Since the cationic intermediate is a highly reactive species, it is expected that it reacts by a transition state very "reactantlike," or in other terms that it is more sensitive to the charge distribution in the initial state than to the stability of the products.

As a matter of fact, if the course of the reaction is determined by the position of attack of the electrophilic center to the arylthio nucleus and independent of the energy and the fate of intermediates **7** and **8**, the results hitherto obtained may be rationalized on the basis of the directing effect of the substituents. Those so far studied are indeed of the *ortho,para*-directing type, and consequently when they are *para* they direct the attack at the 1 position (rearrangement), whereas when they are *meta* they direct the attack at the 2,6-positions (no rearrangement) of the phenylthio nucleus.

Experimental Section

Melting and boiling points are uncorrected. Infrared spectra were determined in carbon disulfide solution on a Perkin-Elmer Model 225 spectrophotometer.

***p*-Bromophenyl *t*-butyl sulfide** was prepared in 61% yield by the method previously reported for the synthesis of phenyl *t*-butyl sulfide[6] as a colorless liquid, bp 153–155° (20 mm).

Anal. Calcd for $C_{10}H_{13}BrS$: C, 48.99; H, 5.34; Br, 32.59; S, 13.08. Found: C, 48.98; H, 5.24; Br, 32.22; S, 12.93.

***p*-Deuteriophenyl *t*-Butyl Sulfide.**—*p*-(*t*-Butylthio)phenylmagnesium bromide from 9.5 g of *p*-bromophenyl *t*-butyl sulfide and 1.2 g of magnesium in 40 ml of anhydrous ether was hydrolyzed with a 15% solution of deuterium chloride in deuterium oxide. The ether solution was separated and dried (Na_2SO_4) and the solvent was removed. The liquid residue was distilled twice to give 4.6 g (71% yield) of *p*-deuteriophenyl *t*-butyl sulfide, bp 106–107° (20 mm) [lit.[6] bp 73° (5 mm) for phenyl *t*-butyl sulfide]; the corresponding sulfone was obtained, mp 99–100° (lit.[6] mp 98–99° for pheny *t*-butyl sulfone).

***p*-Deuteriophenylsulfenyl chloride (3)** was prepared by chlorinolysis of *p*-deuteriophenyl *t*-butyl sulfide (4.6 g) by chlorine in carbon tetrachloride at −10°, following a modification of the procedure reported by Kharasch and Langford[7] for the synthesis of 2,4-dinitrophenylsulfenyl chloride, and purified by distillation. There were obtained 3.5 g (87% yield) of **3**, bp 90–92° (20 mm), identical with that of a sample of phenylsulfenyl chloride prepared by the same method.

1,2-Diphenyl-2-*p*-deuteriophenylthiovinyl 2,4,6-Trinitrobenzenesulfonate (4).—Tolane (1.78 g, 10 mmol) was dissolved in 60 ml of anhydrous methylene chloride, silver 2,4,6-trinitrobenzenesulfonate (acetonitrile complex,[8] 5.23 g, 10 mmol) was added, and the suspension was stirred for a few minutes. A solution of **3** (1.45 g, 10 mmol) in 15 ml of methylene chloride was added dropwise at 15° and the reaction mixture was stirred for 10 min. Filtration of the insoluble AgCl followed by addition of pentane to the clear solution resulted in the precipitation of **4** (2.8 g, 48% yield) as a yellow, crystalline solid, which was purified by crystallization from methylene chloride–pentane, mp 109–110° dec. A mixture melting point with 1,2-diphenyl-2-phenylthiovinyl 2,4,6-trinitrobenzenesulfonate (prepared by the same method)[1a] was 109–110° dec.

2,3-Diphenyl-5-bromobenzo[*b*]thiophene was prepared in 53% yield by cyclization of 2-phenyl-2-*p*-bromophenylthioacetophenone in polyphosphoric acid.[1a] Chromatography on silica gel (hexane) and recrystallization from ethanol gave white crystals, mp 175–176°.

