cipitate (A) was filtered off and treated in one of several ways.

In one run, starting with 50.0 g. of I, the mother liquor was diluted with petroleum ether to precipitate more solid material (5.1 g.), concentrated on a steam-bath, diluted with petroleum ether again to remove a small amount (0.3 g.) of solid product, and distilled. Most of the liquid product distilled between 66–71° at 15 mm. A portion was redistilled at atmospheric pressure. The properties (b.p.[18] 176–183°, $n^{17.4}D$ 1.5375,[19] m.p. and mixed m.p. of β-naphthyl ether[20] 99–100°) identified the product as benzyl chloride (14.9 g., 67.3% yield of crude material).

When (A) was allowed to react with the moisture in the air, it turned almost white. From 50.0 g. of I, 32.9 g. of this material was obtained. The product did not react with cyclohexene or potassium iodide. Two grams of the product was suspended (the material was insoluble) in acetic acid (50 ml.) and water (2 ml.) and chlorine was passed into the mixture for 0.5 hour. The material gradually went into solution. The solution was poured into ice-water (200 ml.). Besides some unidentified products, 4,7-dichloroquinoline, m.p.[17] 84.5–86.0°, and sulfate ions were found by the methods mentioned above.

When (A) was used immediately upon filtration, it was soluble in glacial acetic acid. When potassium iodide was added, the solution turned red and a yellow precipitate formed. The solution was diluted with carbon tetrachloride and the characteristic purple color of iodine appeared. (A) reacted vigorously with concentrated nitric acid. The resulting solution was diluted; one portion gave a precipitate with barium chloride, while another portion yielded 4,7-dichloroquinoline upon neutralization. The melting point,[17] 85–86°, showed no depression when mixed with an authentic sample.

***cis*-2-Butene Adduct of 7-Chloro-4-quinolinesulfenyl Chloride.**—The material (A) (obtained from 25.0 g. of I) was immediately suspended in fresh dry chloroform (175 ml.) and treated with approximately 0.11 mole of *cis*-2-butene. The solid material went into solution almost as fast as the butene could be supplied. The solution was poured into petroleum ether (2 l.) to precipitate the hydrochloride of the butene adduct. The petroleum ether solution was saturated with hydrogen chloride, and more of the hydrochloride was collected. The hydrochloride, after recrystallization from benzene, melted over a wide range (117–125°); further recrystallization from benzene or from ethyl acetate did not improve its melting behavior. Melting point ranges between 85–130° were obtained, and they seemed to be very strongly dependent on the rate of heating and the particle size.

Anal. Calcd. for $C_{13}H_{14}Cl_3NS$: total Cl, 32.96; inorganic Cl, 10.99; S, 9.94; N, 4.34. Found: total Cl, 32.15; inorganic Cl, 12.41; S, 9.54; N, 4.3.

The hydrochloride was dissolved in a small amount of chloroform, and the solution was washed repeatedly with dilute ammonium hydroxide until the wash was free of chloride ions. The chloroform solution was washed with water and evaporated. The solid residue was recrystallized from aqueous ethanol; cooling in Dry Ice–acetone was necessary to avoid greater losses. The 3-chloro-2-butyl 7′-chloro-4′-quinolyl sulfide thus obtained weighed 5.0 g. (20%) and melted at 61–62°. The analytical sample was recrystallized once more without any significant change in the melting point.

Anal. Calcd. for $C_{13}H_{13}Cl_2NS$: Cl, 24.78; S, 11.20. Found: Cl, 24.60; S, 11.14.

Cyclohexene Adduct of 7-Chloro-4-quinolinesulfenyl Chloride.—A portion of (A) obtained from 15.0 g. of I was immediately added to 100 ml. of dry chloroform and about 20 ml. of cyclohexene. A vigorous reaction took place and the material quickly dissolved. The solution was washed with dilute ammonium hydroxide followed by water. The chloroform solution was evaporated to an oil and diluted with petroleum ether. A precipitate (6.8 g.) formed which could be recrystallized from petroleum ether. The cyclohexene adduct (5.2 g., 32% yield) thus obtained was light yellow and melted at 98–100°. After two treatments with decolorizing charcoal and three recrystallizations from hexane the material was white and melted at 100–101°.

Anal. Calcd. for $C_{15}H_{15}Cl_2NS$: C, 57.69; H, 4.84. Found: C, 57.94; H, 4.85.

4-(2,4-Dichlorobenzylthio)-7-chloroquinoline.—The general procedure of Baker, Dodson, and Riegel[1] was followed, except that the reaction mixture was refluxed only 10 minutes. The product after one recrystallization from ethanol was obtained in a 68.4% yield. The analytical sample was recrystallized a second time and melted at 151–152°.

Anal. Calcd. for $C_{16}H_{10}Cl_3NS$: Cl, 29.99; N, 3.95; S, 9.04. Found: Cl, 30.19; N, 3.79; S, 8.84.

Chlorinolysis of 4-(2,4-Dichlorobenzylthio)-7-chloroquinoline.—The procedure was similar to that given for the chlorinolysis of I. The 2,4-dichlorophenylmethanesulfonyl chloride obtained from 40.0 g. of sulfide weighed 5.0 g. (17%) after one recrystallization from hexane. The long colorless needles melted at 80.5–82.5° (lit.[21] m.p. 79–81°). The aqueous solution was diluted to 1 l. A 100-ml. aliquot yielded 1.746 g. (66.3%) of barium sulfate.

