The third group of compounds to be considered in Table IV is benzyl chloride and $\alpha,\alpha,\alpha$-trichlorotoluene. The rate of the $C_6H_5CH_2Cl$ reaction is faster than expected for the $CH_2Cl$ group as an aliphatic substituent, when compared with $\beta$-chloroethanol. We conclude, therefore, that the aromatic nucleus is activated toward a nucleophilic attack by electron withdrawal, both by inductive and by resonance effects. The chlorine atom, on the other hand, is also activated by the aromatic nucleus.[19]

The interaction of $e_{aq}^-$ with $C_6H_5CCl_3$, on the other hand, is in greater part a *direct* interaction with the chlorine atoms.[19] In fact, this rate is *slower* than that with chloroform.[4] This is attributed to a withdrawal of electrons from the aromatic nucleus resulting in partial deactivation of the $-CCl_3$ group.[19] This last case is another example of a direct reaction of $e_{aq}^-$ with a substituent. The use of our $e_{aq}^-$ rate constants as a measure of electron density in the nucleus is therefore limited to substituents which do not readily interact directly with $e_{aq}^-$.

It is interesting to find that comparable rate constants are obtained for the naphthalene and benzyl chloride + $e_{sol}^-$ reactions in water and in ethanol. As the anionic product is a sparingly solvated species, this result corroborates the conclusion that the solvation of the electron in both solvents is comparable.[20]

In conclusion, it can be stated that the hydrated electron may be considered as the most elementary nucleophile as well as the simplest reducing agent. The rules that apply to the $e_{aq}^-$ reaction are governed by the same parameters that determine aromatic substitution[13] and the information gained from the $e_{aq}^-$ reactivity may be applied to aromatic chemistry in general. It is gratifying to observe that the Hammett's free-energy relationship holds up to the limit of diffusion-controlled processes.

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# Optically Active Sulfoxides. The Synthesis and Rotatory Dispersion of Some Diaryl Sulfoxides[2]

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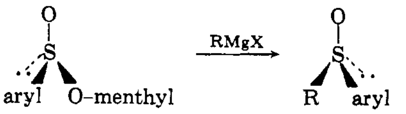
Several optically active diaryl sulfoxides have been prepared by treating optically active (−)-menthyl (−)-arenesulfinates with arylmagnesium bromides. This reaction is shown to produce optically pure sulfoxides. The optical rotatory dispersion curves and ultraviolet spectra of the sulfoxides and the sulfinate esters were determined and are discussed.

Sulfoxides can be synthesized by treating sulfinate esters with Grignard reagents.[4] If the sulfinate esters are optically active at sulfur, optically active sulfoxides are formed. The first example of the use of this method was reported in a preliminary communication.[5] (+)-Ethyl *p*-tolyl sulfoxide (2) was prepared by the reaction of (−)-menthyl (−)-*p*-toluenesulfinate (1) with ethylmagnesium iodide.



(1)

Since then, the syntheses of several other optically active sulfoxides using this method have been reported.[6-9] In this paper we wish to report not only on the synthesis and optical rotatory dispersion (o.r.d.) curves of some diaryl sulfoxides, but also on the mechanism of the reaction used to synthesize them. The diaryl sulfoxides were obtained by treating (−)-menthyl (−)-arenesulfinates with Grignard reagents as in eq. 1. Before discussing the individual sulfoxides, several questions concerning this general reaction should be answered. First, does the reaction proceed with inversion of configuration at sulfur as pictured in eq. (1), with retention, or with some of each? Second, what is the absolute configuration at sulfur?

The chief evidence that inversion takes place at sulfur can be summarized briefly. Phillips[10] demonstrated that alcoholysis of alkyl *p*-toluenesulfinate esters proceeds with inversion. Johnson and Sapp[11] reported that alkoxysulfonium salts, $ROSR_2^+$, prepared from optically active sulfoxides are hydrolyzed to sulfoxides of opposite sign of rotation; that is, the hydrolysis proceeds with inversion. Both of these reactions, the alcoholysis and the hydrolysis, proceed

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[3] (a) University of New Hampshire. (b) National Science Foundation Undergraduate Fellow, Summer, 1963. (c) Some of this work is from the B.S. Thesis (1963) of R. I. P.

[4] H. Gilman, J. Robinson, and N. H. Beaber, *J. Am. Chem. Soc.*, **48**, 2715 (1926); H. Gilman and J. D. Robinson, *Bull. soc. chim. France*, [4] **45**, 636 (1929).

[5] K. K. Andersen, *Tetrahedron Letters*, 93 (1962).

[6] K. K. Andersen, *J. Org. Chem.*, **29**, 1953 (1964).

[7] K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **86**, 1452 (1964).

[8] C. J. M. Stirling, *J. Chem. Soc.*, 5741 (1963).

[9] K. Mislow, A. L. Ternay, Jr., and J. T. Melillo, *J. Am. Chem. Soc.*, **85**, 2329 (1963).

[10] H. Phillips, *J. Chem. Soc.*, **127**, 2552 (1925).

[11] C. R. Johnson and J. B. Sapp, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963, p. 23Q; C. R. Johnson, *J. Am. Chem. Soc.*, **85**, 1020 (1963).

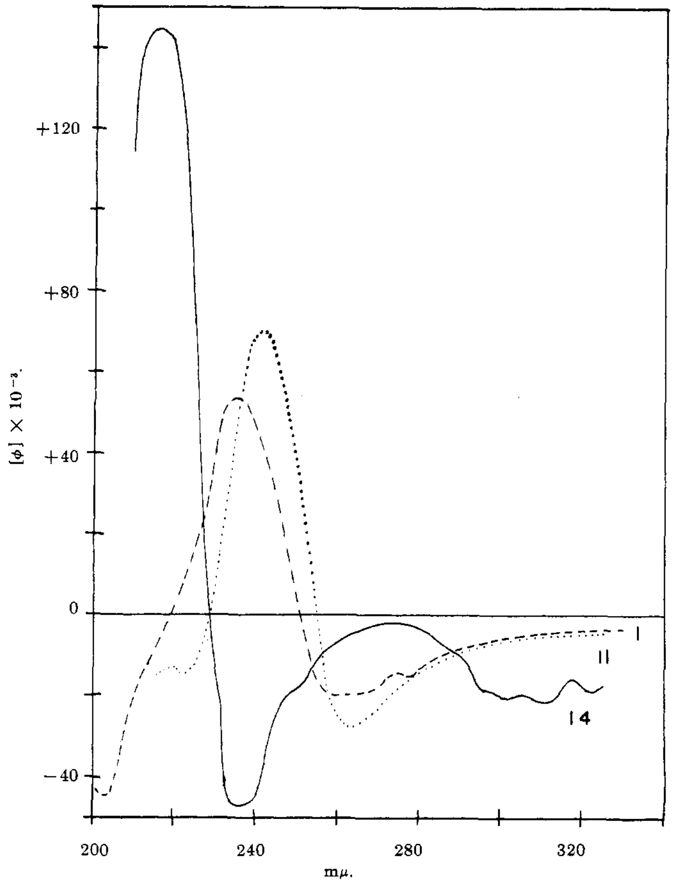


Fig. 1.—Optical rotatory dispersion curves of **1**, **11**, and **14** (see Table III).

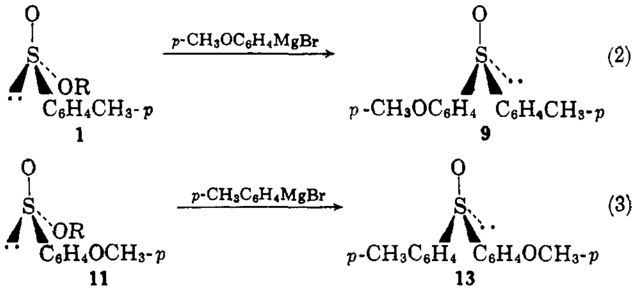
*via* nucleophilic attack on sulfur by oxygen. It seems likely that the nucleophilic Grignard reagent would behave in a similar manner. Further evidence that this is so was presented by Mislow, Ternay, and Melillo.[9] They prepared (+)-ethyl, (+)-isopropyl, and (+)-*t*-butyl *p*-tolyl sulfoxides from (−)-menthyl (−)-*p*-toluenesulfinate (**1**). The sulfoxides and the sulfinate gave Cotton effects opposite in sign. They concluded, assuming that both the conformations and nature of the electronic transitions were comparable, that inversion took place as had previously been suggested.[5] Circular dichroism (c.d.) measurements support these conclusions; the c.d. curves of (+)-ethyl *p*-tolyl sulfoxide (**2**) and (−)-menthyl (−)-*p*-toluenesulfinate (**1**) are practically mirror images of one another.[12]

The optical purities of sulfoxides prepared as in eq. 1 are unknown. The high rotation of the (+)-ethyl *p*-tolyl sulfoxide (**2**) suggests it is of high optical purity. One would expect a completely optically pure product, provided the sulfinate ester is pure, if the reaction proceeds with inversion *via* an $S_N2$-like mechanism. Before discussing this point further, a word on the absolute configurations is in order.