Anal. Calcd for $C_{20}H_{13}BrS$: C, 65.75; H, 3.59; Br, 21.88; S, 8.78. Found: C, 66.04; H, 3.59; Br, 21.77; S, 8.77.

2,3-Diphenyl-5-deuteriobenzo[*b*]thiophene (5a).—The Grignard reagent prepared from 1.0 g of 2,3-diphenyl-5-bromobenzo[*b*]thiophene and 0.15 g of magnesium in 100 ml of anhydrous ether was hydrolyzed with a 15% solution of deuterium chloride in deuterium oxide. The ether solution was separated, the solvent was removed, and the residue was chromatographed on silica gel. Elution with hexane gave 0.6 g (76% yield) of **5a**, which was recrystallized from ethanol, mp 113–114°.[9]

Mass spectrometric data indicated a deuterium content of 0.89 ± 0.02 atoms per molecule.

2,3-Diphenyl-6-bromobenzo[*b*]thiophene was prepared in 89% yield by cyclization of 1,2-diphenyl-2-*p*-bromophenylthiovinyl 2,4,6-trinitrobenzenesulfonate in the presence of gaseous BF_3.[1a] Recrystallization from ethanol gave white crystals, mp 169–171°.[1b]

Anal. Calcd for $C_{20}H_{13}BrS$: C, 65.75; H, 3.59; Br, 21.88; S, 8.78. Found: C, 66.25; H, 3.53; Br, 21.88; S, 8.72.

2,3-Diphenyl-6-deuteriobenzo[*b*]thiophene (5b) was prepared in 73% yield from 2,3-diphenyl-6-bromobenzo[*b*]thiophene by the same procedure reported for the preparation of **5a**, mp 113–114°.[9]

Mass spectrometric data indicated a deuterium content of 0.90 ± 0.02 atoms per molecule.

Treatment of 4 with BF_3 Etherate.—**4** (2.5 g, 4.3 mmol) was dissolved in 200 ml of anhydrous methylene chloride, 20 ml of boron trifluoride diethyletherate was added, and the reaction mixture was allowed to stand for 24 hr at room temperature. The 2,4,6-trinitrobenzenesulfonic acid formed was filtered, and the solution was washed with water and dried (Na_2SO_4). The solvent was evaporated and the residue was chromatographed on silica gel. Elution with hexane gave, after recrystallization from ethanol, 1.05 g (85% yield) of a mixture of deuterated 2,3-diphenylbenzo[*b*]thiophenes **5**, mp 113–114°.[9]

Mass spectrometric data indicated a total deuterium content of 0.90 ± 0.02 atoms per molecule.

The infrared analysis of the mixture was performed by means of calibration curves, based on a band at 821 cm^{-1} for **5a** and a band at 640 cm^{-1} for **5b**, obtained from mixtures of the two model compounds in various ratios.

Registry No.—**3**, 23042-80-0; **4**, 23042-81-1; 2,3-diphenyl-5-bromobenzo[*b*]thiophene, 23042-82-2.

Acknowledgments.—This work was supported by the Consiglio Nazionale delle Ricerche, Rome. We wish to thank Dr. Tito Salvatori, of the SNAM-ENI Laboratories, S. Donato Milanese, for the mass spectra.

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[6] V. N. Ipatieff, H. Pines, and B. S. Friedman, *J. Amer. Chem. Soc.*, **60**, 2731 (1938).

[7] N. Kharasch and R. B. Langford, *J. Org. Chem.*, **28**, 1903 (1963).

[8] D. J. Pettitt and G. K. Helmkamp, *ibid.*, **29**, 2702 (1964).

(9) Identical with that of an authentic sample of 2,3-diphenylbenzo[*b*]-thiophene.[1]

The Photoreactions of 2,4-Dimethoxyacetanilide[1–3]

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Received June 23, 1969

Aryl esters and N-arylamides have been found to undergo photo Fries rearrangements.[4–6] Recently, we reported that, when 2,4-dimethoxyphenyl acetate (I) was irradiated, not only a normal photo-Fries rearrangement to the unoccupied *ortho* position took place but

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(1) Supported by the Research Division, Brigham Young University, and the United Fund of Utah County.