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[21] C. Ziegler and J. M. Sprague, *J. Org. Chem.*, **16**, 621 (1951).

NEWARK, DELAWARE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

Stereoelectronic Factors in the Addition of Sulfenyl Halides to Norbornene

BY HAROLD KWART, ROBERT K. MILLER[1] AND JACK L. NYCE

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The reactions of *o*-nitrobenzenesulfenyl chloride and *p*-nitrobenzenesulfenyl chloride with norbornene give only one product in each case. These products were identified by known degradative processes. A stereoelectronic interpretation has been advanced to explain these observations. Dipole moment studies have been made on the adducts, and an explanation or the deviation of these moments from the calculated result is suggested.

Introduction

We have reported[2] that when 2,4-dinitrobenzenesulfenyl chloride was added to norbornene in non-polar solvents, the normal 1:1 adduct and a smaller amount of nortricyclyl 2,4-dinitrophenyl sulfide resulted. An increase in the amount of the nortricyclyl sulfide was evident when a polar solvent, such as acetic acid, was used. When *p*-toluenesulfenyl chloride was added to norbornene, only the normal 1:1 adduct was obtained.

It has been suggested by Kharasch and coworkers[3] that a three-membered cyclic cationic intermediate is formed by addition of 2,4-dinitrobenzenesulfenyl cation to the double bond. By keeping this in mind, two explanations can be advanced to account for the effect of the structure of the sulfenyl chlorides on the addition reaction:

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[1] National Science Foundation predoctoral fellow, 1954–1955.

[2] H. Kwart and R. K. Miller, THIS JOURNAL, **78**, 5678 (1956).

[3] N. Kharasch and C. M. Buess, *ibid.*, **71**, 2724 (1949).

(1) the steric influence of the *o*-nitro group, or (2) the electronic moment of the cation, which could easily influence the second stage of the reaction.

To learn more about these two influences, *o*- and *p*-nitrobenzenesulfenyl chlorides were allowed to react with norbornene. Both have an electron-withdrawal effect, to a smaller extent than 2,4-dinitrobenzenesulfenyl chloride, but only in one case is there a bulky *o*-group.

The dipole moments of the adducts were measured to establish the possible occurrence or absence of restricted rotation. Since calculation of the theoretical moments requires assumption of free rotation of the aryl sulfide groups, a significant deviation between experimental and calculated results should be evident if a barrier to free rotation is present, as previously suggested.[2]

Results

p-Nitrobenzenesulfenyl Chloride.—The addition of *p*-nitrobenzenesulfenyl chloride to norbornene in ethylene bromide solution gave a mixture which after some difficulty, was separated into pure 1:1 adduct II and an unidentified oil in a 9:1 ratio. The adduct was identified by elemental analysis, chlorinolysis[2,4] to the known *anti*-7-*exo*-2-dichloronorbornane (IV) and *anti*-7-chloro-*exo*-2-norbornyl acetate (V), and by preparation of a pure sulfone derivative, whose analysis agreed with the assigned constitution.

The impure minor product was subjected to chlorinolysis to ascertain the possible formation of a significant amount of a nortricyclyl derivative.[2] No distillable material was formed; consequently, there is no direct evidence for the formation of the nortricyclyl *p*-nitrophenyl sulfide.

o-Nitrobenzenesulfenyl Chloride.—With ethylene bromide as the solvent, the reaction of this sulfenyl chloride with norbornene gave a 78% yield of a yellow, crystalline solid which proved to be the pure, normal 1:1 adduct III. Elemental analysis, chlorinolysis to *anti*-7-*exo*-2-dichloronorbornane and the corresponding ester V, and identification (by analysis) of a pure sulfone derivative confirmed the structure of the adduct. The residual oil from the reaction mixture was chlorinolyzed in the usual fashion in order to convert any nortricyclyl sulfide or 1:1 adduct to the corresponding distillable chlorides. The only product obtained on distillation was the dichloro compound IV formed from the 1:1 adduct. This result established that the addition reaction, here as in the *para* case, yielded only one identifiable product in high yield, unaccompanied by nortricyclyl product.[5]

II, Ar = *p*-nitrophenyl
III, Ar = *o*-nitrophenyl

IV, X = chlorine
V, X = acetoxy

Fig. 1.

To further examine the solvent effect,[2] *o*-nitrobenzenesulfenyl chloride was added to norbornene in glacial acetic acid. The pure 1:1 adduct III was easily isolated in 25% yield with only an oil remaining. The oil was chlorinolyzed but again no trace of nortricyclyl chloride could be detected in the product.

