80-9; **5** (zinc chloride complex), 12321-53-8; **6**, 954-91-6; **8**, 18963-82-1; **8** (acetate), 18963-83-2; **11**, 18963-84-3; **12**, 18963-85-4; **13**, 18963-86-5; **13** (N-methyl derivative), 18975-91-2; **14**, 18964-23-3; **15a**, 551-93-9; **17**, 18963-87-6; **18**, 18963-88-7; **21**, 5363-37-1; **22**, 6622-55-5; benzoin, 119-53-9; N_2-diphenylethylideneanthranilamide, 18964-20-0; 2-diphenylmethyl-2,3-dihydro-4(1H)-quinazolinone, 18964-21-1; 6-methyl-7-phenylindolo[1,2-*a*]-6H-5-quinazolinone, 18964-22-2.

The Application of Polarography to the Kinetics of Aromatic Cyclodehydration

MARTIN O. L. SPANGLER,[1a] JAMES C. WOLFORD,[1b] GEORGE E. TREADWELL,[1c]
AND CHRISTOPHER CRUSENBERRY[1d]

Department of Chemistry, King College, Bristol, Tennessee

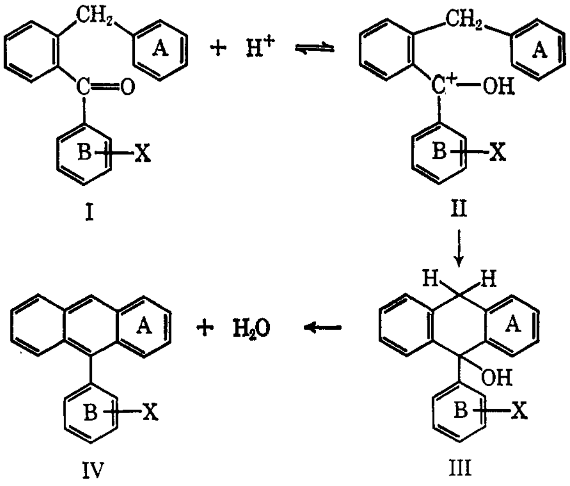
Received August 26, 1968

The kinetics of cyclization of *o*-benzylbenzophenones to 9-phenylanthracenes were studied with reference to variations with temperature. The rate of disappearance of the ketones was followed polarographically in strongly basic aqueous alcohol solutions using KCl as supporting electrolyte. Advantages of this method of analysis are indicated and the results further confirm the previously postulated mechanism.

One of the important methods for the preparation of polynuclear aromatic hydrocarbons is the acid-catalyzed cyclodehydration of certain aromatic aldehydes and ketones.[2] Recent applications of the method include the preparation of 7-phenyldibenz[*a,h*]anthracene,[3] 7- and 12-thienylbenz[*a*]anthracenes,[4] and 9-(2-benzo-[*b*]thienyl)anthracene.[5]

Although other strongly acid media have been used, the most common is a mixture of hydrobromic and acetic acids. Previous kinetic studies, which have all been limited to the simple 9-phenylanthracene series, have led to the proposed mechanism[6–9] outlined in Scheme I which involves a preliminary equilibrium between I and II, the rate-controlling step in which the carbonium ion (II) attacks ring A, followed by a rapid loss of a molecule of water. The reaction is observed to be first order at a given acidity and solvent composition and acid catalyzed and the rate is reported to increase faster than the stoichiometric concentration of the acid catalyst.[10] The rate is very sensitive to the water content of the solution being greatly retarded thereby.[10]

SCHEME I



In previous studies, different investigators used different temperature and different HBr–HOAc–H_2O compositions. It seemed desirable to study the temperature dependence of the rates so that this, along with the known changes with changes in solvent composition,[10] would allow comparison of all the data currently available. The kinetic data reported at 150°,[9] while sufficiently accurate to make the conclusions drawn still valid, was obtained without the benefit of a constant-temperature bath and needed to be restudied.

With these things in mind it was decided to study the kinetics of cyclodehydration of six ketones (I, X = H, 4-Cl, 3-CF_3, 2-F, 2-Cl, and 2-Br) at the two temperatures where most of the previous work was done (100 and 117.5°) and at a higher temperature, 127.5°, so that values for the very slow 2′-chloro- and 2′-bromo-2-benzylbenzophenones could be obtained, all in the same solvent.

