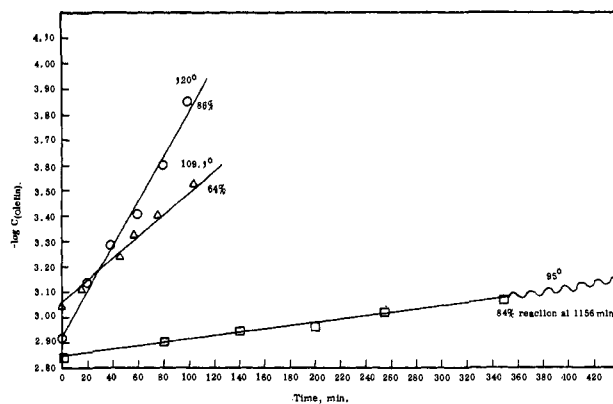


Fig. 2.—The rate of dehydrobromination of *trans*-1-methoxyphenyl-1-phenyl-2-bromoethylene with potassium *t*-butoxide in *t*-butyl alcohol.

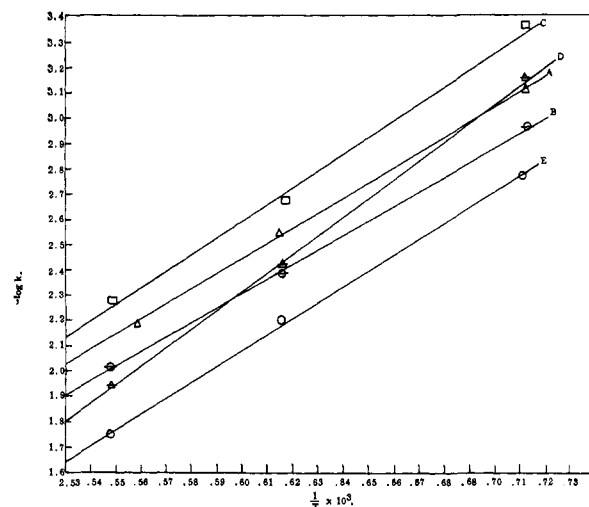


Fig. 3.—Plot for the calculation of the Arrhenius energies of activation for the dehydrobromination of (A) 1,1-diphenyl-2-bromoethylene, (B) *cis*-1-*p*-chlorophenyl-1-phenyl-2-bromoethylene, (C) *trans*-1-*p*-chlorophenyl-1-phenyl-2-bromoethylene, (D) *cis*-1-*p*-methoxyphenyl-1-phenyl-2-bromoethylene, (E) *trans*-1-*p*-methoxyphenyl-1-phenyl-2-bromoethylene.

melting isomer (previously assigned the *trans* configuration) exhibited a dipole moment of 2.65 D. On the other hand, the lower melting material had a dipole moment of 2.15 D. Calculation of theoretical dipole moments using reported bond and group moments<sup>18</sup> and assuming normal bond angles led to a calculated value for the *trans* isomer of 2.05 D. and for the *cis* isomer of 1.45 D. (average between the two extremes resulting from rotation of the methoxy group). The difference between the calculated and experimental moments must be a result of the inherent difficulty in attempting to calculate dipole moments for non-rigid molecules. However, the fact that the difference between the calculated moments is nearly the same as the difference between the observed moments tend to confirm the original assignment of Stoermer and Simon.

The kinetics of the conversion of the vinyl halides were then investigated. The results and activation parameters are reported in Table I.

From these results, it is tempting to conclude that the reaction is proceeding by a concerted displacement of the halide by the migrating aryl group. Thus, as would be expected for a reaction involving the develop-

(18) Cf. C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, pp. 244, 253. For calculated and observed dipole moments of *p*-bromoanisole, an ideal model compound, see R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 599 (1936).