Dipole Moments.—The calculated and measured dipole moments of cycloalkyl aryl sulfides related to this work are listed in Table I. The cyclohexyl derivatives were prepared as standards for the calculations and, therefore, no calculated moments are given in the table. The data on the 1:1 adduct of norbornene and 2,4-dinitrobenzenesulfenyl bromide are included here for comparison with the analogous chlorine compound. The agreement between the observed dipole moments of these compounds gives added support to the structure assigned to the bromo compound.[2]

TABLE I

DIPOLE MOMENT OF CYCLOALKYL ARYL SULFIDES, R–S–Ar

R =	Ar =	μ_D, D. Calcd.	μ_D, D. Found
Cyclohexyl	2,4-Dinitrophenyl		5.88
trans-2-Chlorocyclohexyl	2,4-Dinitrophenyl		5.26
endo-3-Chloro-*exo*-2-norbornyl	2,4-Dinitrophenyl	3.43	5.41
endo-3-Bromo-*exo*-2-norbornyl	2,4-Dinitrophenyl	3.43	5.40
trans-2-Chloro cyclohexyl	*o*-Nitrophenyl		5.09
endo-3-Chloro-*exo*-2-norbornyl	*o*-Nitrophenyl	3.32	4.59
trans-2-Chloro cyclohexyl	*p*-Nitrophenyl		5.32
endo-3-Chloro-*exo*-2-norbornyl	*p*-Nitrophenyl	3.48	5.04

Interpretation and Discussion of Results

The results obtained clearly indicate that while steric hindrance by the aryl group prevents formation of a 2,7-rearranged product,[2] the important factor in formation of the nortricyclyl sulfide is the electronic effect of the aryl group. The bulk of an *o*-nitro group appears to have no effect on the product composition since the same results were obtained with a nitro group in the *p*-position. In analogous cases,[6] it is assumed that anchimeric assistance is afforded by delocalization of a neighboring σ-bond to assist the development of the positive charge on C_3 in the reaction transition state. Although the positive charge could reside on C_3 and C_4, the bulky aryl group prevents reaction at C_4 as indicated by the absence of any 2,7-rearranged prod-

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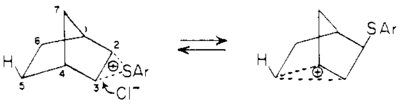
[4] H. Kwart and R. K. Miller, THIS JOURNAL, **78**, 5008 (1956).

[5] A small amount (of the order of a few per cent.) could have escaped detection by this method. In fact, it was possible to subject the entire reaction mixture of the *p*-nitrobenzenesulfenyl chloride adduct to chlorinolysis without obtaining any nortricylyl chloride. It may be pointed out here that chlorinolysis of a very large amount of the 1:1 adduct of norbornene and *o*-nitrobenzenesulfenyl chloride did yield a very small amount of nortricyclyl chloride. On this basis we might have expected to find at least a proportionate quantity in the above experiments with the product formed along with II. Chlorinolysis of the pure *p*-isomer II gave no detectable nortricyclyl chloride, but due to the difficulty in isolating the pure adduct, at no time was a large amount, comparable to that used for the *o*-isomer, chlorinated. In any case, it seems very clear that, at most, only a very small amount of nortricyclyl derivative resulted in the addition of either *o*- or *p*-nitrobenzenesulfenyl chloride to norbornene. This is in sharp contrast to the case of the 2,4-dinitrobenzenesulfenyl chloride which gave a very significant amount (approximately 10%) of nortricyclyl derivative.

[6] S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham, THIS JOURNAL, **75**, 147 (1953).

uct. There are two remaining possibilities: (1) loss of a proton from C_5 to the solvent with resultant formation of nortricyclyl sulfide, or (2) addition of chlorine from the *endo* side to form the 1:1 adduct. Since the aryl sulfide group may be as much as a full carbon–carbon bond distance away from the point of reaction, its electronic effect might be expected to be relatively unimportant. However, in the case where Ar = 2,4-dinitrophenyl, the electron withdrawal apparently is strong enough to induce delocalization of a neighboring σ-bond. With the large steric crowding caused by the aryl sulfide group, the chlorine counter-ion in the intermediate ion pair is unable to completely satisfy this unstable condition, and the result is some loss of proton to the solvent and formation of nortricyclyl sulfide.[2] In a similar view a nortricyclonium ion[7] intermediate is influenced to lose proton to solvent more readily because of the powerful electron withdrawal exerted by the almost contiguous 2,4-dinitrophenyl group. The absence of nortricyclyl sulfide from the products of the reactions reported in this paper indicates that electron withdrawal by a mononitrophenyl sulfide group is not strong enough to affect the reaction center. It follows that in the case of *p*-toluenesulfenyl chloride no second product is to be expected, and this is in accord with what we have reported.[2] Additional evidence for the importance of the electronic effect is found in the result of the reaction of *o*-nitrobenzenesulfenyl chloride with norbornene in glacial acetic acid. Apparently the electronic effect is so important that even in a solvent which greatly enhances the formation of the nortricyclonium ion, no nortricyclyl sulfide is formed in the absence of a sufficiently powerful electron-withdrawing group.



Restricted Rotation in Nitrophenyl Norbornylchlorosulfides.—The calculated values for the dipole moments of the 1:1 adducts differ from the measured values beyond the limits of experimental error (see Table I). In order to understand our proposed explanation for this anomaly, the method of calculation of dipole moments for the bicyclic chlorosulfides must be clearly understood. We shall use the calculations for the 2,4-dinitrophenyl series in the following example.