Results

Our first attempts, using the method of Brice and Katstra[10] in which the production of 9-phenylanthracene

---

[1] (a) To whom correspondence should be addressed: Department of Chemistry, Elizabethtown College, Elizabethtown, Pa. 17022. (b) Undergraduate summer research participant, 1964 and 1965. (c) Undergraduate summer research participant, 1963. (d) Undergraduate summer research participant, 1964.

[2] C. K. Bradsher, *J. Amer. Chem. Soc.*, **62**, 486 (1940).

[3] F. A. Vingiello and P. D. Henson, *J. Org. Chem.*, **30**, 2842 (1965).

[4] F. A. Vingiello, S. G. Quo, and P. Polss, *ibid.*, **30**, 266 (1965).

[5] F. A. Vingiello and P. D. Henson, *ibid.*, **31**, 1357 (1966).

[6] C. K. Bradsher and F. A. Vingiello, *J. Amer. Chem. Soc.*, **71**, 1434 (1949).

[7] F. A. Vingiello and J. G. Van Oot, *ibid.*, **73**, 5070 (1951).

[8] F. A. Vingiello, J. G. Van Oot, and H. H. Hannabass, *ibid.*, **74**, 4546 (1952).

[9] F. A. Vingiello, M. O. L. Spangler, and J. E. Bondurant, *J. Org. Chem.*, **25**, 2091 (1960).

[10] L. K. Brice and R. D. Katstra, *J. Amer. Chem. Soc.*, **82**, 2669 (1960).

is observed spectrophotometrically, gave only fair checks with their results owing mainly to a difference in the rate of decomposition of the 9-phenylanthracene produced which must be applied as a correction. When the method was tried with 3′-trifluoromethyl-2-benzylbenzophenone (I, X = CF_3), no usable results were obtained because of the presence of an extraneous color which could not be removed.[11]

This required the development of a new method of analysis. We have found it convenient to follow the rate of disappearance of the ketone polarographically. The concentration of ketone can be determined quantitatively in strongly basic aqueous alcohol solutions using KCl as supporting electrolyte and brucine as maximum suppressor. Sodium sulfite was included to remove small amounts of bromine that form when the reaction time is very long. Although the polarograph waves are not of ideal shape they are sufficiently reproducible to be used for analysis when careful calibration is made with solutions of known composition. This method of analysis has several advantages. First, the concentration of ketone is measured directly without the necessity of corrections. In the method used by Brice and Katstra,[10] the absorbance of the 9-phenylanthracene had to be corrected in two ways: for the absorbance of the ketone remaining and for the slow decomposition of the 9-phenylanthracene produced. The gravimetric method used by Bradsher and Vingiello[6] required a correction for the solubility of the substituted anthracenes in the reaction medium. In the second place, very small amounts of the ketones are needed since the polarographic analysis is best carried out in very dilute solutions. The amounts needed are about the same as in the spectrophotometric analysis. Finally, any color that may develop in the solution does not interfere. Application of the method to more complex and less soluble ketones may require the use of more nearly completely nonaqueous media and some other supporting electrolyte such as tetramethylammonium chloride in dimethylformamide.

Experimental Section

Materials.—The six ketones were prepared by methods previously reported and had essentially the same physical properties as previously reported.[6,8,9] Reagent grade acetic acid was redistilled at 114–115° (713 mm). Reagent grade 48% hydrobromic acid was distilled twice over red phosphorus, collected at 123° (713 mm), and standardized against sodium carbonate. It was found to have a concentration of 47.8% HBr. Reagent grade acetic anhydride was redistilled at 137–138° (720 mm).

Kinetic Measurements.—Reaction mixtures containing known amounts of the ketone, hydrobomic acid, acetic acid, and water were placed in sealed tubes in a thermostatically controlled oil bath at the desired temperature ±0.1°. The tubes were removed at measured time intervals, cooled in an ice bath, and kept refrigerated until analysis was made. The initial concentration of ketone in each case was 5.00×10^{-3} *M*.