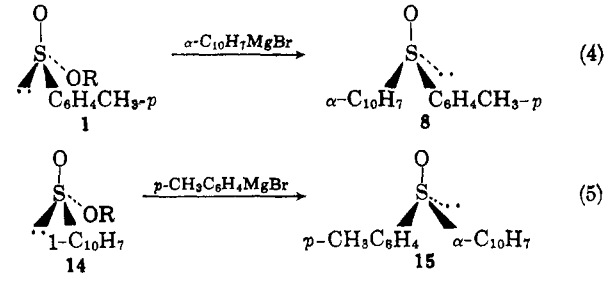
Herbrandson[13] tentatively assigned the *S*-configuration[14] to sulfur in (−)-menthyl (−)-*p*-iodobenzenesulfinate. Assuming that the *p*-iodo atom doesn't influence the sign of rotation of the arenesulfinyl chromophore, then (−)-menthyl (−)-*p*-toluenesulfinate (**1**) should also be of configuration *S* at sulfur.[5]

Thus, assuming inversion, *R*-(+)-ethyl *p*-tolyl sulfoxide (**2**) would arise from (−)-menthyl *S*-(−)-*p*-toluenesulfinate (**1**). Recently, Fleischer, Axelrod, Green, and Mislow[15] using X-ray and chemical methods established the absolute configurations of (−)-menthyl (−)-*p*-iodobenzenesulfinate and of **1**. Both are *S* about sulfur. This is a very significant accomplishment. Using the methods developed by us,[5,6] the absolute configurations may now be assigned to sulfoxides available from optically active sulfinate esters. An example of this method is given by eq. 2, 3, 4, and 5 and is discussed below.

To determine the stereospecificity of the reaction, we carried out the reactions depicted below. Both esters, (−)-menthyl (−)-*p*-toluenesulfinate (**1**) and (−)-menthyl (−)-*p*-methoxybenzenesulfinate (**11**), were recrystallized until of constant rotation. Their similar o.r.d. curves (Fig. 1) indicate that they have the same configuration. The products formed, sulfoxides **9** and **13**, had rotations at the sodium D line equal in magnitude but opposite in sign (see Table I).



An analogous pair of reactions also carried out are indicated by eq. 4 and 5. As before, the esters were recrystallized until their rotations were constant.



(−)-Menthyl (−)-*p*-toluenesulfinate (**1**) and 1-naphthylmagnesium bromide gave *S*-(−)-α-naphthyl *p*-tolyl sulfoxide (**8**) while (−)-menthyl (−)-1-naphthalenesulfinate (**14**) and *p*-tolylmagnesium bromide

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[12] The c.d. measurements on **1** and **2** were made by Professor J. Levisalles at the University of Strasbourg in May, 1962. His values, previously unpublished, for the maximum molecular ellipticities $\times 10^{-4}$ are: (+)-ethyl *p*-tolyl sulfoxide, 7.65 at 242 mμ (*c* 0.0060, ethanol); (−)-menthyl (−)-*p*-toluensulfinate, −4.12 at 250 mμ (*c* 0.00152, ethanol). Smaller peaks of roughly one-tenth the magnitude of the larger peaks appear at about 276 mμ; *c* is in g. per 100 ml.

[13] H. F. Herbrandson and C. M. Cusano, *J. Am. Chem. Soc.*, **83**, 2124 (1961).

[14] R. S. Cahn, *J. Chem. Educ.*, **41**, 116 (1964), and references cited therein. The sequence used in assigning the configuration is RO– > O– > R– > pair of electrons. The pair of electrons are depicted in an $sp^3$-like orbital for ease of visualization only; no other significance is implied. For additional comments on the sequence rule and the relative configurations of sulfoxides see ref. 6.

[15] E. B. Fleischer, M. Axelrod, M. Green, and K. Mislow, *J. Am. Chem. Soc.*, **86**, 3395 (1964). Earlier, Mislow, Ternay, and Melillo[9] pointed out that a conflict existed between configurational assignments made to sulfoxides by us[5] (based on Herbrandson's work[13]) and Montanari (see A. Maccioni, F. Montanari, M. Secci, and M. Tramontini, *Tetrahedron Letters*, No. **17**, 607 (1961), on the one hand, and D. J. Cram and S. H. Pine (*J. Am. Chem. Soc.*, **85**, 1096 (1963)) on the other. Therefore, it was our intention to remain neutral in our most recent publication[6]; it is unfortunate that our position has been interpreted otherwise.

TABLE I

| No. | (−)-Menthyl (−)-arenesulfinate[a] | $[\alpha]_D$, $c$,[b] $T$[c] | M.p., °C. | Analyses,[d] %<br>Calcd.: C, H | <br>Found: C, H |
|---|---|---|---|---|---|
| 1 | *S*-(−)-*p*-Toluenesulfinate[e] | −199°, 2, 25 | 106–107 | ... | ... |
| 11 | *S*-(−)-*p*-Methoxybenzenesulfinate[f] | −189, 1.20, 24 | 106–108 | ... | ... |
| 14 | *S*-(−)-1-Naphthalenesulfinate | −433, 2.07, 24 | 118–119 | 72.69, 7.93 | 72.74, 7.71 |
| | RR′ sulfoxide[a] | | | | |
| 3 | *S*-(−)-*o*-Tolyl *p*-tolyl[g,h] | −86, 2.04, 23 | 72–73 | 73.01, 6.12 | 73.20, 6.40 |
| 4 | *R*-(+)-Phenyl *p*-tolyl[g,i] | +22, 2.00, 23 | 92–93 | ... | ... |
| 5 | *S*-(+)-*m*-Tolyl *p*-tolyl[g,h] | +17, 2.015, 25 | 61–63 | 73.01, 6.12 | 73.19, 6.13 |
| 6 | *S*-(−)-Mesityl *p*-tolyl[g,h] | −286, 2.00, 26 | 106–108 | 74.38, 7.02 | 74.54, 7.13 |
| 7 | *S*-(−)-*p*-N,N-Dimethylaminophenyl *p*-tolyl[g] | −85, 2.05, 24 | 161–162 | 69.46, 6.61 | 69.51, 6.50 |
| 8 | *S*-(−)-α-Naphthyl *p*-tolyl[g] | −414, 2.00, 26 | 136–137 | 76.66, 5.30 | 76.40, 5.43 |
| 9 | *S*-(−)-*p*-Anisyl *p*-tolyl[g] | −25, 1.99, 30 | 79.5–80.5 | See no. 13 | |
| 10 | Hydrochloride of no. 7[g,j] | +30, 2.02, 28 | ... | ... | ... |
| 12 | *S*-(−)-*o*-Anisyl *p*-anisyl[k] | −217, 2.01, 22 | 114.5–115.5 | 64.10, 5.38 | 64.37, 5.28 |
| 13 | *R*-(+)-*p*-Tolyl *p*-anisyl[k] | +24, 2.005, 20 | 81.0–81.5 | 68.26, 5.73 | 68.21, 5.85 |
| 15 | *R*-(+)-*p*-Tolyl α-naphthyl[l] | +416, 2.12, 25 | 136–137 | See no. 8 | |

[a] Configurations absolute (see ref. 15). [b] Concentration in g./100 ml. in acetone. [c] Temperature in °C. [d] Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. [e] H. F. Herbrandson, R. T. Dickerson, Jr., and J. Weinstein, *J. Am. Chem. Soc.*, **78**, 2576 (1956). [f] H. F. Herbrandson and R. T. Dickerson, Jr., *ibid.*, **81**, 4102 (1959), report m.p. 116–117.5°. [g] Prepared from ester no. 1. [h] Previously prepared by K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *J. Am. Chem. Soc*, **86**, 1452 (1964). [i] Previously prepared by K. Mislow, A. L. Ternay, Jr., and J. T. Melillo, *ibid.*, **85**, 2329 (1963). [j] A solution of **7** acidified with gaseous HCl. The optical activity disappears slowly. Therefore, the rotations are minimum values. See ref. *h*. [k] Prepared from ester **11**. [l] Prepared from ester **14**.

gave *R*-(+)-α-naphthyl *p*-tolyl sulfoxide (**15**). These enantiomers had rotations at the sodium D line equal in magnitude, but opposite in sign (see Table I).

The simplest explanation of the results obtained from reactions 2, 3, 4, and 5 is that the reactions are 100% stereospecific. In other words, optically pure sulfinate esters yield optically pure sulfoxides. We feel that the general synthetic reaction (eq. 1) is completely stereospecific proceeding with inversion at sulfur.

If the reaction is not completely stereospecific, we have recorded a remarkable series of events. Several situations consistent with the results of eq. 2, 3, 4, and 5 are conceivable. The three sulfinate esters might have been resolved incompletely but to the same extent. These esters when treated with the different Grignard reagents then would have had to react either in completely stereospecific reactions or reactions with the same percentage of incomplete stereospecificity to yield sulfoxides of the same optical purity. Another possibility involves resolution of the three esters to differing extents of optical purity. Reaction with the Grignard reagents would have had to proceed with different percentages of stereospecificity in order to yield enantiomeric sulfoxides fortuitously of the same optical purity. These situations seem most improbable.

There is one final objection one could make about our interpretation. One might grant that the sulfoxides as isolated are optically pure, but that this was attributed to the method of isolation. That is, upon the several recrystallizations needed to isolate the sulfoxide, any of its enantiomer might have been removed. Thus, a competing reaction leading to racemization or retention of configuration would have been overlooked. This is possible if a small amount of the enantiomer is present as was demonstrated by the following experiment. A mixture of the enantiomeric α-naphthyl *p*-tolyl sulfoxides (89 parts of (−)-**8**, 11 parts of (+)-**15**) was recrystallized once from acetone. The recovered sulfoxide had a rotation equal to that of the (−)-**8** used to prepare the partially racemic mixture. The (+)-**15** was removed by one recrystallization. Since the pure sulfoxides are isolated in high yields, often over 80%, any reactions leading to racemization or retention must be minor, but, as the above recrystallization experiment demonstrates, they cannot be entirely ruled out.