The dipole moment of an unsymmetrical sulfide RSR′ is the vector sum of the two carbon–sulfur dipoles. Calculation of the moments of the sulfides is complicated by the fact that the molecules are not linear; even symmetrical sulfides have finite dipole moments.[8] In the case of the adducts under consideration, the problem is further complicated by these facts: (1) the direction of the sulfur–aryl bond with respect to the carbon–halogen bond is variable, (2) the direction of the *o*-nitro group with respect to the carbon–halogen bond is variable (this would be so even if complication (1) did not exist), and (3) resonance due to the nitro groups affects the cycloaryl–sulfur and sulfur–phenyl dipoles to an unknown, but probably considerable, extent. We do not know enough about these factors to calculate dipole moments without some simplifying assumptions, and the following are used here: (a) the resonance effect of the nitro groups is constant throughout a given series of cycloalkylnitrophenyl sulfides, and (b) free rotation about the cycloalkyl–sulfur and sulfur–phenyl bonds is possible, all positions being equally likely.

Because of the high value of the nitro group moment (and probably the resonance effect also) the sulfur–aryl group contribution to the dipole moment of the molecule probably is directed toward the phenyl ring. Then, assuming free rotation about the sulfur–phenyl bond, the moment, *m*, of a cycloalkylnitrophenyl sulfide is the resultant of the two moments, *p* and *q* (Fig. 2). However, if the cycloalkyl group holds an electronegative substituent, X, the moment of the molecule is the resultant of components, *d* and *f* (Fig. 3).

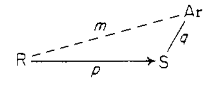


Fig. 2.—Cycloalkyl aryl sulfide.

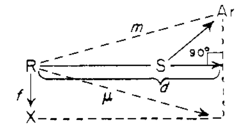


Fig. 3.—Chlorocycloalkyl aryl sulfide.

If one can prepare a compound X–R–S–Ar, in which the angle between the R–X and R–S bonds is known, then the value of *d* can be calculated. In the case of the adduct of cyclohexene and 2,4-dinitrobenzenesulfenyl chloride,[9] the measured dipole moment is 5.26 *D*. There is abundant evidence[10] that the cyclohexane ring exists in the "chair" form and that this compound has a *trans*[9] relationship of the chloro and aryl sulfide groups. With a carbon–chlorine bond moment of 2.18 *D*,[11] component *d* for an axial–axial (a–a) conformation can be calculated to be 7.44 *D;* for the equatorial-equatorial (e–e) conformation the calculated value is 4.12 *D*. The dipole moment of cyclohexyl 2,4-dinitrophenyl sulfide was measured in order to allow a choice between these two possibilities. The experimental result, 5.88 *D*, corresponds to a resultant *m*, which must be greater than *d;* hence, the chlorosulfide must be entirely or largely in the e–e conformation, and the only acceptable value for component *d* is 4.12 *D*.

With the value calculated above for *d*, and the assumption of tetrahedral angles for all carbons in the norbornane structure, the moment for the structure considered most probable for the norbornene-

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[7] J. D. Roberts and C. C. Lee, THIS JOURNAL, **73**, 5009 (1951).

[8] (a) E. C. E. Hunter and J. R. Partington, *J. Chem. Soc.*, 2062 (1931); 2812 (1932); (b) W. S. Walls and C. P. Smyth, *J. Chem. Phys.*, **1**, 337 (1933).

[9] (a) N. Kharasch, H. L. Wehrmeister and H. Tigerman, THIS JOURNAL, **69**, 1612 (1947); (b) N. Kharasch and C. M. Buess, *ibid.*, **71**, 2724 (1949).

[10] (a) O. Massel, *Quart. Revs.*, **7**, 221 (1953); (b) D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953).

[11] M. T. Rogers and M. B. Panish, THIS JOURNAL, **77**, 4230 (1955).

2,4-dinitrobenzenesulfenyl chloride adduct can be calculated to be 3.43 *D*.

The other experimental data in Table I were treated in the same way to arrive at the calculated values for the norbornene adducts.

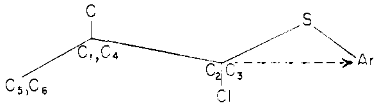

Fig. 4.—*endo*-3-Chloro-*exo*-2-norbornyl aryl sulfide projection.

Chemical degradation has shown unequivocally the structures of the norbornene adducts; the dipole moment calculations obviously do not support the chemical evidence. We must seek the explanation for this anomaly among the assumptions that we have used in calculating the dipole moments. Furthermore, we must seek a source or sources that would produce an error of considerable magnitude. The latter consideration eliminates at once the possibility that the discrepancy is introduced by our assumption of tetrahedral angles for the norbornane carbons. Previous work[2,12] has shown that, provided the substituents are simple, calculations of dipole moments in this way gives results which are well in accord with observed values. This is also supported by calculation of the molecular geometry using the vector analysis scheme suggested by Corey and Sneen[13a] and applied by Martin and Bartlett[13b] to a skeleton with geometry similar to the present cases. It appears unlikely, since the halogens are electronegative, that our assumption of constant nitro resonance effect is seriously in error. We are thus led to the conclusion that either the 2-chlorocyclohexylnitrophenyl sulfides are not entirely in the e–e form, or else that free rotation does not exist in the norbornyl-aryl sulfides.