Analysis of the reaction mixtures was made on 5-ml aliquots which were prepared for polarography by adding 25 ml[12] of 5 *N* aqueous NaOH, 1 ml of 0.2% brucine (in 95% ethanol), 5 ml of 1 *N*[13] aqueous KCl, and 2 ml of 1 *N* aqueous Na_2SO_3 and diluting to 100 ml with 95% ethanol. Dilution to 50 ml could be used in all cases except with 4′-chloro-2-benzylbenzophenone which was insoluble under these conditions.

After deaerating the solutions with oxygen-free nitrogen,[14] polarograms were recorded at 25 ± 0.1° using a Sargent Model XXI polarograph. The concentration of ketone was determined from the diffusion current using a calibration curve prepared from known solutions. The diffusion current-concentration plots were linear in the range desired for the kinetic study which was 5 to 25×10^{-5} *M*. This range could be extended on up to 50×10^{-5} *M* when the ketone solubility permitted dilution to 50 ml instead of 100 ml. The lower limit that could be determined conveniently was about 5×10^{-5} *M*. The half-wave potentials and i_d/C values are listed in Table I.

TABLE I

POLAROGRAPHIC BEHAVIOR OF 2-BENZYLBENZOPHENONES (I)[a]

X	$-E_{1/2}$ V *vs.* sce	i_d/C, A mmol^{-1} l.
H	1.55	1.37
4-Cl	1.48	1.51
3-CF_3	1.39	1.55
2-F	1.48	1.70
2-Cl	1.53	2.36
2-Br	1.41	2.67

[a] In a few cases a double wave was observed but usually this fused into one. See M. Ashwroth, *Coll. Czech. Chem. Commun.* **13,** 229 (1948), in I. M. Kolthoff and J. J. Lingane, *Polarography*. second ed, Vol. II, Interscience, New York, N.Y., 1952, p 683. The value of the diffusion current and, to a lesser extent, the half-wave potentials, depends on how these are obtained from the polarogram.

The rate of disappearance of the ketones was found to be first order. The rate constants were calculated from the slope of the straight line formed when log *C* was plotted against time where *C* is the concentration taken directly from the i_d *vs.* *C* calibration curve. A typical set of data is shown in Table II. This data gives an apparent rate constant of 39.6×10^{-3} hr^{-1} or 11.0×10^{-6} sec^{-1}. This was averaged with a second value to give that reported in Table III.

TABLE II

KINETIC DATA FOR THE CYCLIZATION OF 2-BENZYLBENZOPHENONE TO 9-PHENYLANTHRACENE[a]

Time, hr	Diffusion current, μA	Concentration[d] $\times 10^3$, mol/l.
0.00	0.510	5.00
2.00	0.500	4.80
6.00	0.428	3.65
9.00	0.400	3.25
12.00	0.368	2.80
18.00	0.328	2.25
21.00	0.320	2.10

[a] Temperature, 118°; solvent composition, 0.972 *M* HBr[b] at 118°; mole fraction of HOAc = 0.748.[c] [b] Corrected for volume expansion. [c] Where mole fraction of HOAc + H_2O = 1.00. [d] Concentration of ketone at 25°.

Discussion

Kinetic results are summarized in Table III. The 2-chloro- and 2-bromo-substituted compounds cyclize at immeasurably slow rates at 101.2 and 118°. They

---

[11] Compounds studied in this way were the 2-benzylbenzophenones in which X = H, 4-Cl and 3-CF_3. The rate constants at 101° for the first two of these were both 5.5×10^{-6} sec^{-1}. These studies were made by Janet C. Peake and Merry Jean Beres, undergraduate research participation students, 1961 and 1962, respectively.

[12] Increasing this volume by 20% gave no appreciable change in the appearance of the polarograph curves.

[13] Increasing this to 4 *N* gave no appreciable change in the appearance of the polarograph curves.

[14] Requires at least 15 min of vigorous bubbling.