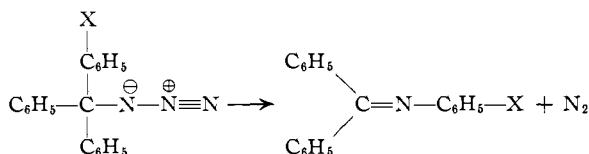
TABLE I  
RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE REACTIONS OF 1,1-DIARYL-2-BROMOETHYLENES (EH) WITH POTASSIUM *t*-BUTOXIDE

EH	$k \times 10^6, \text{sec.}^{-1a}$			$E_a, \text{kcal.}^b$	$\Delta H^*, \text{kcal.}^c$	$\Delta S^*, \text{e.u.}^d$	Base, (moles per l.)
	95.6°	109.1°	119.2°				
I	1.26 <sup>e</sup> ±0.068	4.65 ±0.33	10.8 ±1.0	26.2 ±1.8	25.5 ±1.8	-12.3 ±4.6	0.206 (95.6) .198 (109.1) .200 (119.2)
<i>cis</i> -III	1.78 ±0.078	6.85 ±0.25	15.5 ±0.60	26.5 ±1.1	25.7 ±1.1	-11.0 ±2.8	.206 (95.6) .198 (109.1) .201 <sup>f</sup> (119.2)
<i>trans</i> -III	0.703 <sup>g</sup> ±0.027	3.60 <sup>g</sup> ±0.058	8.97 <sup>g</sup> ±0.27	31.3 ±0.85	30.5 ±0.85	+0.30 ±0.34	.202 (95.6) .199 (109.1) .202 (119.2)
<i>cis</i> -IV	1.17 ±0.030	6.48 ±0.68	19.0 ±0.76	34.5 ±1.3	33.7 ±1.3	+10.0 ±3.4	.202 (95.6) .197 (109.1) .204 (119.2)
<i>trans</i> -IV	2.78 ±0.095	10.5 ±0.24	28.6 ±0.38	28.3 ±0.68	27.5 ±0.68	-5.18 ±1.9	.200 <sup>f</sup> (95.6) .204 (109.1) .204 (119.2)

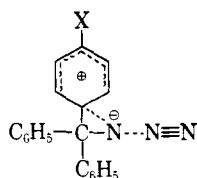
<sup>a</sup> Errors in  $k$  are the average deviations from the least squares line of the first-order plots. <sup>b</sup> Errors in  $E_a$  are calculated from the maximum and minimum values of the slope in the Arrhenius equation. <sup>c</sup> Uncertainties in  $\Delta H^*$  are the same as those in  $E_a$ . <sup>d</sup> Uncertainties in  $\Delta S^*$  are derived from those in  $\Delta H^*$ . <sup>e</sup> Pritchard and Bothner-By<sup>6</sup> have reported  $k = 1.21 \times 10^{-6}$  for this same reaction at 95° employing 0.215 *M* potassium *t*-butoxide in *t*-butyl alcohol. <sup>f</sup> Average of 2 runs. <sup>g</sup> Maximum value since *trans*-III was contaminated with *cis*-III (see Experimental).

ment of an electron-deficient migrating group, the *trans*-*p*-methoxy group accelerates the reaction (relative to its *cis* isomer) and the *p*-chlorine retards the migration. Furthermore, although the rate differences are quite small, they reflect quite large differences in activation enthalpies which are almost completely offset by compensating activation entropies.

However, an interpretation of these compensating enthalpy and entropy effects is difficult. Thus, despite the fact that this type of "compensation effect" is extremely common<sup>19</sup> it is apparently a point for debate as to correct interpretation of large enthalpy effects accompanying large entropy effects. For example, Saunders and Ware<sup>20</sup> have examined the thermal decomposition of a series of substituted triphenylmethyl azides to yield the corresponding anils.



This reaction is quite similar to the F.B.W. rearrangement in that the aryl group is migrating to a high electron density center with (possibly concomitant) loss, in their case, of a molecule of nitrogen. In this reaction Saunders and Ware found that the substituent groups had very little effect on the rates of the rearrangement but did cause quite large changes in the activation parameters; electron-donating groups caused decreases in the activation enthalpies. From these results they concluded that the enthalpy changes were indeed indicative of potential energy effects of the substituent groups and suggested the following transition state for their reaction.



(19) For discussions of this subject, see: (a) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955); (b) R. F. Brown, *ibid.*, **27**, 3015 (1962).

(20) W. H. Saunders, Jr., and J. C. Ware, *J. Am. Chem. Soc.*, **80**, 3328 (1958).

Another striking example of this type of interpretation of enthalpy effects appeared in a recent paper by Smith and Hall.<sup>21</sup> In an investigation of the thermal decomposition of substituted aryl azides they found that substituent groups had relatively small effects on the reaction rates but that, again, rather large activation enthalpy differences were encountered. From these results, the existence of an isokinetic temperature and the fact that *m*-substituents had relatively small effects on the activation enthalpies, they felt that "an attempt to interpret the effects of substitution would be more fruitful in terms of activation enthalpies than rate constants." Thus, again, it was concluded that, even in the presence of large compensating entropy effects, the enthalpy differences were indications of potential energy effects of the substituent groups.