Returning again to our calculations in the 2,4-dinitrophenyl series, it is obviously unlikely that the magnitude of component *d* is higher than the dipole moment of cyclohexyl 2,4-dinitrophenyl sulfide (5.88 *D*), and thus the cyclohexene adduct cannot be entirely in the a–a form. The possibility remains, however, that the adduct is a mixture of the a–a and e–e conformations such that the *d*-value lies in the range 4.12–5.88 *D*. Recalculation of the data using these limits shows that this source of error is of considerable magnitude. Kozima and co-workers[14] have shown that *trans*-1,2-dichloro- and *trans*-1,2-dibromocyclohexane both exist as dynamic equilibrium mixtures of a–a and e–e forms and these authors propose that the increased van der Waals radius of the halogen accounts for the increase in amount of a–a form in going from the chloro to the bromo compound. This idea calls attention to the steric factor in the sulfides under consideration and points out what is probably the major source of discrepancy in our dipole calculations, namely, the free rotation assumption.

We have contended, in a previous paper,[2] that free rotation of the aryl sulfide group may be seriously restricted in a norbornene–sulfenyl halide adduct. The conformation in which there is least interference between the nitrophenyl and norbornyl groups is depicted in Fig. 4, which is a projection of the adduct on the plane bisecting perpendicularly the line joining C_1 and C_4.

Lack of free rotation should, in effect, reduce the apparent angle between the aryl sulfide group and the chlorine, with a corresponding increase in the dipole moment of the molecule. Although it cannot be calculated accurately, the magnitude of this effect is large probably and, in combination with the wide margin of error in calculation from the moments of the cyclohexene adducts, is probably sufficient to account for the discrepancies seen in Table I. The results of the dipole calculations are thus entirely consistent with our stereoelectronic interpretation of the mechanism of norbornene addition reactions, wherein the Ar group comes very close to the C_3 position.

One fact which requires some comment is the unexpected order of the moments observed for the three 1:1 adducts; 2,4-dinitro > *p*-nitro > *o*-nitro. One should expect on the basis of a simple vector calculation that the order should be *p* > 2,4 > *o*. A simple assumption which might account for this discrepancy is that there can be free rotation around the norbornyl–sulfur bond but restriction about the sulfur–phenyl bond (see Fig. 5). Vector calculations based on this assumption show that the moments of the *o*- and *p*-isomers should both be less than the 2,4-dinitro. However, this assumption also leads to the conclusion that the *o*- and *p*-isomers must have identical moments which is in-

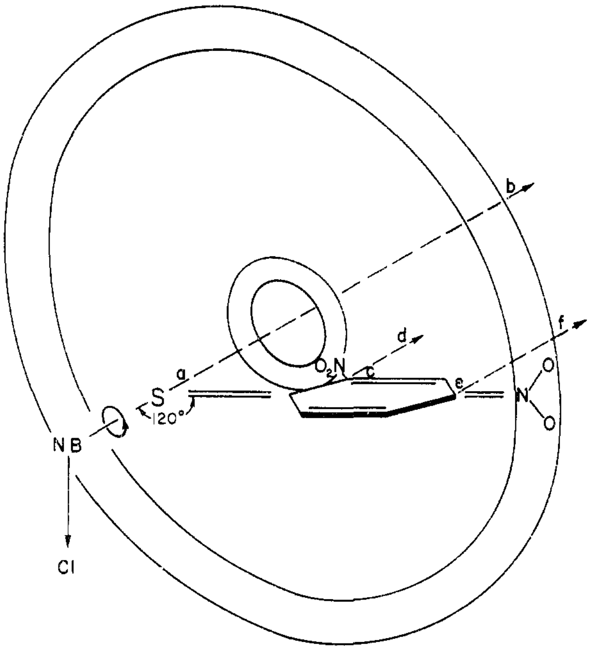

Fig. 5.—Line ab represents the resultant vector of cd and ef when the sulfur–phenyl bond is considered rigid.

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(12) (a) H. Kwart, THIS JOURNAL, **75**, 5942 (1953); (b) H. Kwart and R. Kaplan, *ibid.*, **75**, 3356 (1953); **76**, 4072, 4078 (1954); (c) J. D. Roberts, F. O. Johnson and R. A. Carboni, *ibid.*, **76**, 5692 (1954).

(13) (a) E. J. Corey and R. A. Sneen, *ibid.*, **77**, 2505 (1955); (b) J. C. Martin and P. D. Bartlett, *ibid.*, **79**, 2534 (1957).

(14) K. Kozima, K. Sakashita and S. Maeda, *ibid.*, **76**, 1965 (1954).

consistent with the data obtained. But this, too, can be brought in line by the further assumption that the *o*-nitro groups are tilted out of coplanarity and have reduced moments because of sterically inhibited resonance. We are investigating this latter possibility with suitable model compounds.

Experimental

***p*-Nitrobenzenesulfenyl Chloride.**—*p*,*p*′-Dinitrodiphenyl disulfide, prepared by the method described in reference[15] and purified as described by Price, *et al.*,[16] was stirred in a chloroform solution with ice-bath cooling, according to the directions of Zincke and Lenhardt,[17] while a stream of chlorine was allowed to enter slowly. After an hour the reaction usually was complete and the solvent was removed with aspirator vacuum. Since it is quite sensitive to moist air, the sulfenyl chloride was then immediately put into solution with freshly distilled ethylene bromide.