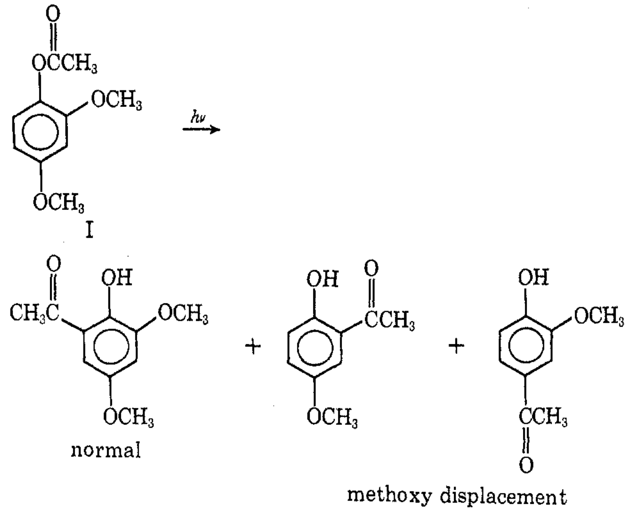
(2) Nuclear magnetic resonance spectra were obtained on a Varian A-60A spectrometer purchased under the National Science Foundation Grant GP-6837.

(3) Presented at the Pacific Northwest Regional Meeting, Salt Lake City, Utah, June 1969.

(4) (a) J. C. Anderson and C. B. Reese, *Proc. Chem. Soc.*, 217 (1960); (b) J. C. Anderson and C. B. Reese, *J. Chem. Soc.*, 1781, (1963).

(5) See D. Bellus and P. Hrdlovic, *Chem. Rev.*, **67**, 599 (1967), for a review of the photo-Fries and related reactions.

(6) (a) D. Elad, *Tetrahedron Lett.*, 873 (1963); (b) D. Elad, D. V. Rao, and V. I. Stenberg, *J. Org. Chem.*, **30**, 3252 (1965).



also a methoxy group could be displaced if it were in the *ortho* or *para* position. In addition, decarboxylation and cleavage products were obtained.[7]

In the present study, we have irradiated 2,4-dimethoxyacetanilide (II) to see if methoxy-displaced rearrangements would also take place in the N-arylamide system. We also wanted to see if a reaction similar to the decarboxylation of certain phenyl esters[7,8] could be observed in this system (that is the loss of CONH). This latter reaction was not observed even with 2,4,6-trimethylacetanilide where no photo-Fries rearrangement could take place.[9]

The products of the ultraviolet (uv) irradiation of II in benzene were found to be 2-amino-3,5-dimethoxyacetophenone (III, 63%) from the *ortho* photo-Fries reaction to the unoccupied position; 2-amino-5-methoxyacetophenone (IV, 5%) and 4-amino-3-methoxyacetophenone (V, 11%) from displaced *ortho*- and *para*-methoxy photo-Fries reactions; 2,4-dimethoxyaniline (8%) from the cleavage reaction; and five other products which could not be isolated in sufficient quantity to characterize.

The structures of the photo-Fries rearrangement products (III, IV, and V) were determined by their spectra. The nuclear magnetic resonance (nmr) spectra were quite definitive. Compounds IV and V each exhibited a peak attributable to NH_2 groups at δ 5.65 for IV and 4.3 for V. The difference in chemical shift for these two peaks is a result of hydrogen bonding in 2-aminoacetophenone-type compounds. This hydrogen bonding causes the NH_2 bond to shift from about δ 4.3 to 5.5–6.0.[10] The carbonyl bond in the infrared (ir) may also be shifted to lower wavenumbers by as much as 50 cm^{-1} owing to hydrogen bonding in the *ortho* position.[11] Such a shift was exhibited by the ir spectrum for compound IV (1640 cm^{-1}) in comparison with V (1660 cm^{-1}). Thus we feel confident that IV is 2-amino-5-methoxyacetophenone and V is 4-amino-3-methoxyacetophenone. The nmr and ir spectra of 2-amino-3,5-dimethoxyacetophenone (III), the major photo-Fries reaction product, also exhibit the typical 2-aminoacetophenone spectra (1640 cm^{-1} in the ir spectrum and a singlet at δ 6.1 in the nmr spectrum).