The diaryl sulfoxides and the sulfinate esters used in this preparation are listed in Table I. The three sulfinate esters, **1**, **11**, and **14**, were prepared from (−)-menthol and racemic arenesulfinyl chlorides. The least soluble epimers were purified by repeated recrystallization until their rotations were constant. In each case the levorotatory sulfinate was isolated. The configurational relationships among these esters were established by means of eq. 2, 3, 4, and 5. Since the configuration at sulfur in (−)-menthyl (−)-*p*-toluenesulfinate (**1**) is *S*,[15] then the other two esters, (−)-menthyl (−)-*p*-methoxybenzenesulfinate (**11**) and (−)-menthyl (−)-1-naphthalenesulfinate (**14**), are also *S*.

The ultraviolet spectral data for the sulfinate esters and sulfoxides are listed in Table II. The ultraviolet spectra for sulfoxides in general has been conveniently summarized by Jaffé and Orchin.[16] While dialkyl sulfoxides absorb near 220 mμ (log ε ~3.2), presumably an n → π* transition, the situation becomes complex when the sulfoxide chromophore is bonded to one or two aromatic rings. As a first approximation, the spectra of such compounds will be considered as benzene spectra perturbed by resonance interaction between the aromatic π-system and the sulfinyl chromophore. Further perturbations are caused by additional substituents on the aromatic ring. Absorption occurs in three regions of the spectrum for the compounds listed in Table II with the exception of **8**, **14**, and **15** which contain naphthalene rings and N,N-dimethylaminophenyl *p*-tolyl sulfoxide (**7**). These latter compounds will be discussed separately. The long wave length absorption between 262 and 285 mμ (log ε 3.0–3.8) in ethanol has been designated the secondary band

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(16) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 466 ff. See also G. Leandri, A. Mangini, and R. Passerini, *J. Chem. Soc.*, 1386 (1957).

TABLE II

| Compd. no. | Ultraviolet spectra[a] Second primary band | Primary band | Secondary band | Cotton effect midpoints and amplitudes[b] Second primary | Primary | Secondary |
|---|---|---|---|---|---|---|
| 1 | 225(4.06) | 246(3.82) | 273$^s$(3.05) | (−)[c] | 248(−73,000) | [d] |
| | 223(4.09)[e] | 256(3.66)[e] | | (−)[c] | 253(−61,000)[e] | [d] |
| 11 | | 247(4.05) | 281$^s$(2.94) | (−)[c] | 252(−97,000) | |
| 14 | 223(4.75) | 291(3.95) | 304$^s$(3.75) | 225(−192,000) | 299–289(−20,000) | [d] |
| | | | 314(3.34) | | | |
| | | | 319(3.22) | | | |
| 2 | 215$^s$(3.96) | 238(3.84) | 262$^s$(3.31) | (+)[c] | 243(+123,000) | [d] |
| | | | 274$^s$(3.01) | | | |
| | | 251(3.78)[e] | | (+)[c] | 252(+71,000)[e] | [d] |
| | | 239(3.96)[f] | 268$^s$(3.16) | | 236(+53,000) | [d] |
| | | | 274$^s$(2.99) | | | |
| 3 | | 239(4.31) | 264$^s$(3.78) | 230(−32,000)[e] | | 270(−31,000) |
| | | | 276$^s$(3.73) | | | |
| 4[g] | | 236(4.24) | 265$^s$(3.62) | (+)[c] | | 262–255(+17,000)[d] |
| | | | 272$^s$(3.51) | | | |
| 5 | | 238(4.23) | 268$^s$(3.83) | (+)[c] | | 260–256(+13,000)[d] |
| | | | 276$^s$(3.78) | | | |
| 6 | | 244(4.26) | 269(3.68) | 221(−179,000) | | 275(−120,000) |
| | | | 277(3.66) | | | |
| | | | 285(3.57) | | | |
| | 229$^s$(4.38)[f] | 256(4.40)[f] | | 229(−79,000)[f] | | 278(−43,000)[f] |
| 7 | 220$^s$(4.23) | 293(4.36) | | (−)[c] | | 298(−30,000)[d] |
| | | 280(4.44)[e] | | | | 292(−51,000)[e] |
| 8 | 223(4.61) | 291(3.92) | Shoulders | 234(−468,000) | 300–295(−15,000)[g] | [d] |
| 9 | | 246(4.34) | | (−)[c] | | 270–261(−29,000)[d] |
| 10 | | 238(4.39) | 265$^s$(3.82) | (+)[c] | | 263–255(+11,000)[d] |
| 12 | | 244(4.29) | 278(3.84) | | 239(−90,000)[h] | 281(−109,000) |
| 13 | | 246(4.34) | | (+)[c] | | 270–261(+31,000)[d] |
| 15 | 223(4.61) | 291(3.92) | Shoulders | 234(+485,000) | 299–278(+19,000) | [d] |

[a] $\lambda_{max}$ in mμ, log ε in parentheses; solvent, 95% ethanol unless specified otherwise. [b] Midpoints calculated as halfway between the peak and trough of the o.r.d. curve. Where multiple peaks or troughs occur, a range is given. Amplitudes are apparent since multiple Cotton effects are often involved. [c] Apparent sign of a shorter wave length c.e. Instrumental limitations preclude its measurement. These c.e. are not necessarily associated with the second primary ultraviolet band. [d] One or more c.e. in this region apparent as shoulder on o.r.d. curve. [e] In isooctane. [f] In 1 volume 70% perchloric acid, 1 volume 95% ethanol. [g] G. Leandri, A. Mangini, and R. Passerini, *J. Chem. Soc.*, 1386 (1957), report 237 mμ (4.20) and 270 mμ (3.28). [h] Assignment to primary band doubtful; see Discussion.

while the more intense absorption between 236 and 247 mμ (log ε 3.8–4.4) has been designated as the primary band. The secondary and primary bands may be perturbed $^1L_b$ and $^1L_a$ benzene transitions, respectively. Any absorption below 230 mμ has been designated as a second primary band. The position of the sulfoxide n → π* transition in these aryl sulfinyl compounds is unclear. This transition presumably involves promotion of electrons to an unoccupied orbital of the aromatic ring rather than to the sulfinyl group as postulated for dialkyl sulfoxides. The aryl sulfinyl n → π* absorption should occur at longer wave lengths and it is suspected that the transition occurs in the same region as the perturbed $^1L_a$ transition. These two transitions may together make up the primary band.[16]

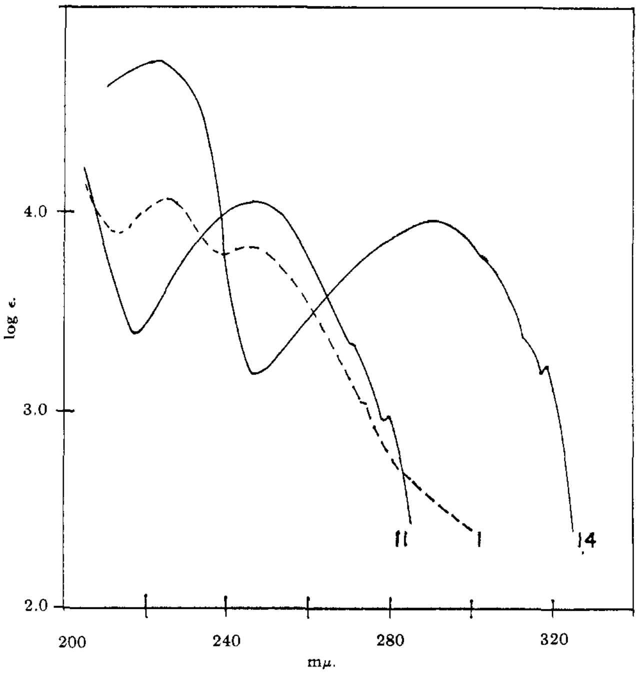

Fig. 2.—Ultraviolet spectra of 1, 11, and 14 (see Table II).

The ultraviolet spectral data for specific compounds will now be discussed together with the o.r.d. data.