On the other hand, it has been pointed out, particularly by Hammett<sup>22</sup> and by Leffler,<sup>19a</sup> that activation enthalpies can be safely used as measures of potential energy effects only when activation entropies do not change, a situation which is obviously not the case either in our work or the work cited above.<sup>23</sup>

Thus, despite the fact that there is apparently some real danger in ascribing the substituent effects in our system to potential energy effects, the effects are definitely analogous to the triphenylmethyl azide system of Saunders and Ware.<sup>20</sup> Furthermore, they are also similar to substituent effects in the formally analogous Beckmann rearrangement. For example, Pearson, Baxter and Martin<sup>24</sup> have found that the rates of reaction of substituted acetophenone oximes with sulfuric acid are not greatly affected by substituent groups (*p*-methoxy:H:*p*-chloro, 12.1:1.0:0.64).<sup>25</sup> However, an

(21) P. A. S. Smith and J. H. Hall, *ibid.*, **84**, 480 (1962).

(22) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 120.

(23) However, Leffler<sup>19a</sup> has pointed out the fact that there is a possibility that a linear relationship between activation enthalpy and entropy might actually indicate a linear correlation between the activation enthalpies and potential energy effects. Unfortunately, at least to our knowledge, this has not yet been demonstrated. The activation parameters given in Table I, when adjusted for the acidity of the hydrogens, give an isokinetic temperature relationship with an isokinetic temperature of 149°.

(24) D. E. Pearson, J. F. Baxter and J. C. Martin, *J. Org. Chem.*, **17**, 1511 (1952).

(25) Compare with migratory aptitudes in the pinacol rearrangement in which the *p*-methoxy group causes a five-hundred fold increase in the rate: W. E. Bachmann and J. W. Ferguson, *J. Am. Chem. Soc.*, **56**, 2081 (1934); W. E. Bachmann and H. R. Steinberger, *ibid.*, **56**, 170 (1934).

examination of the activation parameters shows that the *p*-methoxyacetophenone oxime exhibits an activation enthalpy of over 8 kcal./mole less than the unsubstituted compound, again a situation in which the electron-donating group causes a large decrease in activation enthalpy which is nearly offset by a compensating entropy effect.<sup>26</sup>

Thus, although it is not possible to distinguish unequivocally between displacement of the halide ion by the migrating aryl group (mech. 1) and a two-step reaction involving the slow formation of an intermediate anion (mech. 2), the accumulated data certainly suggest that the F.B.W. rearrangement is proceeding by a mechanism which is quite similar to both the rearrangement of the triphenylmethyl azides and the Beckman rearrangement. In view of the fact that at least the latter of these two rearrangements certainly proceeds through a transition state involving an electron-deficient migrating group<sup>12</sup> we feel that mech. 1 is the best representation of the rearrangement step in the reaction at hand.

### Experimental<sup>27</sup>

**1,1-Diphenyl-2-bromoethylene.**—1,1-Diphenylethylene was prepared by the method of Allen and Converse.<sup>28</sup> Bromination and dehydrohalogenation were performed using the procedure of Hepp.<sup>29</sup> Recrystallization of the crude product from methanol gave the pure olefin, m.p. 42–43°, reported<sup>24</sup> m.p. 40°.

***cis*- and *trans*-1-*p*-Chlorophenyl-1-phenyl-2-bromoethylene (*cis*- and *trans*-III).**—*cis*- and *trans*-III were prepared according to the method of Curtin, Flynn and Nystrom.<sup>11</sup> In a typical run, 50 g. (0.232 mole) of 1-*p*-chlorophenyl-1-phenylethylene was brominated with 44.2 g. (0.245 mole, 6% excess) of bromine in 200 ml. of carbon tetrachloride at room temperature. The mixture was then refluxed for 18 hr. to eliminate hydrogen bromide. The solvent was removed by distillation and the resultant oil refluxed for 1 hr. with 14 g. (0.25 mole) of potassium hydroxide in 100 ml. of absolute ethanol. To the resultant mixture was added water and ether. Following separation of the organic layer and washing the aqueous layer with ether, the ether was dried and removed by distillation. The remaining oil was distilled through a 6-in. column packed with glass helices. The fraction with b.p. 149–155° (1.0–1.3 mm.) was collected to give 49 g. of colorless liquid. Upon standing at room temperature white crystals separated from the oil. These were removed and recrystallized from ethanol to constant melting point; m.p. 88–89°; reported<sup>11</sup> for the *cis* isomer, m.p. 88–89°.