TABLE III

RATES OF CYCLODEHYDRATION OF 2-BENZYLBENZOPHENONES (I) TO 9-PHENYLANTHRACENES (IV)

X	Temp, °C	Mole fraction[a] of HOAc	HBr,[b] mol/l.	$k \times 10^6$, sec^{-1}	H_0[c]
H	99.8	0.566	0.987	0.636[d]	−1.33
H	99.8	0.650	0.987	1.04[d]	−1.66
H	99.8	0.748	0.987	2.86[d]	−2.12
H	101.2	0.748	0.987	2.28	−2.12
H	99.8	0.866	0.987	11.7[d]	−2.83
H	99.8	0.996	0.987	33.6[d]	−3.71
3-CF_3	101.2	0.748	0.987	3.00	−2.12
4-Cl	101.2	0.748	0.987	1.97	−2.12
2-F	101.2	0.748	0.987	1.30	−2.12
2-Cl	101.2	0.748	0.987	0.083[e]	−2.12
2-Br	101.2	0.748	0.987	. . .[f]	−2.12
H	117.5	0.561	1.523	12.2[g]	−1.96
3-CF_3	117.5	0.561	1.523	17.8[g]	−1.96
4-Cl	117.5	0.561	1.523	11.7[g]	−1.96
H	118.0	0.748	0.972	11.8	−2.12
3-CF_3	118.0	0.748	0.972	12.6	−2.12
4-Cl	118.0	0.748	0.972	9.7[h] (14.0)	−2.12
2-F	118.0	0.748	0.972	7.67	−2.12
2-Cl	118.0	0.748	0.972	1.61	−2.12
2-Br	118.0	0.748	0.972	. . .[f]	−2.12
H	118.0	0.748	0.962	26.0	−2.12
3-CF_3	128.1	0.748	0.962	29.0[h] (18.3)	−2.12
4-Cl	128.1	0.748	0.962	25.5	−2.12
2-F	128.1	0.748	0.962	21.5[h] (26.4)	−2.12
2-Cl	128.1	0.748	0.962	8.28	−2.12
2-Br	128.1	0.748	0.962	1.67	−2.12
2-F	128.1	0.996	1.214	44.2	
2-Cl	128.1	0.996	1.214	14.7	
2-Br	128.1	0.996	1.214	9.24	

[a] Mole fraction of HOAc + H_2O = 1.00. [b] Corrected for volume expansion of the solvent. [c] At 25°. Tentative values obtained by Andrew Anderson, undergraduate summer research participant at King College, 1965. [d] From ref 10. [e] Approximate value because of the very slow rate. [f] No appreciable reaction after 120 hr. [g] These and their solvent composition were calculated from the data in ref 5 and 8. [h] Corrected to correspond to the isokinetic principle. The experimental values are given in parentheses.

are observable at 128° and proceed even more rapidly at higher acidity and lower water content as can be seen from the last two rate values in Table III. However, these cannot be compared with data at other acidities until H_0 determinations have been made in HBr–HOAc–H_2O solutions of this composition. The activation parameters, calculated from the temperature dependence of the rates, are collected in Table IV.

TABLE IV

ACTIVATION PARAMETERS FOR THE CYCLODEHYDRATION OF 2-BENZYLBENZOPHENONES

X	E_a[a]	$\Delta H^{\ddagger}$[a]	$\Delta S^{\ddagger}$[b]
H	26.6	25.8	−25.3
3-CF_3	25.6	24.8	−27.8
4-Cl	29.3	28.5	−18.8
2-F	31.8	31.0	−12.8
2-Cl	60.2	59.4	57.0

[a] Kcal/mol. [b] Cal/(mol)(deg), calculated at 117.5° and at unit h_0 as calculated by dividing the rate constants by h_0.