The c.d.[12] and o.r.d. curves for (−)-menthyl (−)-*p*-toluenesulfinate (**1**) and (+)-ethyl *p*-tolyl sulfoxide (**2**) permit unambiguous assignments to be made to the Cotton effects (c.e.) for these compounds. The c.d. maximum in ethanol for **1** occurs at 250 mμ while the o.r.d. midpoint occurs at 248 mμ. For **2**, the c.d. maximum is at 242 mμ and the o.r.d. midpoint at 243 mμ. These values correlate well with the ultraviolet absorption maxima at 246 mμ for **1** and 238 mμ for **2**. The less intense c.d. peaks at about 276 mμ correspond to shoulders on the o.r.d. curves (see Fig. 1 and Fig. 1 of ref. 9) and also to the secondary ultraviolet bands (Fig. 2). In isooctane the primary bands undergo a bathochromic shift from 246 to 256 mμ for **1** and from 238 to 251 mμ for **2**; the secondary bands are no longer apparent. The o.r.d. midpoints in isooctane shift similarly: from 248 to 253 mμ for **1** and from 243 to 252 mμ for **2**. Such bathochromic shifts are typical

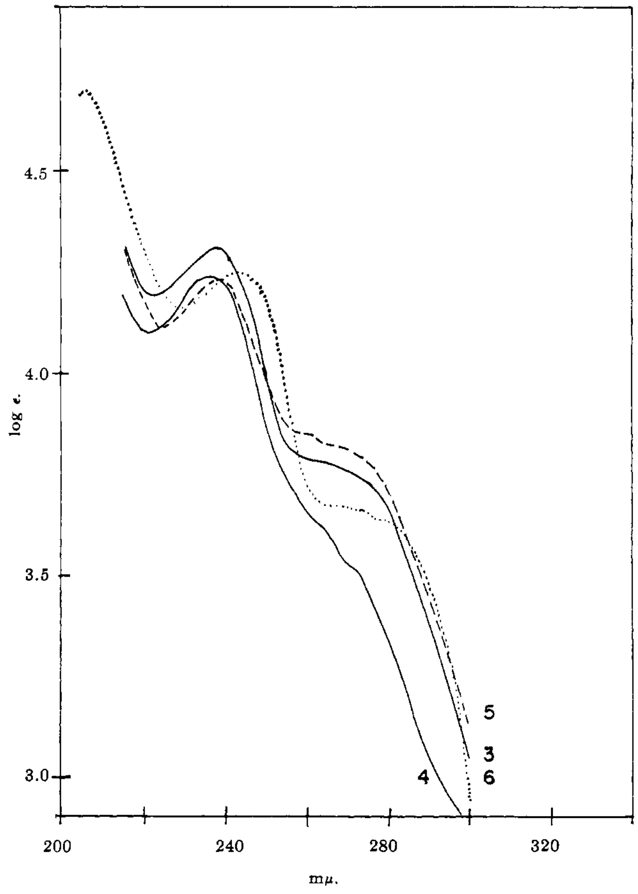

Fig. 3.—Ultraviolet spectra of **3**, **4**, **5**, and **6** (see Table II).

for n → π* transitions. It may be that the primary band is a perturbed $^1L_a$ transition and an n → π* transition with the two transitions occurring close together and giving only one absorption band. Some support for this latter interpretation comes from ultraviolet and o.r.d. measurements in strong acid solution. The ultraviolet spectrum of **2** remains almost unchanged, but the o.r.d. midpoint shifts hypsochromically to 236 mμ. This would be expected for an n → π transition. Protonation of the oxygen would increase the positive charge on the sulfur atom which in turn should increase the energy needed to promote the n electrons to a π*-orbital. The optically active transition may be an n → π* transition.

The ultraviolet spectrum and o.r.d. curve for (−)-menthyl (−)-*p*-methoxybenzenesulfinate (**11**) are depicted in Fig. 1 and 2. The c.e. midpoint at 252 mμ agrees well with the ultraviolet absorption maximum at 247 mμ. However, no minor c.e. corresponding to the secondary ultraviolet bands are apparent.

Compounds **1** and **2** have been classified as dissymmetric chromophores by Mislow, *et al.*[9]; **11** also fits this classification.

The ultraviolet spectra and o.r.d. curves for the methyl-substituted diphenyl sulfoxides **3**, **4**, **5**, and **6** are depicted in Fig. 3 and 4. The ultraviolet spectra are quite similar. A clear-cut *ortho* steric effect is not apparent in the spectra of (−)-*o*-tolyl *p*-tolyl sulfoxide (**3**) and (−)-mesityl *p*-tolyl sulfoxide (**6**). This has been commented on before for other diaryl sulfoxides.[16,17]

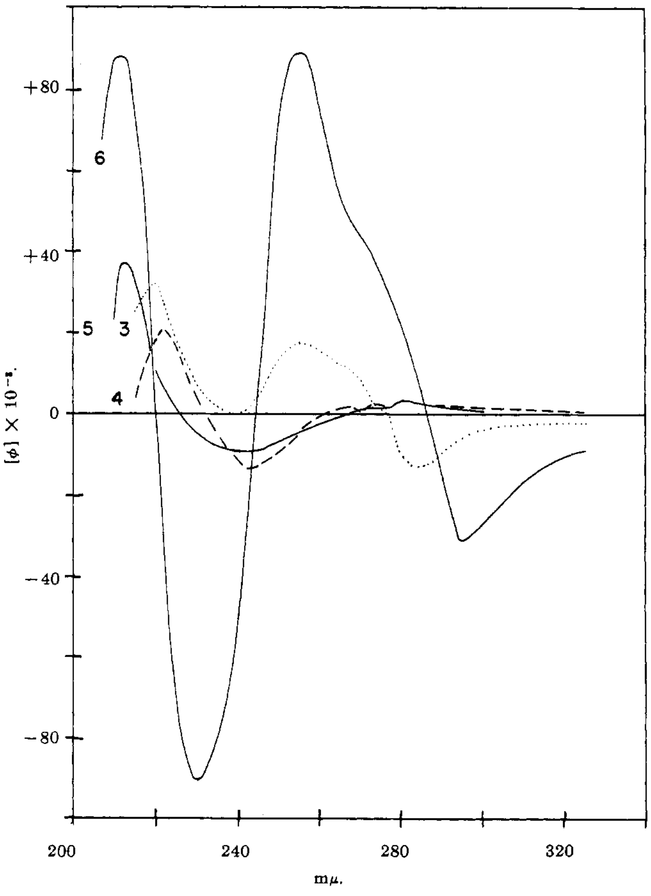

Fig. 4.—Optical rotatory dispersion curves of **3**, **4**, **5**, and **6** (see Table III).

For **3** and **6** the short wave length c.e. midpoints do not correlate with any ultraviolet absorption maximum. Either the optically active transitions are weak in the ultraviolet, obscurred by the primary band, or the Cotton effects have been incorrectly assigned. When the ultraviolet spectrum for **6** was determined in strong acid, however, a shoulder at 229 mμ became apparent. The primary band shifts bathochromically and probably obscures the secondary bands, since they are no longer visible. The long wave length c.e. remains at the same position, but the short wave length c.e. shifts to 229 mμ in perfect correlation with the ultraviolet absorption. This is a bathochromic shift compared to ethanol for the c.e. and would be unusual for an n → π* transition but not for an $^1L_a$ transition. The data in Table III indicate that the long wave length c.e. is multiple in acid solution. This was suggested by the shape of the o.r.d. curve in ethanol (Fig. 4). We feel this makes our c.e. assignments somewhat uncertain; c.d. studies would be most helpful in determining the location of the optically active transitions with greater surety.

Analogous to **6**, (−)-*o*-tolyl *p*-tolyl sulfoxide (**3**) also has a short wave length c.e. at 230 mμ which does not correlate very well with the 239 mμ primary ultraviolet band. The short wave length c.e. midpoints for **4** and **5** cannot be obtained from our data; c.d. studies would help to clarify the position of the optically active transitions.

Omitting **7** and **8** for the moment, (−)-*p*-anisyl *p*-tolyl sulfoxide (**9**), (+)-*p*-N,N-dimethylaminophenyl *p*-tolyl sulfoxide hydrochloride (**10**), and (−)-*o*-anisyl

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(17) Recently evidence for a steric effect has been presented by K. Mislow, P. Schneider, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **86**, 2957 (1964).