***o*-Nitrobenzenesulfenyl Chloride.**—The corresponding disulfide[15] was stirred in a carbon tetrachloride solution while chlorine was passed through, according to the directions outlined by Hubacker.[18] Iodine was added in some cases to accelerate the reaction, which usually was complete in two hours. The sulfenyl chloride was isolated in a pure condition (m.p. 73–74.5°) and in an average yield of about 80%. After several recrystallizations from carbon tetrachloride, the melting point was constant at 74–75°. When bottled immediately, no appreciable decomposition of the sulfenyl chloride occurred on standing for three months.

Addition of *p*-Nitrobenzenesulfenyl Chloride to Norbornene. Run 1.—The solution of sulfenyl chloride (128 g., 0.63 mole; based on the theoretical yield in the preparation) in 200 ml. of ethylene bromide was added slowly to a stirred solution of norbornene (92 g., 0.97 mole) in 100 ml. of freshly distilled ethylene bromide. The addition was complete in 45 minutes with the temperature kept always below 25° with ice-bath cooling. The solution, which turned pale yellow, was allowed to stir for an hour and then refrigerated for 48 hours. All attempts to obtain a crystalline product failed, so the solution was washed three times with a 10% sodium bicarbonate solution, twice with water, and dried over anhydrous sodium sulfate. The solvent was then removed under reduced pressure and an oil remained which refused to crystallize. A separation finally was effected by counter-current distribution between acetonitrile and heptane. Five cuts were obtained; a light yellow oil (about 90%) and four other cuts (about 10%), none of which was large enough to merit individual treatment. The yellow oil was the expected pure *endo*-3-chloro-*exo*-norbornyl *p*-nitrophenyl sulfide. Upon long standing (about 5 months) the oil gradually crystallized. All attempts to recrystallize the solid from different solvents only succeeded in the return of the oil, so it was crushed finely in a mortar and washed repeatedly with hexane. The melting point never rose above 57.5–59.5°.

Anal. Calcd. for $C_{13}H_{14}O_2NSCl$: C, 55.02; H, 4.92. Found: C, 55.90; H, 5.09.

The other four cuts were combined and subjected to chlorinolysis in acetic acid–water solution. Under these conditions[2] if any nortricyclyl sulfide existed as a second product, it would be found on distillation of the chlorinolysis products as nortricyclyl chloride. Upon careful work up of the products no distillable material was found.

Run 2.—This time a large excess of the sulfenyl chloride was used to ensure the absence of any unreacted norbornene at the end of the reaction. The same procedure previously described was used, but, after removal of the unreacted material and the solvent, the entire reaction mixture was chlorinolyzed in an acetic acid–water mixture. Upon distillation of the chlorinolysis products a special effort was made to isolate any low boiling nortricyclyl chloride. A small cut was obtained between 39–60° at 6 mm. which would be expected to contain the nortricyclyl chloride if any were present. The high refractive index $n^{20}D$ 1.5037 (lit.[19] $n^{25}D$ 1.4948) and the absence in the infrared of any of the prominent bands of the known[19] nortricyclyl chloride indicated the absence of nortricyclyl chloride in this cut, and, therefore, the absence of any significant amount of nortricyclyl sulfide in the original reaction mixture; 14.56 g. (33.3% of theoretical) of material boiling between 79.8–83.2° at 10 mm., and whose infrared spectra and refractive index $n^{20}D$ 1.5093 corresponded very well with the known[2] *anti*-7-*exo*-2-dichloronorbornane, was obtained. This product is what would be expected from chlorinolysis of the 1:1 adduct. The remaining material balance could be partly accounted for by a higher boiling cut whose infrared spectrum was identical with that of the known *anti*-7-chloro-*exo*-norbornyl acetate.

***endo*-3-Chloro-*exo*-2-norbornyl *p*-Nitrophenyl Sulfone.**—An excess of hydrogen peroxide (30%, 60 ml.) was added to a solution of 8.12 g. of *endo*-3-chloro-*exo*-2-norbornyl *p*-nitrophenyl sulfide in 200 ml. of glacial acetic acid and the mixture heated on a steam-bath for two hours. It was filtered from a slightly flocculent precipitate and allowed to stand for six hours. On chilling in an ice-bath and diluting with water, 7.9 g. (86.8% of theoretical) of pure *endo*-3-chloro-*exo*-2-norbornyl *p*-nitrophenyl sulfone was recovered which melted at 173.5–175.0°. Several recrystallizations from a benzene–carbon tetrachloride mixture did not change the melting point.

Anal. Calcd. for $C_{13}H_{14}NSClO_4$: S, 10.15; Cl, 11.23. Found: S, 10.21; Cl, 11.57.