It was hoped that the data presented here along with some measure of the acidity of the solutions would allow comparison of data taken at different temperatures and acidities. However, precise measurement of the acidity of the types of solutions under consideration are not available. Brice and Katstra have shown[10] that the molarity of HBr is not a good index of the proton-donating property of the solutions; *i.e.*, the rate of cyclodehydration does not increase linearly with the stoichiometric concentration of HBr. This is particularly true when the water content of the solution is changing. They have suggested that H_0 might be a good measure of acidity in this solvent system. This seems to be correct because the tentative values of H_0 in this solvent system which we have recently obtained (Table III) give a linear plot with the log k values obtained by Brice (Figure 1). It should be emphasized that the stoichiometric concentration of HBr is not changing in this particular series, only the water concentration. The slope of the line is 0.841. The H_0 values may require some refinement but the fact that in the lower acidity range they check with the values reported by Zajac and Nowicki[15] and can be used to calculate rate constants that check with measured values increases our confidence that future changes in these values will be minor. For example, the rate constant for the cyclization of 2-benzylbenzophenone at 99.8° (HBr = 0.987 M and mole fraction of HOAc = 0.748) is 2.86×10^{-6} sec^{-1}. Using the activation energy, the Arrhenius equation, and the expression $\log k = -0.814H_0 + \text{constant}$, one can calculate that the rate should be 10.3×10^{-6} sec^{-1} under the conditions used by Bradsher and Vingiello[6] (117.5°, HBr =

---

[15] W. W. Zajac, Jr., and R. B. Nowicki, *J. Phys. Chem.*, **69**, 2649 (1965).

1.523 *M* and the mole fraction of HOAc = 0.561). This compares favorably with the values of 12.2×10^{-6} sec^{-1} actually measured.

However, further comparisons require the following more questionable assumptions: (1) the H_0 values do not vary appreaciably with temperature and (2) the variation of *k* with H_0 for the substituted ketones is the same as that for the unsubstituted compound. The first of these has been shown to be a fair approximation in H_2SO_4-H_2O in the 20-80° range,[16] but similar determinations have not been made in HBr-HOAc-H_2O solvent mixtures. The variation of H_0 with temperature may be fairly large especially at temperatures as high as 128°. The second seems reasonable since the mechanism appears to be the same for all the compounds studied.

Table V shows the results of our attempts to compare our data and that of Brice with that of Bradsher and Vingiello. Changes in *k* due to changes in acidity were estimated graphically, assuming that all three compounds follow the log *k vs.* H_0 relationship in Figure 1.

TABLE V

CALCULATED RATE CONSTANTS[a] AT 117.5°

X	From data[b] at 101.2°	From data[c] at 118.0°	From data[b] at 128°	Measured values[d]
H	7.34	8.6	7.5	12.2
H	10.3[e]			12.2
3-CF_3	9.1	9.3	8.7	17.8
4-Cl	7.4	10.2	6.6	11.7

[a] $\times 10^6$ (sec^{-1}). [b] Calculations involve both temperature and acidity change. [c] Calculations involve only acidity change. The differences in temperatures (0.5°) is considered negligible. [d] Obtained from ref 8 by changing from hr^{-1} to sec^{-1}. [e] From ref 10.

The calculated values check fairly well with those actually measured at 117.5° considering the uncertainties mentioned above and the fact that three different methods of analysis are being compared. It should also be noted that the polarographic method measures the disappearance of ketone while the other two methods measure the appearance of cyclized product. The calculated values are consistently lower than those given by Vingiello and Van Oot.[8] The reason for this is not known. For the one point at which experimental values can be compared directly, the check is quite good (2.28×10^{-6} sec^{-1} *vs.* 2.86×10^{-6} sec^{-1}).

The *meta*- and *para*-substituted compounds show a fairly constant activation energy as might be expected by the compensating factors in the proposed mechanism.[7] The entropies of activation are rather large negative values as would be expected from a cyclic transition state. The activation energies show a sharp increase when the substituents are *ortho*, increasing with the size of the substituent. This is probably due to the severe steric crowding postulated.[9] This increase in activation energy is paralleled by an increase in entropy of activation which may be interpreted as being due to a longer and weaker incipient bond in the transition state between the carbon that was originally the carbonyl carbon and the carbon at the *ortho* position of ring A as the large *ortho* group in ring B increases the crowding at the point of reaction.