TABLE III

| No | Optical rotatory dispersion[a] | Concentration[b] | |
|---|---|---|---|
| 1 | $[\phi]_{350}$ −2670, $[\phi]_{277}$ −15,500, $[\phi]_{274}$ −14,200, $[\phi]_{260}$ −19,800, $[\phi]_{251}$ 0, $[\phi]_{235}$ 53,300, $[\phi]_{219}$ 0 $[\phi]_{203}$ −44,000, $[\phi]_{200}$ −41,900 | 0.116, 0.0116 | E |
| 1 | $[\phi]_{300}$ −6540, $[\phi]_{277}$ −19,600, $[\phi]_{274}$ −19,100, $[\phi]_{272}$ −20,200, $[\phi]_{258}$ 0, $[\phi]_{233}$ 40,900, $[\phi]_{219}$ 0 $[\phi]_{212}$ −32,700, $[\phi]_{210}$ −27,300 | 0.0054 | I |
| 11 | $[\phi]_{350}$ −2810, $[\phi]_{263}$ −27,500, $[\phi]_{255}$ 0, $[\phi]_{241}$ 69,500, $[\phi]_{228}$ 0, $[\phi]_{222}$ −14,600, $[\phi]_{220}$ −12,900 $[\phi]_{215}$ −14,600 | 0.096, 0.0096 | E |
| 14 | $[\phi]_{400}$ −4800, $[\phi]_{322}$ −19,400, $[\phi]_{318}$ −15,200, $[\phi]_{310}$ −21,700, $[\phi]_{305}$ −19,100, $[\phi]_{302}$ −20,100 $[\phi]_{275}$ −1810, $[\phi]_{235}$ −46,500, $[\phi]_{228}$ 0, $[\phi]_{215}$ 145,000, $[\phi]_{210}$ 108,000 | 0.064, 0.0064 | E |
| 2 | $[\phi]_{350}$ 1720, $[\phi]_{277}$ 11,800, $[\phi]_{275}$ 10,500, $[\phi]_{260}$ 19,400, $[\phi]_{247}$ 0, $[\phi]_{227}$ −104,000, $[\phi]_{215}$ 0 $[\phi]_{200}$ 62,500, $[\phi]_{195}$ 60,900 | 0.099, 0.0020 | E |
| 2 | $[\phi]_{300}$ 6170, $[\phi]_{272}$ 13,500, $[\phi]_{268}$ 12,000, $[\phi]_{265}$ 12,500, $[\phi]_{256}$ 0, $[\phi]_{232}$ −57,200, $[\phi]_{221}$ 0, $[\phi]_{212}$ 39,300 $[\phi]_{210}$ 28,100 | 0.003 | I |
| 2 | $[\phi]_{300}$ 3440, $[\phi]_{278}$ 7960, $[\phi]_{273}$ 7240, $[\phi]_{270}$ 8500, $[\phi]_{267}$ 7960, $[\phi]_{250}$ 16,300, $[\phi]_{240}$ 0, $[\phi]_{221}$ −36,700, $[\phi]_{210}$ −10,400, $[\phi]_{205}$ −14,000 | 0.0093, 0.0019 | A |
| 3 | $[\phi]_{350}$ −1430, $[\phi]_{284}$ −13,300, $[\phi]_{277}$ 0, $[\phi]_{255}$ 17,600, $[\phi]_{240}$ 0, $[\phi]_{220}$ 32,100, $[\phi]_{215}$ 25,500 | 0.097, 0.0097, 0.0019 | E |
| 4 | $[\phi]_{350}$ 320, $[\phi]_{280}$ 3300, $[\phi]_{277}$ 1850, $[\phi]_{273}$ 2800, $[\phi]_{270}$ 1400, $[\phi]_{267}$ 1500, $[\phi]_{260}$ 0, $[\phi]_{243}$ −13,500 $[\phi]_{232}$ 0, $[\phi]_{222}$ 21,000, $[\phi]_{215}$ 4000 | 0.216, 0.0216, 0.00216 | E |
| 5 | $[\phi]_{350}$ 501, $[\phi]_{280}$ 3460, $[\phi]_{277}$ 1610, $[\phi]_{272}$ 2030, $[\phi]_{265}$ 0, $[\phi]_{240}$ −9700, $[\phi]_{226}$ 0, $[\phi]_{212}$ 37,000 $[\phi]_{210}$ 22,400 | 0.193, 0.0193, 0.0038 | E |
| 6 | $[\phi]_{350}$ −4630, $[\phi]_{295}$ −31,200, $[\phi]_{287}$ 0, $[\phi]_{255}$ 89,200, $[\phi]_{244}$ 0, $[\phi]_{230}$ −90,100, $[\phi]_{220}$ 0 $[\phi]_{211}$ 88,800, $[\phi]_{207}$ 67,800 | 0.043, 0.0079, 0.0043 | E |
| 6 | $[\phi]_{350}$ −2750, $[\phi]_{301}$ −20,200, $[\phi]_{287}$ 0, $[\phi]_{278}$ 16,200, $[\phi]_{270}$ 13,700, $[\phi]_{254}$ 22,600 $[\phi]_{244}$ 0 $[\phi]_{237}$ −15,300, $[\phi]_{231}$ 0, $[\phi]_{221}$ 63,800, $[\phi]_{215}$ 62,200 | 0.016, 0.0016 | A |
| 7 | $[\phi]_{400}$ −2030, $[\phi]_{311}$ −8880, $[\phi]_{291}$ 0, $[\phi]_{272}$ 41,900, $[\phi]_{258}$ 0, $[\phi]_{245}$ −30,100, $[\phi]_{228}$ −15,300 $[\phi]_{223}$ −19,500, $[\phi]_{220}$ −17,700 | 0.011 | I |
| 7 | $[\phi]_{400}$ −1190, $[\phi]_{325}$ −7690, $[\phi]_{316}$ −1100, $[\phi]_{315}$ −2200, $[\phi]_{312}$ 0, $[\phi]_{287}$ 8800, $[\phi]_{285}$ 7700 $[\phi]_{270}$ 22,000, $[\phi]_{240}$ 0, $[\phi]_{218}$ −35,200, $[\phi]_{215}$ −26,400 | 0.118, 0.0118, 0.0024 | E |
| 8 | $[\phi]_{400}$ −3160, $[\phi]_{320}$ −12,700, $[\phi]_{318}$ −9270, $[\phi]_{310}$ −15,400, $[\phi]_{280}$ 0, $[\phi]_{242}$ −152,000 $[\phi]_{235}$ 0, $[\phi]_{226}$ 316,000, $[\phi]_{215}$ 168,000 | 0.027, 0.0027, 0.00054 | E |
| 9 | $[\phi]_{350}$ −502, $[\phi]_{289}$, −4330, $[\phi]_{283}$ −2280, $[\phi]_{278}$ −4100, $[\phi]_{273}$ −1820, $[\phi]_{271}$ −2280, $[\phi]_{269}$ 0 $[\phi]_{250}$ 25,100, $[\phi]_{240}$ 0, $[\phi]_{228}$ −31,900, $[\phi]_{215}$ −9100 | 0.054, 0.0054, 0.0011 | E |
| 10[c] | $[\phi]_{400}$ 362, $[\phi]_{281}$ 4600, $[\phi]_{276}$ 2960, $[\phi]_{273}$ 3950, $[\phi]_{268}$ 1640, $[\phi]_{265}$ 1970, $[\phi]_{258}$ 0, $[\phi]_{244}$ −6580 $[\phi]_{239}$ 0, $[\phi]_{227}$ 27,900, $[\phi]_{220}$ 19,000, $[\phi]_{215}$ 32,900 | 0.158, 0.0158, 0.0032 | E |
| 12 | $[\phi]_{350}$ −4710, $[\phi]_{293}$ −46,500, $[\phi]_{283}$ 0, $[\phi]_{268}$ 62,000, $[\phi]_{251}$ 0, $[\phi]_{247}$ −16,100, $[\phi]_{242}$ 0 $[\phi]_{230}$ 73,900, $[\phi]_{220}$ 19,100, $[\phi]_{215}$ 35,800 | 0.044, 0.0044 | E |
| 13 | $[\phi]_{350}$ 384, $[\phi]_{290}$ 6400, $[\phi]_{283}$ 4430, $[\phi]_{278}$ 6400, $[\phi]_{274}$ 2960, $[\phi]_{272}$ 3450, $[\phi]_{266}$ 0, $[\phi]_{250}$ −24,600 $[\phi]_{242}$ 0, $[\phi]_{227}$ 49,300, $[\phi]_{220}$ 22,200, $[\phi]_{215}$ 27,100 | 0.005, 0.001 | E |
| 15 | $[\phi]_{400}$ 3690, $[\phi]_{322}$ 16,400, $[\phi]_{318}$ 13,300, $[\phi]_{310}$ 19,000, $[\phi]_{285}$ 1900, $[\phi]_{280}$ 2140, $[\phi]_{276}$ 0 $[\phi]_{241}$ 164,000, $[\phi]_{235}$ 0, $[\phi]_{226}$ −321,000, $[\phi]_{210}$ −140,000 | 0.112, 0.0112, 0.0012 | E |

[a] All curves plain from 589 mμ to first value listed. [b] G./100 ml. of solvent. Solvents: E, 95% ethanol; I, isooctane; A, 1 volume 70% perchloric acid and 1 volume 95% ethanol. [c] Solution of 7 in ethanol acidified using gaseous hydrogen chloride and run immediately after acidification; see Table I, footnote *j*.

*p*-anisyl sulfoxide (**12**) will be considered next (Fig. 5–8). Although the secondary ultraviolet bands for **9** are not evident, probably as a result of a bathochromic shift of the primary band induced by the methoxy group, multiple Cotton effects occur in this region in analogy to the other substituted diphenyl sulfoxides **3**, **4**, **5**, and **6**. Both **10** and **12** also follow this pattern. Multiple Cotton effects centered at 255–263 mμ corresponding to the 265 mμ secondary ultraviolet band are evident for **10** while a c.e. centered at 281 mμ corresponding to the 278 mμ secondary ultraviolet band is evident for **12**. It is tempting to assign the short wave length 239 mμ c.e. for **12** to the primary ultraviolet band at 244 mμ. However, the short wave length Cotton effects for sulfoxides **3** and **6**, the only other diaryl sulfoxides which permit measurement of these Cotton effects, do not correspond to their primary bands. The same situation may be true for **12** as discussed above for **3** and **6**.

The compounds discussed above seem to follow one of two patterns. The monoarylsulfinyl compounds **1**, **2**, and **11** have major Cotton effects large in amplitude which correlate well with their respective primary ultraviolet absorption bands, and minor Cotton effects occurring as shoulders on the o.r.d. curves which correlate with their secondary ultraviolet absorption bands. On the other hand, the diarylsulfinyl compounds **3**, **4**, **5**, **6**, **9**, **10**, and **12** follow a different pattern. They have long wave length Cotton effects well correlated with their secondary ultraviolet bands, but the short wave length Cotton effects are not correlated with the primary ultraviolet bands; these Cotton effects occur at wave lengths shorter than the primary ultraviolet bands. It should be remembered, however, that c.d. studies on the diaryl sulfoxides should be carried out in order to check our Cotton effect assignments.