Shizuka and Tanaka have shown that the acetanilide photo-Fries reaction occurred from the lowest lying excited singlet state resulting in the fission of the C–N bond and the liberation of C_6H_5NH and $COCH_3$ radicals.[12] They also found that rearrangements to the 4 position did not take place when it was occupied by methyl or chloro groups; however, 4-iodo and 4-bromo groups were displaced by the migrating acyl group.[12c] They attributed the latter results to a predissociation of C–Br and C–I bonds caused by the irradiation.[12c] The fact that the chloro group was not displaced is somewhat surprising since Kobsa observed a displacement of the chloro group when he irradiated 4-*t*-butyl-2,6-dichlorophenyl acetate.[13]

The mechanism of the photo-Fries reaction of 2,4-dimethoxyacetanilide is probably the same as that reported by Shizuka and Tanaka.[12] However, we do not believe that the methoxy displacement reaction is taking place by way of a predissociation of the C–OCH_3 bond. If this were the case, we could have expected to find some 2-methoxyacetanilide as well as some 4-methoxyacetanilide in the reaction products. Neither of these compounds could be isolated in our reaction. We, therefore, propose a concerted type of mechanism for this reaction as we previously postulated.[7]

Experimental Section

Materials and Apparatus.—2,4-Dimethoxyaniline and 2,4,6-trimethylaniline were purchased from the Aldrich Chemical Co. Acetyl chloride, reagent grade benzene, and pyridine were purchased from J. T. Baker Co. An Aerograph 202-B temperature-programming vapor phase chromatograph was used to analyze and separate all photochemical products. All ir spectra were obtained on a Perkin-Elmer Model 700 spectrophotometer. The nmr spectra were taken on a Varian A-60A spectrometer.[2] A Hanovia 450-W, medium-pressure lamp was used.

Preparation of 2,4-Dimethoxyacetanilide (II).—An excess of acetyl chloride was slowly added to 20 g (0.13 mol) 2,4-dimethoxyaniline in 80 ml of cold pyridine. The resulting dark red solution was allowed to warm to room temperature and then added to 100 ml of ice water. The crude 2,4-dimethoxyacetanilide (II) was filtered (11.5 g, 47%). The product II was purified by recrystallization from water, mp 114–115°.[14]

Anal. Calcd for $C_{10}H_{13}O_3N$: C, 61.53; H, 6.71. Found: C, 61.51; H, 6.67.

Preparation of 2,4,6-Trimethylacetanilide.—This was prepared by the above procedure to obtain an 80% yield, mp 215–216°.

Anal. Calcd for $C_{11}H_{15}ON$: C, 74.54; H, 8.53. Found: C, 74.63; H, 8.75.

Irradiation of 2,4-Dimethoxyacetanilide (II).—The substrate (2 g) was dissolved in 200 ml of benzene and the solution was placed in the reactor. A quartz immersion well was fitted into the reactor. A small stream of pure nitrogen was sparged into the bottom of the reactor for 40 min before the reaction was started and then continued throughout the irradiation. The irradiation was carried out for 19 hr. Upon completion of the irradiation, the solvent was removed under vacuum (30–40 mm). The remaining almost-black oil was subjected to vpc analysis using a 20% SE-30 on Chromosorb W column and programming the temperature from 100 to 275°. Ten vpc peaks were observed. Some of these fractions were collected and analyzed.

Fractions 1–3 (4%) could not be isolated.

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[7] J. S. Bradshaw, E. L. Loveridge, and L. White, *J. Org. Chem.*, **33**, 4127 (1968).

[8] See R. A. Finnegan and D. Knutson, *J. Amer. Chem. Soc.*, **89**, 1970 (1967), and other papers of that series.

[9] *ortho* and *para* displacements of alkyl groups in the photo-Fries reaction have never been observed; see ref 5.