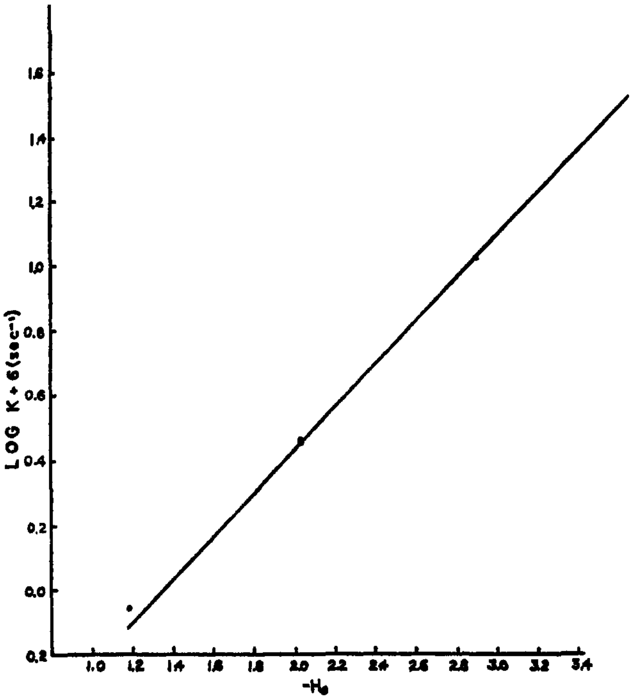


Figure 1.—The effect of solvent acidity on the rate of aromatic cyclodehydration.

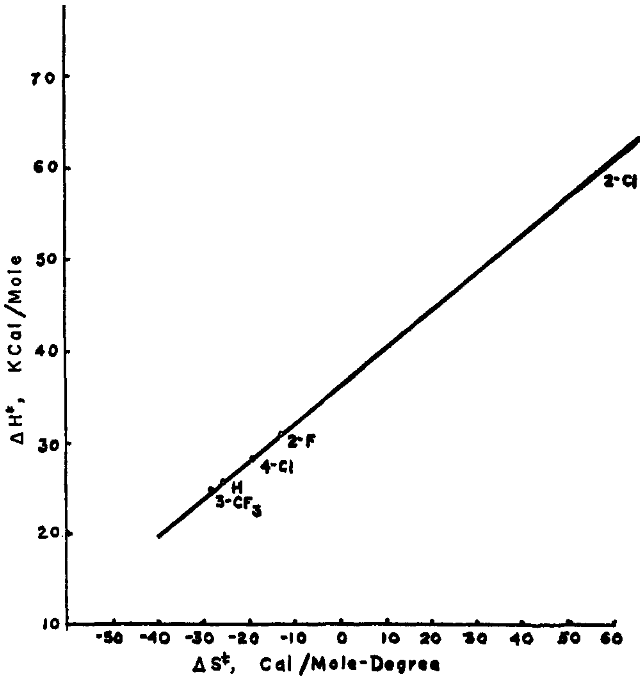


Figure 2.—Isokinetic plot for the aromatic cyclodehydration of 2-benzylbenzophenones (I). The points are identified by the substituents on ring B.

These reactions make up an isokinetic relationship[17] as can be seen from Figure 2. The slope of the line gives an isokinetic temperature of ~415°K (142°C) which is well above the highest experimental tempera-

---

(16) A. I. Gelbshtein, G. G. Sheglova, and A. I. Tempkin, *Dokl. Akad. Nauk SSSR*, **107**, 108 (1956), in J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963.

(17) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

ture used. This tends to confirm the previous interpretation of two compensating factors, both having the same isokinetic temperature, by eliminating the possibility that the reactions had been studied at the isokinetic temperature. The 2-fluoro compound shows no deviation that might be attributed to some proximity effect such as an intramolecularly hydrogen-bonded intermediate[9] or a steric effect. The slow cyclization of both the 2- and 4-fluoro ketones has been interpreted[8,9] as being due to a strong resonance interaction at the reaction center. Even the 2-chloro ketone is only slightly off the straight line although the steric crowding at the reaction center must be quite severe in the transition state. It would be interesting to determine the location of the 2-methyl and 2-bromo compounds on this plot.

Registry No.—I (X = H), 4919-84-0; I (X = 4-Cl), 18793-94-7; I (X = 3-CF$_3$), 394-75-2; I (X = 2-F), 740-35-2; I (X = 2-Cl), 18793-96-9; I (X = 2-Br), 18793-97-0.

Acknowledgments.—This work was supported by the Research Corp. with supplementary support from the National Science Foundation and from the American Association for the Advancement of Science, administered by the Tennessee Academy of Science.