Chlorinolysis of *endo*-3-Chloro-*exo*-2-norbornyl *p*-Nitrophenyl Sulfide.—Chlorine was passed through a solution of 12.3 g. (0.043 mole) of *endo*-3-chloro-*exo*-norbornyl *p*-nitrophenyl sulfide in 250 ml. of glacial acetic acid and 8 ml. of water until further absorption had ceased. After the solution was allowed to stir for two hours it was poured into 500 g. of cracked ice. When the ice had melted the precipitate of *p*-nitrobenzenesulfonyl chloride was filtered off (m.p. 79–80°) and both the solid and water solutions were extracted repeatedly with petroleum ether. The solvent was then washed twice with a 10% solution of sodium bicarbonate, twice with water, and dried over calcium chloride for several days. The solvent was then removed by distillation at atmospheric pressure with a Skinner–Noyes column and the rest distilled at reduced pressure through a Vigreux column. After a small forecut (probably residual solvent), 2.06 g. of *anti*-7-*exo*-2-dichloronorbornane was recovered with boiling point of 77–82° at 10 mm. ($n^{20}D$ 1.5085). The product balance could be partly accounted for by 1.3 g. of higher boiling material which was identified as *anti*-7-chloro-*exo*-2-norbornyl acetate since it gave a strong hydroxamic acid test for esters and the infrared spectrum was identical with the known spectrum[2] of the compound.

Addition of *o*-Nitrobenzenesulfenyl Chloride to Norbornene.—A solution of *o*-nitrobenzenesulfenyl chloride (94.8 g., 0.5 mole) in 340 ml. of freshly distilled ethylene bromide was added slowly to a solution of norbornene (62.7 g., 0.66 mole) in 75 ml. of ethylene bromide. Ice-bath cooling was used to keep the temperature below 50°. Addition was complete in 20 minutes and the reaction mixture was allowed to stir for 45 minutes at room temperature. After standing for 24 hours the clear solution was chilled in an ice-bath and filtered from a bright yellow precipitate. Upon repeated concentration of the filtrate and filtration, a total of 110.2 g. (77.7%) of pure *endo*-3-chloro-*exo*-2-norbornyl *o*-nitrophenyl sulfide was recovered, m.p. 108–109°. It was recrystallized from carbon tetrachloride to constant melting point, 108.5–109.5°.

Anal. Calcd. for $C_{13}H_{14}O_2NSCl$: C, 55.02; H, 4.97; S, 11.30. Found: C, 54.54; H, 4.92; S, 11.71.

A black oily residue remained from which no solid material could be obtained. This was chlorinated and worked up in the manner previously described in order to find any nortricyclyl sulfide, if present, which would appear as the nortricyclyl chloride. Upon distillation of the chlorinolysis product a complete absence of low boiling material was observed, but 3.2 g. of the *anti*-7-*exo*-2-dichloronorbornane was recovered which would correspond to about 5.5 g. of the 1:1 adduct. Thus, the total yield of *endo*-3-chloro-*exo*-2-norbornyl *o*-nitrophenyl sulfide was 81.7% with no trace of a second product obtained.

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[15] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 220.

[16] C. C. Price, G. W. Gardner and W. Stacey, THIS JOURNAL, **68**, 498 (1946).

[17] T. Zincke and S. Lenhardt, *Ann.*, **400**, 9 (1913).

[18] M. H. Hubacker, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 455.

[19] J. D. Roberts and W. Bennett, THIS JOURNAL, **76**, 4623 (1954).

***endo*-3-Chloro-*exo*-2-norbornyl *o*-Nitrophenyl Sulfone.**—An excess of hydrogen peroxide (40 ml., 30%) was added to a solution of 5.4 g. of *endo*-3-chloro-*exo*-2-norbornyl *o*-nitrophenyl sulfide in 130 ml. of glacial acetic acid on a steam-bath. An immediate precipitate occurred which dissolved on further heating. The solution slowly turned from a pale yellow to a clear colorless solution and after nearly two hours it was allowed to cool slowly. When it was diluted with about four times its volume of water, 4.8 g. of white crystalline sulfone (79.5% yield) was recovered which melted at 123–126°. Upon repeated recrystallization from cyclohexane the melting point remained at 123–125°.

Anal. Calcd. for $C_{13}H_{14}NSClO_4$: S, 10.15; Cl, 11.23. Found: S, 10.02; Cl, 11.82.

Chlorinolysis of *endo*-3-Chloro-*exo*-2-norbornyl *o*-Nitrophenyl Sulfide.—The sulfide (57 g., 0.21 mole) was chlorinated in 300 ml. of glacial acetic acid and 12 ml. of water and then treated as previously described. Upon distillation, after removal of a small forecut (whose infrared spectra showed all the prominent bands of nortricyclyl chloride[19]), 9.43 g. of *anti*-7-*exo*-2-dichloronorbornane was collected between 80–87° at 10–12 mm. A higher boiling cut was obtained which was identified as the same chloroester as was obtained from the chlorinolysis of the *p*-nitro adduct.

Addition of *p*-Nitrobenzenesulfenyl Chloride to Cyclohexene.[9]—The *p*-nitrobenzenesulfenyl chloride was prepared as usual in chloroform solution. The chloroform was removed at aspirator vacuum until only an oil remained. To this rapidly stirred slurry cyclohexene was added dropwise with ice-bath cooling used to keep the temperature below 28°. An immediate reaction took place and the addition was complete in one hour. After the solution was allowed to stir for a half-hour at reflux temperature the excess cyclohexene and residual chloroform were removed at aspirator pressure while the solution was warmed gently on a water-bath. An oily residue remained which solidified when cooled in an ice-bath. The crude pale yellow crystals which formed melted at 63–65°. After several recrystallizations from ethanol the melting point was constant at 66.5–67.5°.