The remaining oil was then redistilled and a slightly yellow oil collected, b.p. 155–157° (1.0–1.3 mm.). The infrared spectrum of this oil indicated that it had no more than 30% of the *cis* isomer as an impurity (based on the strong absorption of the *cis* isomer at 723 cm.<sup>-1</sup>). Attempts to crystallize this oil both before and after chromatography failed.

*Anal.* Calcd. for C<sub>14</sub>H<sub>10</sub>BrCl (*trans*-III used for kinetics): C, 57.27; 3.42. Found: C, 57.45; H, 3.29.

***cis*- and *trans*-1-*p*-Methoxyphenyl-1-phenyl-2-bromoethylene (*cis*- and *trans*-IV).**—1-*p*-Methoxyphenyl-1-phenylethylene was prepared by the Grignard reaction of *p*-methoxyacetophenone with phenylmagnesium bromide followed by dehydration of the resulting alcohol. The method used was that of Nielson and McEwen<sup>30</sup> in the preparation of a similar compound.

The ethylene (4.0 g., 0.019 mole) was brominated with 3.2 g. (0.020 mole, 5% excess) of bromine in carbon tetrachloride. Hydrogen bromide was eliminated by refluxing the reaction mixture for 7 hr. Following removal of carbon tetrachloride by

distillation, the residual oil was dissolved in ethanol and cooled to give a colorless solid. One recrystallization from ethanol gave 1.8 g. of colorless solid, m.p. 79–81°. Repeated recrystallization from ethanol raised the melting point to 81–82°; reported<sup>18</sup> for *trans*-IV, m.p. 82.5°. All kinetic studies were made with the 81–82° material.

The filtrate from which the *trans* isomer had been isolated was cooled for 1 week at 0°. During this time some more of the impure *trans* isomer separated. This was removed and the resultant mother liquor was evaporated to dryness to give 0.9 g. of solid, m.p. 45–50°. Chromatography over alumina (eluted with pentane-ether) gave 0.10 g. of pure *cis*-IV, m.p. 60–61°, reported<sup>18</sup> m.p. 52°.

**Diphenylacetylene** was prepared according to the method of Smith and Falkof.<sup>31</sup> Recrystallization from ethanol gave a pure product, m.p. 60–61°, reported<sup>28</sup> m.p. 60–61°.

***cis*-Monobromostilbene.**—To 3.6 g. (10.5 mmoles) of *meso*-stilbene dibromide, prepared by brominating *trans*-stilbene, was added 0.59 g. (10.5 mmoles) of potassium hydroxide in 10 ml. of absolute ethanol. The mixture was refluxed for 1 hr., neutralized and extracted with ether. The ether was dried over sodium sulfate and removed under a stream of nitrogen. A reddish oil remained which solidified at 16° (reported<sup>32</sup> solidification point, 19°).

***trans*-Monobromostilbene.**—Stilbene dibromide (*dl*) was prepared by brominating *cis*-stilbene. The dibromide was dehydrohalogenated as follows: To 0.8 g. (2.3 mmoles) of the dibromide was added 0.13 g. (2.3 mmoles) of potassium hydroxide in 5 ml. of absolute ethanol. The mixture was refluxed for 1 hr., neutralized with aqueous hydrochloric acid and extracted with ether. The ether solution was washed twice with water and dried over sodium sulfate. Removal of the ether under a stream of nitrogen gave a yellow oil. This oil was crystallized from ethanol in a Dry Ice-acetone bath to give white crystals, m.p. 29–30°, reported<sup>31</sup> m.p. 30°.

**Reaction of 1,1-Diphenyl-2-bromoethylene (I) with Potassium *t*-Butoxide.**—One gram (3.9 mmoles) of the olefin was dissolved in a solution of potassium *t*-butoxide prepared by dissolving 0.240 g. (6.1 mmoles) of potassium in 50 ml. of dry *t*-butyl alcohol. The reaction was refluxed for 72 hr. and then quenched by adding dilute nitric acid until the mixture was neutral. Water was added until an oil separated. The oil was allowed to crystallize from ethanol to yield 0.44 g. (65%) of diphenylacetylene, m.p. 57–58°, reported<sup>31</sup> m.p. 60–61°. A mixture melting point with an authentic sample of diphenylacetylene showed no depression. Infrared spectra of the two samples were identical.