A discussion of (−)-*p*-N,N-dimethylaminophenyl *p*-tolyl sulfoxide (**7**) has been deferred until now, since its spectral properties differ from the other diaryl sulfoxides discussed above. The primary band occurs at 293 mμ. The amino group has caused a large bathochromic shift. No shoulders indicative of secondary bands are present. A second primary band, however, occurs as a shoulder at 220 mμ. While a c.e. centered at 298 mμ might be assigned to the 293 mμ ultraviolet band, the measurements in isooctane cast doubt on such an assignment. In isooctane, the ultraviolet

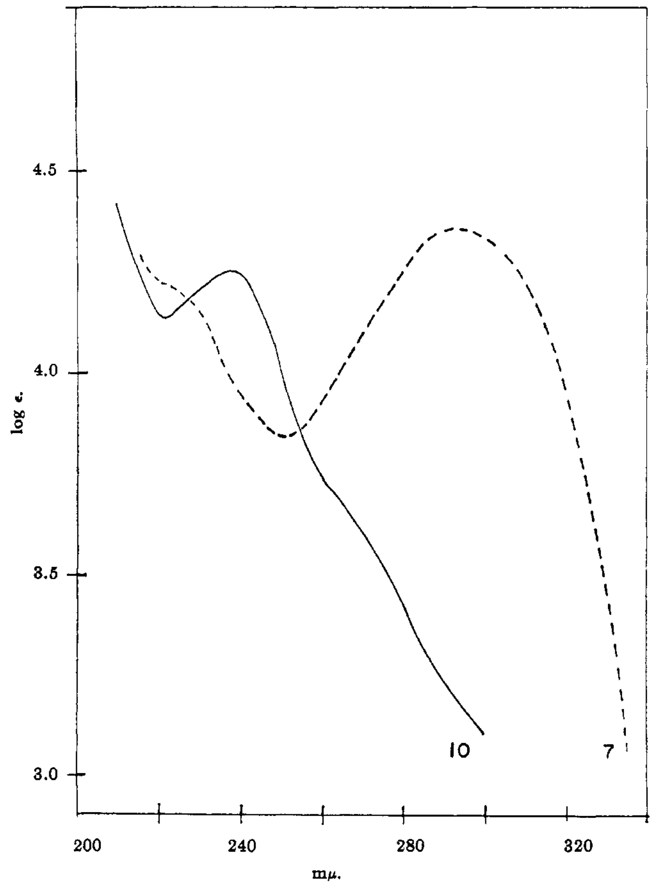

Fig. 5.—Ultraviolet spectra of **7** and **10** (see Table II).

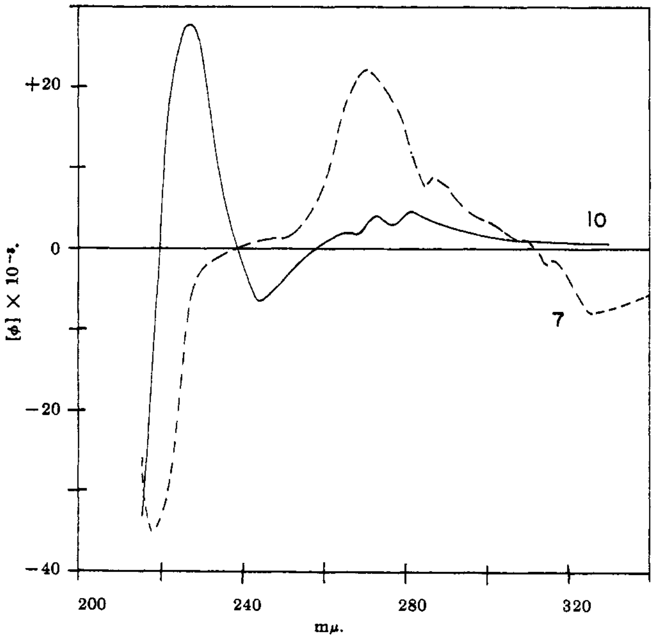

Fig. 6.—Optical rotatory dispersion curves of **7** and **10** (see Table III).

primary band shifts to 280 mμ, but the c.e. moves only slightly to 292 mμ. It seems probable that secondary bands obscured by the more intense primary ultraviolet band are to be correlated with the multiple Cotton effects. This would be in keeping with the results obtained from the other diaryl sulfoxides.

The compounds containing naphthyl groups, (−)-menthyl (−)-1-naphthalenesulfinate (**14**), (−)-$\alpha$-naphthyl $p$-tolyl sulfoxide (**8**), and its enantiomer **15**,

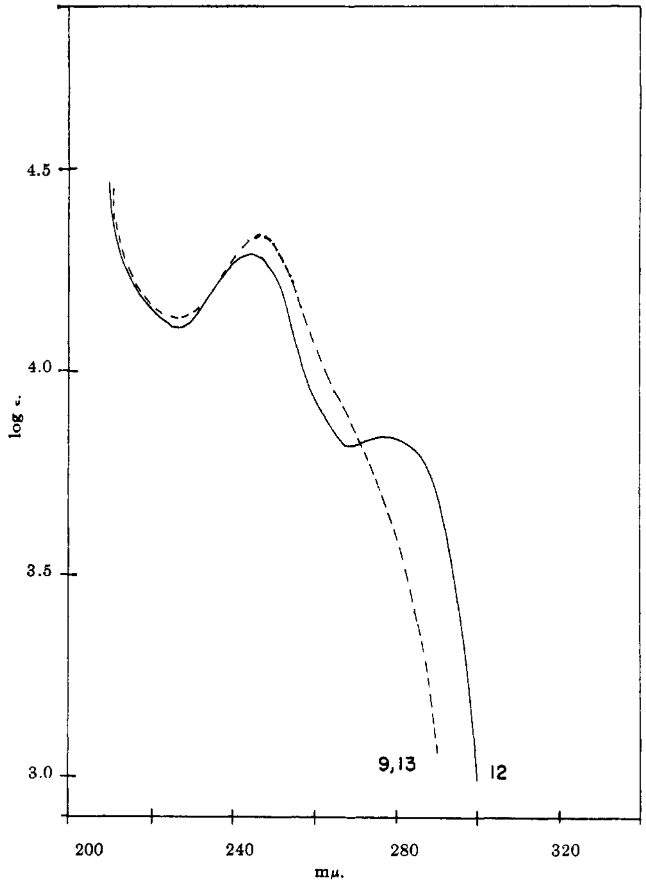

Fig. 7.—Ultraviolet spectra of **9**, **13**, and **12** (see Table II).

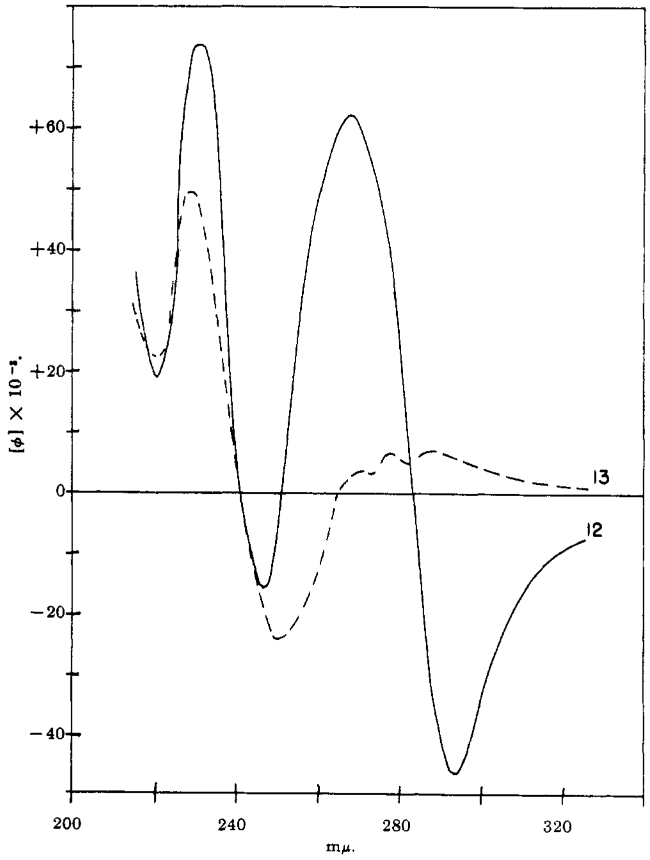

Fig. 8.—Optical rotatory dispersion curves of **12** and **13** (see Table III).

have similar ultraviolet and o.r.d. properties. A primary band with several shoulders at 291 mμ and a

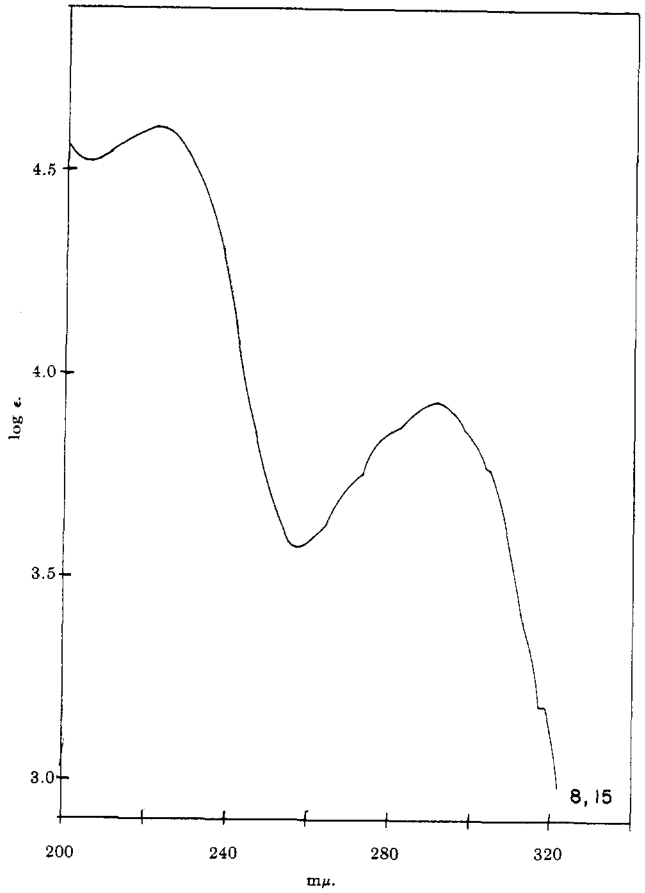

Fig. 9.—Ultraviolet spectra of **8** and **15** (see Table II).