[10] Similar shifts have been observed in the case of 4-aminoacetophenone (NH_2 peak at δ 4.43) and 2-aminoacetophenone (NH_2 peak at δ 6.12). See Sadtler Nuclear Magnetic Resonance Spectra No. 242 and No. 4987, published by Sadtler Research Laboratories Inc., Philadelphia, Pa.

[11] See K. Nakanishi "Infrared Absorption Spectroscopy," Holden-Day Inc., San Francisco, Calif., 1962, p 42.

[12] (a) H. Shizuka and I. Tanaka, *Bull. Chem. Soc. Jap.*, **41**, 2343 (1968); (b) H. Shizuka, *ibid.*, **42**, 52 (1969); (c) H. Shizuka, *ibid.*, **42**, 57 (1969).

[13] H. Kobsa, *J. Org. Chem.*, **27**, 2293 (1962).

[14] All melting points are uncorrected.

Fraction 4 (8%) exhibited ir and nmr spectra that were the same as those of 2,4-dimethoxyaniline.

Fraction 5, compound IV (5%), exhibited ir (KBr) 3450, 3340, and 1640 cm^{-1}; nmr (CCl_4) δ 2.45 (s, 3), 3.75 (s, 3), 5.7 (s, 2), and 6.8 (m, 3).

Fraction 6, compound V (11%), exhibited ir (KBr) 3460, 3360, and 1660 cm^{-1}; nmr (CCl_4) δ 2.40 (s, 3), 3.85 (s, 3), 4.30 (s, 2), 6.55 (m, 1), and 7.30 (m, 2).

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71. Found: C, 65.17; H, 6.79.

Fraction 7, compound III (63%), exhibited ir (KBr) 3460, 3340, 1640 cm^{-1}; nmr (CCl_4) δ 2.45 (s, 3), 3.70 (s, 3), 3.85 (s, 3), 6.10 (s, 2), and 6.50 (m, 2).

Anal. Calcd for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71. Found: C, 61.29; H, 6.59.

Fraction 8, compound II, exhibited ir and nmr spectra which were the same as those of the starting material.

Fractions 9 and 10 (9%) could not be isolated.

Irradiation of 2,4,6-Trimethylacetanilide.—The substrate (1 g) was dissolved in 240 ml of pure benzene and irradiated as described above. After the solvent was removed, only 2,4,6-trimethylaniline and starting anilide could be isolated from the reaction mixture. No material was observed in the vpc chromatogram with a retention time the same that of as 1,2,3,5-tetramethylbenzene.

Registry No.—II, 23042-75-3; III, 23042-76-4; IV, 23042-77-5; V, 22106-40-7; 2,4,6-triethylacetanilide, 5096-21-9.