**Incomplete Reaction of 1,1-Diphenyl-2-bromoethylene with Potassium *t*-Butoxide.**—This reaction was carried out in exactly the same manner as the reaction described above except that the reaction time was 24 hours. The recovered oil (0.65 g.) was analyzed by g.l.p.c. using a 6-ft. column of Tide at 190° and a pressure of 10 p.s.i. Under these conditions, the reaction product showed two peaks with retention times of 2.7 and 4.7 min. Authentic samples of diphenylacetylene and starting material showed the same two peaks. There was no detectable trace of *trans*-monobromostilbene (retention time, 7.9 min.). *cis*-Monobromostilbene had a peak at 3.8 min. which, due to the nature of the peaks, could not be resolved from the peak arising from the starting material. However, the infrared spectrum of the crude reaction mixture was found to be identical with the infrared of a mixture of starting material and diphenylacetylene. *cis*-Monobromostilbene has several strong peaks (2900, 1360, 1190, 1095, 890 and 792 cm.<sup>-1</sup>) which did not appear in the spectrum of the crude reaction mixture.

**Reaction of *cis*-1-*p*-Chlorophenyl-1-phenyl-2-bromoethylene (III) with Potassium *t*-Butoxide.**—*cis*-III (0.54 g., 1.84 mmoles) was refluxed for 69 hr. with a large excess of potassium *t*-butoxide in 20 ml. of *t*-butyl alcohol. Water was then added to the reaction mixture until it became cloudy. Upon cooling, 240 mg. (62%) of 1-*p*-chlorophenyl-2-phenylacetylene separated. Recrystallization from ethanol gave a pure product, m.p. 81–83°, reported<sup>11</sup> m.p. 82–83°.

**Reaction of *trans*-1-*p*-Methoxyphenyl-1-phenyl-2-bromoethylene (IV) with Potassium *t*-Butoxide.**—*trans*-IV (1.0 g., 3.5 mmoles) was dissolved in 25 ml. of 0.4 *M* potassium *t*-butoxide in *t*-butyl alcohol. The mixture was refluxed for 6 days. After cooling, the mixture was neutralized and extracted with ether. Evaporation of the ether gave 0.50 g. (69%) of light yellow solid. Recrystallization from ethanol gave a white crystalline material, m.p. 57–58°, reported<sup>33</sup> m.p. 89–90°. Similar results were obtained with the *cis* isomer.

*Anal.* Calcd. for C<sub>15</sub>H<sub>12</sub>O: C, 86.54; H, 5.75. Found: C, 86.56; H, 5.82.

(26) Attempts to compare this reaction with other similar rearrangements (e.g., Hofmann, Curtius, Lossen) led to no real conclusions. Thus, although a negative charge on the migrating terminus seems to reduce the sensitivity of the rearrangement to electron-donating groups (*p*-methoxy accelerates the Hofmann by a factor of ten and the Lossen by a factor of six; W. B. Renfrow, Jr., and C. R. Hauser, *J. Am. Chem. Soc.*, **59**, 121, 2308 (1937)), no activation parameters were reported. Furthermore, in the Curtius rearrangement in which activation parameters have been determined, conclusions are frustrated by strong ground-state resonance interactions between certain of the substituent groups on the migrating aryl group and the carbonyl that is present in this type of reaction (cf. Y. Yukawa and Y. Tsuno, *ibid.*, **79**, 5530 (1957)).

(27) Melting points are uncorrected.

(28) C. F. H. Allen and S. Converse, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 226.

(29) E. Hepp, *Ber.*, **7**, 1410 (1874).

(30) D. R. Nielson and W. E. McEwen, *J. Am. Chem. Soc.*, **76**, 4042 (1954).

(31) L. I. Smith and M. M. Falkof, "Organic Syntheses," Coll. Vol. III John Wiley and Sons, Inc., New York, N. Y., 1955, p. 350.

(32) P. Rumpf and M. Gillois, *Bull. soc. chim.*, 1348 (1955).

(33) A. Orekhoff and M. Tiffeneau, *ibid.*, **37**, 1414 (1925).