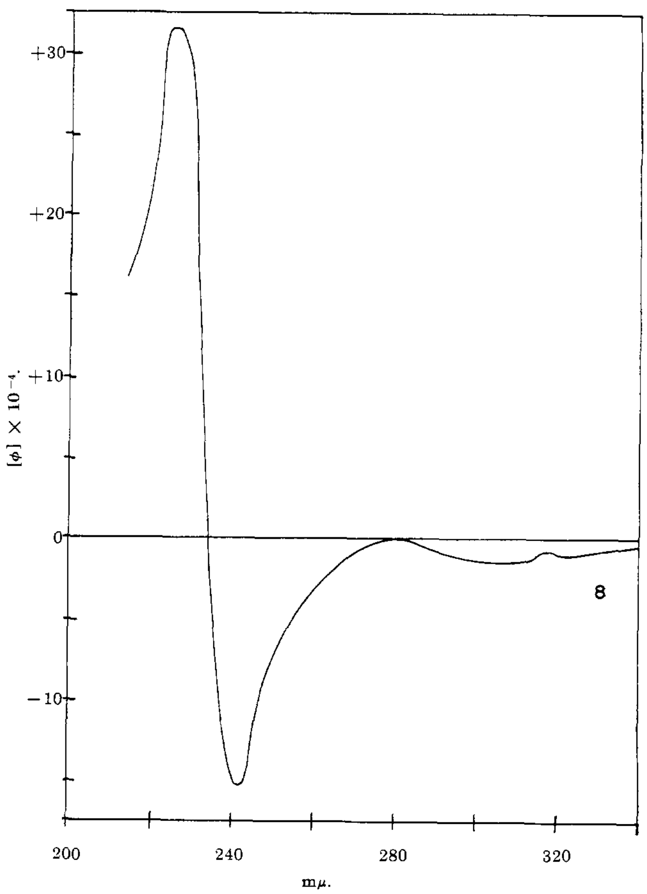

Fig. 10.—Optical rotatory dispersion curve of **8** (seeTable III).

second primary band at 223 mμ occur for all three compounds. The o.r.d. curves are also quite similar. For **14**, a short wave length c.e., at 225 mμ, correlates well with the 223 mμ ultraviolet band. A multiple c.e. at 289–299 mμ correlates with the primary band at 291 and its accompanying secondary bands. For **8** and **15**, the situation is less clear. A short wave length c.e. occurs at 234 mμ but this doesn't correlate too well with the 223 mμ ultraviolet band. A longer wave length multiple c.e. at 300–281 mμ correlates with the primary 291 mμ band and/or shoulders.

Since the configuration of the various sulfinyl compounds relative to one another is known, one can study the influence of structure on the sign of the Cotton effects. In addition, the influence of structure on the amplitude of the Cotton effects can also be studied, since the compounds are believed to be optically pure. The arenesulfinate esters will be considered first.

Figure 1 indicates that the three arenesulfinate esters **1**, **11**, and **14**, all of the same configuration, give negative long wave length Cotton effects which determine their sign of rotation at the sodium D line. In addition, Phillips[10] prepared ethyl and *n*-butyl *p*-toluenesulfinate both of the same configuration and both levorotatory. These five examples suggest that alkyl arenesulfinates of the same configuration have the same sign of rotation at the sodium D line. The effect of changes in the configuration of the aromatic ring relative to the sulfinyl group on the sign and amplitude of the c.e. is not known.

The sign of the long wave length c.e. likewise determines the sign of rotation at the sodium D line for the diaryl sulfoxides. First the diaryl sulfoxides excluding those with *ortho* substituents or a naphthyl group will be considered and an attempt to correlate the sign of rotation to structure will be made.

In their classic paper on the octant rule, Moffitt, Woodward, Moscowitz, Klyne, and Djerassi[18] noted that the perturbing ability of atoms on rotation was correlated with their atomic refractivity. This correlation does not seem to work for the *meta*- and *para*-substituted diaryl sulfoxides. However, a correlation of sign of rotation with Hammett's sigma ($\sigma$) constants was found. With the limited number of substituents, this correlation may be fortuitous. While additional examples may invalidate the correlation, we shall nevertheless point out how it was determined and how it operates. This correlation is proposed simply as an empirical rule.

In order to predict how substituents determine the sign of the long wave length Cotton effect, a standard molecule was needed; (+)-phenyl *p*-tolyl sulfoxide (**4**) was chosen. The substituent which supplied the highest electron density to the sulfur atom as measured by Hammett's $\sigma$-constant was considered as determining the sign of the c.e. In **4**, this is the *p*-$CH_3$ ($\sigma = -0.170$)[19]; the c.e. is positive.

Sulfoxides **5**, **7**, **9**, and **10** all have a *p*-toluenesulfinyl group of the same configuration in common since they were all synthesized from the same ester (**1**). The $\sigma$-constant of the substituent on the other ring in comparison with the $\sigma$-constant for *p*-$CH_3$ determines the sign of the c.e. and thus the sign of rotation at the

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[18] W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Am. Chem. Soc.*, **83**, 4013 (1961).

[19] R. W. Taft, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

sodium D line. Sulfoxides **5** and **10** give positive Cotton effects. Their substituents have $\sigma$-constants more positive than that for $p$-$CH_3$ and so impart less electron density to the sulfur atom, *i.e.*, $\sigma = -0.069$ for $m$-$CH_3$ (**5**) and $+0.859$ for $p$-$(CH_3)_3N^+$ in analogy with $p$-$(CH_3)_2NH^+$ for **10**. On the other hand, the $\sigma$-constants for the substituents on **7** and **9** are all more negative than that for $p$-$CH_3$; negative Cotton effects are observed in both cases. For example, $\sigma = -0.600$ for $p$-$(CH_3)_2N$ (**7**) and $-0.268$ for $p$-$CH_3O$ (**9**).

The *ortho*-substituted diaryl sulfoxides and the naphthyl aryl sulfoxides are not covered by the rule postulated above. (−)-*o*-Tolyl *p*-tolyl sulfoxide (**3**), (−)-mesityl *p*-tolyl sulfoxide (**6**), (−)-$\alpha$-naphthyl *p*-tolyl sulfoxide (**8**), and (−)-*o*-anisyl *p*-anisyl sulfoxide (**12**) all have *para*-substituted arenesulfinyl groups of the same configuration. The other aromatic ring contains one or more *ortho* substituents; the naphthalene ring is considered to be an *ortho*-substituted benzene ring. All of these compounds are levorotatory. Consideration of a Dreiding model of *ortho*-substituted diaryl sulfoxides[20] indicates that these substituents can approach the sulfinyl oxygen rather closely and that a steric repulsion would be expected. Some conformations arising from rotation of the benzene ring relative to the sulfinyl group would be of higher energy if the ring were *ortho* substituted, rather than *meta* or *para* substituted. The populations of these states would be reduced. Intuitively, one would expect such a molecule to be "more" asymmetric since the two aryl groups bonded to the same sulfinyl groups would possess an additional factor contributing to their dissimilarity. This seems to be reflected in the amplitudes of their Cotton effects. In general, the *ortho*-substituted diaryl sulfoxides have Cotton effects larger in amplitude than the *meta*- and *para*-substituted compounds. Since the Cotton effects tend to be multiple, the measured amplitudes are the summation of a series of amplitudes. Any amplitudes which were measured for these multiple Cotton effects have been designated as "apparent" since they are made up of several contributions. In spite of this added complication, it seems clear that the *ortho* substituents increase the apparent amplitudes.

Essentially, the diaryl sulfoxide chromophore is symmetric when *meta* or *para* substituted. When *ortho* substituted, however, the molecule gives Cotton effects increased in apparent amplitude. Its chromophore can then be classified as inherently dissymmetric.[21]

Further work is needed to explain satisfactorily the nature of both the ultraviolet spectra and o.r.d. curves of the mono- and diarylsulfinyl compounds.

## Experimental

(−)-Menthyl (−)-*p*-toluenesulfinate (**1**) and (−)-menthyl *p*-methoxybenzenesulfinate (**11**) were prepared as described in the literature.[22]

**(−)-Menthyl (−)-1-Naphthalenesulfinate (14).**—Powdered 1-naphthalenesulfonyl chloride (200 g., 0.882 mole) was added in small portions over a 10-min. period with vigorous stirring to a suspension of zinc dust (180 g., 2.75 g.-atom) in 1.5 l. of wate preheated to 80°. The mixture was stirred for 1 hr. at 90° after which 100 ml. of 12 *N* NaOH was added. Powdered sodium bicarbonate was added until the mixture was basic. The salts were filtered off, stirred with 100 ml. of hot water, and refiltered. The combined filtrates were placed in an evaporating dish and heated until a crust began to form. Upon cooling, crystals formed. These were filtered off, placed in a flask, and heated for 3 hr. on the steam bath at aspirator pressure with occasional shaking until dry. The salt was ground in a mortar and added in portions with stirring over a 2.5-hr. period to 210 ml. of thionyl chloride in 200 ml. of ether. After stirring for 2 hr. more, the excess thionyl chloride was removed using an aspirator. The solid was filtered using suction and washed twice with dry ether. The combined filtrates were concentrated to give 140 g. of a yellow oil. The oil was dissolved in 150 ml. of ether and cooled to 5 to 10°. (−)-Menthol (104 g., 0.666 mole) and pyridine (53 g., 0.67 mole) in 150 ml. of ether were added dropwise with shaking over a 30-min. period. After standing for 30 min. more with occasional shaking, the mixture was washed 3 times with water, 2 times with dilute hydrochloric acid, and 2 times with dilute aqueous sodium bicarbonate. After drying over magnesium sulfate, the solution was concentrated to about 200 ml. Upon cooling, crystals were obtained. More ether was boiled off and the solution cooled again, whereupon more crystals formed. A total of 17 g. of **14** was obtained. No attempt was made to improve the yield.[23]

After several recrystallizations from an acetone–water mixture and from petroleum ether (b.p. 110–115°), pure **14**, with the properties described in Tables I, II, and III, was obtained.