Sulfur-Bridged Carbocycles. III. Photocyclization of β,β'-Diphenyldivinyl Sulfide[1]

Eric Block and E. J. Corey

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

Received September 6, 1968

β,β'-Diphenyldivinyl sulfide (**2a**) has been found to undergo facile cyclization on irradiation to *trans*-2,3-diphenyl-5-thiabicyclo[2.1.0]pentane (**3a**), the first known example of a cyclobutene episulfide. Bicyclic sulfide **3a** undergoes desulfurization with trivalent organophosphorus compounds giving *trans,trans*-1,4-diphenylbutadiene, presumably by way of thermally unstable *trans*-3,4-diphenylcyclobutene (**9**). A second product of the irradiation of sulfide **2a** has been identified as 2,3-dihydro-3,4-diphenylthiophene (**10**).

With the objective of synthesizing 2-thiabicyclo[1.1.1]pentane (**1**), the simplest symmetrical sulfur-bridged carbocycle,[2] we have investigated the photochemistry of divinyl sulfides. It was anticipated that photocyclization of the type observed by Srinivasan in the acyclic diene series[3] would occur affording bicyclic sulfides. In contrast to the nonconjugated dienes (such as 1,4-pentadiene) which are transparent in the ultraviolet region above 180 mμ, vinyl sulfides absorb strongly at 230 mμ (see Table I). Furthermore, a bathochromic shift is observed on going from vinyl sulfides to divinyl sulfides. This shift is thought to indicate through-conjugation of the double bonds.[4]

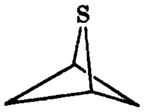
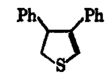

1

Table I

Ultraviolet Spectra of Vinyl Sulfides

Compound	λ_{max}, mμ	ε	Ref
$CH_2{=}CHSCH(CH_3)_2$	230	6000	4a
$CH_2{=}CHSCH{=}CH_2$	240, 255	8350,.7600	4a
 **10**	226, 306	16,200, 15;200	This work
$C_6H_5CH{=}CHSCH_3$	286	15,500	4b
$C_6H_5CH{=}CHSCH{=}CHC_6H_5$ (**2a**)	229, 320	24,000, 36,000	This work

Although irradiation of divinyl sulfide[5] itself under various conditions was unproductive,[6] brief irradiation of the isomers of β,β'-diphenyldivinyl sulfide[7] (**2a**, preparation outlined in eq 1) afforded a new compound, characterized as *trans*-2,3-diphenyl-5-thiabicyclo[2.1.0]-

---

[1] Paper II: E. J. Corey and E. Block, *J. Org. Chem.*, in press.

[2] For the synthesis and reactions of the second and third members of the class of symmetrical sulfur-bridged carbocycles, see the preceding paper and E. J. Corey and E. Block, *J. Org. Chem.*, **31**, 1663 (1966); also see E. Block, Ph.D. Thesis, Harvard University, 1967 [*Dissertation Abstr.*, **28**, 1849B (1967)].

[3] (a) R. Srinivasan and K. H. Carlough, *J. Am. Chem. Soc.*, **89**, 4932 (1967); (b) also see J. Meinwald and G. W. Smith, *ibid.*, **89**, 4923 (1967).

[4] (a) C. E. Scott and C. C. Price, *ibid.*, **90**, 2202 (1968); (b) M. C. Caserio, R. E. Pratt, and R. J. Holland, *ibid.*, **88**, 5747 (1966).

[5] For the preparation of divinyl sulfide, see K. K. Georgieff and A. Dupré, *Can. J. Chem.*, **37**, 1104 (1959).

[6] Wynberg and coworkers have similarly reported that irradiation of bis(1-propenyl) sulfide gives no detectable amounts of cyclization products: S. H. Groen, R. M. Kellogg, J. Buter, and H. Wynberg, *J. Org. Chem.*, **33**, 2218 (1968).

[7] (a) Reaction i: O. Scherer and G. Stähler, German Patent 1,080,101 (1960); *Chem. Abstr.*, **55**, 16422*i* (1961). (b) Reactions ii and iii: K. Dimroth, H. Follmann, and G. Pohl, *Chem. Ber.*, **99**, 642 (1966).