We were naturally concerned by the difference in the reported and observed melting points of the *p*-methoxy diphenylacetylene. Hence, we attempted to prepare this material by the method of Orekhoff and Tiffeneau.<sup>33</sup> All attempts resulted in a yellow solid which melted between 60 and 100°, most of it melting at 60°. Attempts to purify this material by recrystallization from a variety of solvents were unsuccessful; g.l.p.c. analysis of the material showed two peaks, one with a retention time identical to the retention time of the product from the reaction of *cis*- and *trans*-IV with potassium *t*-butoxide and the other identical with 1-*p*-methoxyphenyl-2-phenylethylene. Except for a peak at 859 cm.<sup>-1</sup>, every peak in the infrared spectrum could be accounted for by assuming the reaction product was a mixture of the acetylene and 1-*p*-methoxyphenyl-2-phenylethylene.

**Product Analysis.**—The products from the reaction of potassium *t*-butoxide in *t*-butyl alcohol with all of the starting materials were determined by isolation, spectroscopic analysis and, in some cases, by g.l.p.c. Isolation from each reaction mixture gave between 60 and 70% yields of the pure diarylacetylenes. Spectroscopic analysis indicated that in every case, at least 85% of each of the reactions proceeds by the elimination-rearrangement reaction path. Furthermore, g.l.p.c. analysis of the 1,1-diphenyl-2-bromoethylene reaction mixture showed it to contain no volatile material other than diphenylacetylene and a little unreacted starting material.

**Spectra.**—Ultraviolet absorption spectra were employed to determine the concentrations of starting materials and products used in the kinetic measurements. All spectra were run in 95% ethanol. Extinction coefficients were determined with a Beckman spectrophotometer, model DU. The extinction coefficients and wave lengths employed were: 1-*p*-methoxyphenyl-2-phenylacetylene,  $2.02 \pm 0.007 \times 10^4$  (306 m $\mu$ ); *trans*-IV,  $1.98 \pm 0.015 \times 10^3$  (306 m $\mu$ ); *cis*-IV,  $4.76 \pm 0.03 \times 10^2$  (306 m $\mu$ ); 1-*p*-chlorophenyl-2-phenylacetylene,  $2.58 \pm 0.03 \times 10^4$  (302 m $\mu$ ); and diphenylacetylene,  $2.48 \pm 0.015 \times 10^4$  (296.5 m $\mu$ ). Neither *cis*- nor *trans*-1-*p*-chlorophenyl-1-phenyl-2-bromoethylene showed any absorption at 302 m $\mu$ .

A Varian high-resolution nuclear magnetic resonance spectrometer, model 4300-2, with a field homogeneity control was used to obtain the n.m.r. spectra at a frequency of 60 Mc. Chemical shifts were determined by the side band technique.

The samples were dissolved in carbon tetrachloride containing tetramethylsilane as an internal reference.

The chemical shifts of the vinyl hydrogens are: I, 3.32  $\tau$ ; *cis*-III, 3.32  $\tau$ ; *trans*-III, 3.30  $\tau$ ; *cis*-IV, 3.40  $\tau$ ; *trans*-IV, 3.43  $\tau$ . These are all sharply defined singlets.

**Kinetics.**—All kinetic studies were run in the presence of a large excess of base (*ca.* 200-fold). All runs of *cis*-*trans* pairs of olefins were effected with identical base concentrations (approximately 0.20 *M*), thus eliminating differences in the rate constants resulting from the base term inherent in these constants.<sup>6</sup> In all cases a plot of  $-\log C_{(\text{ethylene})}$  vs. time gave a straight line representative of a first-order reaction. Values of the specific rate constant were calculated from the slope of the lines by the method of least squares and activation energies were obtained from the data fit of the simple Arrhenius equation, using the method of least squares. Values of  $\Delta H^*$  and  $\Delta S^*$  were calculated from the equations  $\Delta H^* = E_a - RT$  and  $k = \frac{RT}{Nh} e^{-\Delta H^*/RT} e^{\Delta S^*/R}$

The temperature used was 119.2°. All the values are included in Table I.