**Diaryl Sulfoxides.**—The diaryl sulfoxides were prepared by adding the appropriate arylmagnesium bromide to the (−)-menthyl (−)-arenesulfinate in ether. After hydrolysis of the reaction mixture with aqueous ammonium chloride or dilute hydrochloric acid followed by separation and drying of the organic layer, the sulfoxides were isolated by concentrating the ether layer until crystallization was possible. The one exception was (−)-*p*-N,N-dimethylaminophenyl *p*-tolyl sulfoxide which was isolated by acid extraction of the ether solution followed by precipitation from the acid by base. Sulfoxides **7**, **8**, and **15** were insoluble in the ether layers after hydrolysis of the reaction mixture. Some ethyl acetate was added to facilitate the work-up. If traces of unreacted arenesulfinate ester were present in the ether layer as revealed by an infrared band at about 1140 cm.$^{-1}$ (sulfinate S–O stretching), these traces were removed by stirring the ether overnight with aqueous base which hydrolyzed the ester. The preparation of (+)-phenyl *p*-tolyl sulfoxide illustrates the general procedure.

All of the sulfoxides had infrared bands at about 1050 cm.$^{-1}$ (sulfoxide S–O stretching).

**(+)-Phenyl-*p*-tolyl Sulfoxide (4).**—(−)-Menthyl (−)-*p*-toluenesulfinate (30.0 g., 0.102 mole) and anhydrous ethyl ether (250 ml.) were placed in a 1-l. 3-neck flask equipped with a stirrer, addition funnel with a nitrogen inlet, and a condenser with a drying tube. A solution of phenylmagnesium bromide prepared from bromobenzene (34.0 g., 0.216 mole) and magnesium (7.5 g., 0.313 g.-atom) in ether (100 ml.) was added dropwise over a 1.5-hr. period with stirring and cooling in an ice bath. After stirring for an additional 60 min., saturated aqueous ammonium chloride was added until the inorganic salts precipitated, leaving a clear ether solution. The ether was removed by decanting. The inorganic residue was extracted by stirring with ether. The combined ether solutions were dried over magnesium sulfate, concentrated, and cooled in an ice bath. Crystals of (+)-phenyl *p*-tolyl sulfoxide (20.5 g., 0.0845 mole, 90% yield) precipitated and were removed by filtration. After several recrystallizations from anhydrous ether, the sulfoxide had the properties listed in Tables I, II, and III.

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[20] Diaryl sulfoxide models were constructed using the bond angles and lengths determined for phenyl sulfoxide; S. C. Abrahams, *Quart. Rev.* (London), **10**, 407 (1956).

[21] The concept of "inherently dissymmetric chromophores" has been discussed by A. Moscowitz in C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, Chapter 12, and *Tetrahedron*, **13**, 48 (1961). This concept was applied to alkyl *p*-tolyl sulfoxides by Mislow, Ternay, and Melillo.[9] These authors also mentioned the "essential symmetry of the diphenyl sulfoxide chromophore" in phenyl *p*-tolyl sulfoxide. That *ortho* substituents might influence this symmetry was to be expected from analogy with their work in the area of twisted chromophores. See K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon, and G. H. Wahl, Jr., *J. Am. Chem. Soc.*, **86**, 1710 (1964), and references therein.

[22] H. F. Herbrandson and R. T. Dickerson, Jr., *ibid.*, **81**, 4102 (1959).

[23] The reduction of the 1-naphthalenesulfonyl chloride is based on the procedure of F. C. Whitmore and F. H. Hamilton, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 492. Conversion of the sulfinate salt to the sulfinyl chloride is based on the procedure of F. Kurzer, *Org. Syn.*, **34**, 93 (1954).

**Instruments.**—Infrared spectra were run on Perkin–Elmer Model 337 and Model 21 spectrophotometers, ultraviolet spectra on a Cary Model 14 spectrophotometer, and optical rotatory dispersion curves on a Cary Model 60 recording spectropolarimeter.[24] Ultraviolet spectra were determined by Miss Saima Karp.

**Acknowledgment.**—The authors wish to thank Dr. G. G. Lyle for some helpful discussions.

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[24] Reference to a company or product does not imply approval or recommendation of the product by the U. S. Department of Agricultural to the exclusion of others that may be suitable.

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[Contribution from the Department of Chemistry, Massachusetts Institute of Technology,
Cambridge 39, Massachusetts]

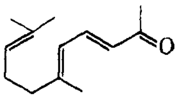
# Bicycloionones and Tricycloionones

By G. Büchi, E. Koller, and C. W. Perry[1]

Received August 14, 1964

Treatment of *cis*-pseudoionone with titanium tetrachloride in benzene solution yielded an ill-defined mixture of chlorine-containing ketones. After dehydrohalogenation with collidine, bicycloionone and epibicycloionone were isolable in 32 and 3% yields, respectively. The structures of the two bicycloionones were established and their formation is discussed in terms of a speculative scheme. The mineral-acid-catalyzed cyclization of pseudoionone was known to yield minor amounts of tricycloionone. Mechanistic considerations led to a hypothetical structure for this ketone which was fully supported by chemical and spectroscopic arguments.

The strikingly simple synthesis of α-ionone (2) and β-ionone (3) from pseudoionone (1) was discovered at the end of the last century.[2] This acid-catalyzed cyclization has received a great deal of attention ever since because the ionones are bulk perfumes and starting materials for the syntheses of vitamin A and of the carotenes. More recent investigations[3–5] have shown that minor quantities of γ-ionone (4) are formed also in the cyclization. In the course of efforts to improve yields and to vary the ratio of cyclic products formed the catalytic action of many acidic reagents was studied.[6–8]



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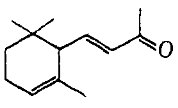

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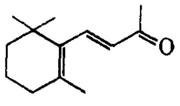

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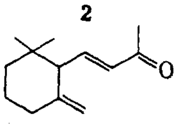

4

Titanium tetrachloride was among the catalysts investigated and reported[7] to yield a product with the composition $C_{13}H_{19}Cl$. According to Schinz and Vogt,[9] treatment of pseudoionone (1) with titanium tetrachloride produced varying amounts of β-ionone (3) in addition to a mixture of halogen-containing substances. Dehydrochlorination with hot collidine furnished a halogen-free product, $C_{13}H_{20}O$, which we shall call bicycloionone. Because it did not combine with Girard reagent and did not form other carbonyl derivatives, the investigators believed it to be an oxide. Catalytic hydrogenation furnished a saturated dihydro derivative and oxidation with potassium permanganate gave both a ketodicarboxylic acid ($C_{13}H_{20}O_5$) and a yellow triketone ($C_{13}H_{18}O_3$). These transformations suggested the presence of a disubstituted cyclic double bond in the molecule and, although the evidence available did not reveal the structure of bicycloionone, the problem was not pursued further.

When *cis*-pseudoionone (5)[10] was added to excess titanium tetrachloride in an inert solvent, a mixture of unstable, chlorine-containing compounds was produced. From this a halogen-free mixture consisting of α-ionone (**2**, 7%), β-ionone (**3**, 2%), bicycloionone (32%), and a fourth isomer (3%) was procured by exposure to hot collidine. Similar treatment of *trans*-pseudoionone (1)[10] resulted in a multitude of products, but neither bicycloionone nor the fourth isomer was detected. Bicycloionone was purified carefully and obtained as a low melting solid. Its infrared spectrum possessed absorptions attributable to a carbonyl group and a *cis*-disubstituted double bond. An n.m.r. spectrum[11] revealed four methyl groups all attached to carbon atoms bearing no hydrogen atoms, and one of these methyl substituents apparently was part of an acetyl function (7.98 τ). A singlet corresponding in intensity to one proton at 7.60 τ suggested an additional hydrogen atom adjacent to this carbonyl group. Furthermore, the spectrum confirmed the presence of a disubstituted double bond and the splitting pattern observed required at least one allylic hydrogen atom. In agreement with the earlier report,[9] catalytic hydrogenation of bicycloionone gave the saturated dihydrobicycloionone. Treatment of this ketone with sodium ethoxide in deuterioethanol at room temperature produced a trideuterioketone, but at elevated temperature a fourth deuterium atom was introduced. Examination of the mass spectra of these deuterated compounds showed that they were indeed methyl ketones. These observations completed the characterization of the functional groups and the transformations to be described now revealed the skeletal structure.

The α-diketone **7**,[9] available from bicycloionone (**6**)

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