A Photochemical Preparation of 4,11-Diphenylbisanthene

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Received June 27, 1969

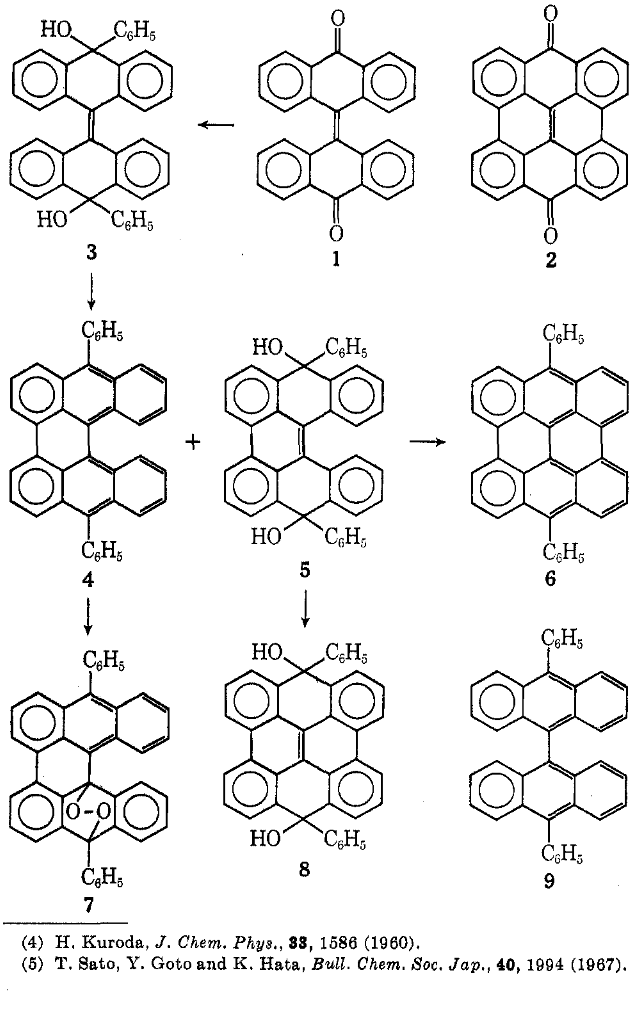
4,11-Diphenylbisanthene (**6**) is one of a few aromatic hydrocarbons from which fluorescence ($\Phi_F = 0.18$, λ_{max} 720 mμ in benzene) of moderate intensity has been detected in the infrared region.[1] A three-step synthesis of **6** with an overall yield of 20% had been described earlier by the sequence bianthrone (**1**) → 4,11-bisanthenequinone (**2**) → 4,11-dihydroxy-4,11-diphenyldihydrobisanthene (**8**) → **6**.[2] A more convenient approach appeared to be the photocyclization of the diphenylbianthracenediol **3**, which can be prepared from bianthrone in good yield.[3]

Ultraviolet irradiation of benzene solutions of **3** [λ_{max} 327 mμ (log ϵ 4.08)] and iodine exposed to the atmosphere did indeed produce hydrocarbon **6** in moderate yield. The only two products isolated were the deep blue diphenylbisanthene and the highly blue-fluorescing photooxide **7**. The easily identifiable intense bands at 683 and 625 mμ for product **6** facilitated the following of the reaction spectrophotometrically. A maximum buildup of diphenylbisanthene was quickly attained, but on prolonged irradiation the product was slowly decomposed. The concurrent appearance of a broad band centered near 400 mμ and the decrease in intensity of the peaks at 683 and 625 mμ imply the formation of a photooxide, since the absorption at shorter wavelengths is in the same region as that of the photooxide of bisanthene.[4] The photooxide of **6** could not be isolated; instead, only resinous material was obtained, as had been observed previously.[2]

Thus, the limiting factor in maximizing the yield of **6** is the photoinstability of the hydrocarbon. While yields were greatest when the reaction was carried out open to the atmosphere, the photooxidation of the product was also occurring. When following the reaction of 5.9×10^{-5} *M* **3** and 5.9×10^{-5} *M* iodine in a 1-cc cell, a yield of **6** as high as 59% was detected. On a larger scale, however, diphenylbisanthene was isolated in 20% yield.

Contrary to the observation that the yield of triphenylene in the photoaryl coupling of *o*-terphenyl is dependent on the iodine concentrations,[5] varying the amounts of iodine in the reaction of **3** to **6** had little affect on the yield, as demonstrated by the yields of **6** (50, 59, and 49%) when the ratios of diol **3**/I_2 were 10, 1.0, and 0.5. Iodine is essential to the reaction, however, since, without it, **6** was not formed as **3** was slowly consumed. Heating the product of the noncatalyzed reaction with hydriodic acid did not yield diphenylbisanthene. This result rules out dihydroxydiphenyldihydrobisanthene **8** as a product in the photochemical reaction in which iodine is not used.

Since the decomposition of **6** was much slower when irradiated under nitrogen, rather than when exposed to the air, solutions of **3** and iodine were irradiated in a nitrogen atmosphere. Under these conditions the yield of diphenylbisanthene was decreased to 5% and



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(3) A. Schonberg and A. Ismail, *J. Chem. Soc.*, 201 (1945).

(4) H. Kuroda, *J. Chem. Phys.*, **33**, 1586 (1960).

(5) T. Sato, Y. Goto and K. Hata, *Bull. Chem. Soc. Jap.*, **40**, 1994 (1967).