Essentially, the kinetic method described by Pritchard and Bothner-By<sup>6</sup> was used. *t*-Butyl alcohol was purified by refluxing with a small amount of sodium for 1 hr. and then distilling

through a 3-ft. column packed with stainless steel sponge, b.p. 82–82.5°. Standard base was prepared in a nitrogen atmosphere by dissolving potassium metal (cut under white mineral oil and dipped once in dry pentane) in *t*-butyl alcohol. Concentrations of the solutions were determined by titrating aliquots added to water against standard acid. In each run, a weighed amount of 1,1-diaryl-2-bromoethylene was dissolved in 25 ml. of *t*-butyl alcohol. To this was added standard base to give a total volume of 50 ml. Five-ml. samples were then transferred to dry 10-ml. ampoules which had been previously flushed well with nitrogen. The tubes were then sealed, pre-heated for 20 seconds and immediately transferred to a constant temperature silicone oil-bath which was maintained throughout the reactions at temperatures of 95.6, 109.1 and 119.2  $\pm$  0.05°. Zero time was taken when the tubes were placed in the bath. Ampoules were withdrawn at intervals and the reaction was quenched by placing in an ice-bath. While frozen, the tubes were opened and distilled water was added to convert any remaining potassium *t*-butoxide to the hydroxide. After warming to room temperature, the contents of the tubes were diluted with 95% ethanol to standard volumes. The spectra were run with ethanol as a blank.

Optical densities were measured at wave lengths corresponding to maxima of the acetylenes. These were selected because the starting olefins either absorbed very little or not at all at these wave lengths. In those cases where the starting olefin did show some absorption at these wave lengths (the two *p*-methoxyphenyl-olefins), the following equations were used to calculate the concentration of the acetylene.

$$A_{\text{Total}} = e_T b c_T + e_{EH} b c_{EH}$$

$$c_{EH} + c_T = c_0$$

$A_{\text{Total}}$  = total absorbance of the mixture

$e_T$  = extinction coefficient of the pure acetylene (tolan)

$c_T$  = concentration of the acetylene

$e_{EH}$  = extinction coefficient of the pure olefin

$c_{EH}$  = concentration of the olefin

$b$  = thickness of the cell

$c_0$  = initial concentration of the olefin

**Dipole Moments.**—Dielectric constants of *cis*- and *trans*-1-*p*-methoxyphenyl-1-phenyl-2-bromoethylene (*cis*- and *trans*-IV) were measured in pure benzene previously prepared for dielectric studies ( $n_D^{25}$  1.4982,  $d_4^{25}$  0.8736). Dielectric constants were measured with a General Radio type 716-C capacitance bridge containing the measuring cell (unknown capacitor) and a precision capacitor (balancing capacitor).<sup>34</sup> Dipole moments were calculated using the equation

$$\mu = 0.01281 \times 10^{-18} [(P_\infty - R_2)T]^{1/2}$$

where  $R_2$  is the molar refraction of the solute and  $P_\infty$  is the polarization of the solute at infinite dilution;  $P_\infty$  was determined by the method of Hendstrand.<sup>35</sup> All measurements were made at 25  $\pm$  0.02°.

**Acknowledgment.**—The authors are most grateful to the National Science Foundation for support of a portion of this work. They would also like to acknowledge their appreciation to Dr. W. S. Brey, Jr., for the n.m.r. data.

(34) For a more detailed discussion of this method see C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p. 212, and references cited therein.

(35) G. Hendstrand, *Z. physik. Chem.*, **B2**, 428 (1929).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA 4, PA.]

## Thiabenzene. IV. 1- and 2-Thianaphthalenes and 10-Thiaanthracenes. Evidence for Cyclic Conjugation

By CHARLES C. PRICE, MIKIO HORI, THYAGARAJA PARASARAN AND MALCOLM POLK<sup>1</sup>

RECEIVED FEBRUARY 25, 1963

By reaction of appropriate thiopyrylium salts with phenyllithium, four new thiabenzene analogs have been prepared. The new compounds are much more stable to heat, light and oxygen than 1,2,4,6-tetraphenylthiabenzene. Covalent conjugated bonding in all five compounds is indicated by the single aromatic band in the proton n.m.r. spectra and by the low dipole moments (1.5–1.9 D.).

The preparation of the first example (I) of a new aromatic heterocyclic ring system, called thiabenzene, was reported earlier.<sup>2</sup> By similar procedures, two

(1) Supported in part by NSF Grant No. G19740.

(2) (a) G. Sulz and C. C. Price, *J. Am. Chem. Soc.*, **83**, 1770 (1961); (b) **84**, 2090 (1962); (c) **84**, 2094 (1962).

thianaphthalenes and two thiaanthracenes have now been prepared. We wish to report here on their properties, particularly their stability, n.m.r. spectra and dipole moments, which have particular significance to the type of bonding which may exist in this new ring system.