Anal. Calcd. for $C_{12}H_{14}SClNO_2$: Cl, 13.04; S, 11.80. Found: Cl, 12.65; S, 11.82.

Addition of *o*-Nitrobenzenesulfenyl Chloride to Cyclohexene.—A large excess of cyclohexene was added to 56.5 g. of *o*-nitrobenzenesulfenyl chloride at room temperature with no solvent. The solution was stirred rapidly and after ten minutes a reaction began to occur, as noted by the heat evolution, and it was controlled by ice-bath cooling. After the initial reaction subsided the solution was heated at reflux temperature for two hours and then cooled in an ice-bath. A nearly quantitative yield of yellow crystals was recovered (m.p. 101.5–103.5°). After three recrystallizations from ethanol the melting point was constant at 103–105° (lit.[9] 100–102°).

Anal. Calcd. for $C_{12}H_{14}SClNO_2$: Cl, 13.04; S, 11.80. Found: Cl, 13.30; S, 11.88.

Addition of *o*-Nitrobenzenesulfenyl Chloride to Norbornene in Acetic Acid.—A solution of 16 g. (0.085 mole) of *o*-nitrobenzenesulfenyl chloride in 250 ml. of glacial acetic acid was added slowly to a stirred solution of 9.5 g. (0.1 mole) of norbornene in 23 ml. of glacial acetic acid while the temperaure was kept below 28° with ice-bath cooling. Very little heat seemed to be evolved from the reaction after about one-half of the solution was added. The reaction mixture was allowed to stir for an hour at room temperature after addition was complete and then to stand for two more hours. No precipitate was observed. It was then frozen solid in an ice-bath and allowed to melt slowly. By repeating this method, 6.03 g. (25.2% of theoretical) of the 1:1 adduct was recovered, m.p. 105–108°, mixed m.p. 106–108.5°. The residue was poured into twice its volume of water and an oil separated which was extracted repeatedly with a liter of benzene. The benzene was washed with 10% sodium bicarbonate solution, water, and dried over sodium sulfate, after which the bulk of the benzene was removed by distillation and the last traces with a stream of warm air. The yellow oil remaining refused to crystallize, so it was subjected to chlorinolysis and worked up in the manner previously described in order to detect any significant amount of a second product, if formed. On distillation of the chlorinolysis product about 0.5–1.0 ml. of material was obtained between 47–78° at 20–32 mm. which would be expected

TABLE II

DIPOLE MOMENT DETERMINATIONS

Concn., moles/cc. × 10^5	e	n^2	$e - n^2$
2-Chlorocyclohexyl *p*-nitrophenyl sulfide			
1.93	2.3466	2.2440	0.1026
3.82	2.4106	2.2457	.1649
5.74	2.4832	2.2470	.2362
7.91	2.5577	2.2509	.3068
9.18	2.6039	2.2530	.3509
$S^0 = 3.49 \times 10^3$ cc./mole, $\mu = 5.32$ *D.*			
2-Chlorocyclohexyl *o*-nitrophenyl sulfide			
1.98	2.3360	2.2440	0.0920
3.64	2.3896	2.2454	.1442
5.77	2.4584	2.2473	.2111
8.13	2.5373	2.2503	.2870
9.45	2.5824	2.2512	.3312
$S^0 = 3.19 \times 10^3$ cc./mole, $\mu = 5.09$ *D.*			
2-Chlorocyclohexyl 2′,4′-dinitrophenyl sulfide			
0.97	2.3065	2.2435	0.0630
3.00	2.3775	2.2458	.1317
5.29	2.4583	2.2485	.2098
7.02	2.5195	2.2506	.2689
9.73	2.6155	2.2540	.3615
$S^0 = 3.42 \times 10^3$ cc./mole, $\mu = 5.26$ *D.*			
Cyclohexyl 2,4-dinitrophenyl sulfide			
1.22	2.3244	2.2410	0.0834
2.94	2.3972	2.2427	.1545
5.38	2.5034	2.2452	.2582
6.67	2.5618	2.2470	.3148
8.34	2.6332	2.2494	.3838
$S^0 = 4.25 \times 10^3$ cc./mole, $\mu = 5.88$ *D.*			
endo-3-Chloro-*exo*-2-norbornyl *p*-nitrophenyl sulfide			
2.20	2.3437	2.2440	0.0997
3.87	2.3972	2.2446	.1526
6.59	2.4844	2.2473	.2371
7.64	2.5191	2.2491	.2700
11.93	2.6569	2.2523	.4046
$S^0 = 3.14 \times 10^3$ cc./mole, $\mu = 5.04$ *D.*			
endo-3-Chloro-*exo*-2-norbornyl *o*-nitrophenyl sulfide			
2.15	2.3303	2.2440	0.0863
3.95	2.3795	2.2463	.1332
6.42	2.4457	2.2485	.1972
7.36	2.4713	2.2497	.2216
10.66	2.5614	2.2523	.3091
$S^0 = 2.60 \times 10^3$ cc./mole, $\mu = 4.59$ *D.*			
endo-3-Chloro-*exo*-2-norbornyl 2′,4′-dinitrophenyl sulfide			
1.51	2.3285	2.2452	0.0833
3.67	2.4083	2.2476	.1607
5.80	2.4883	2.2503	.2380
8.17	2.5762	2.2530	.3232
10.01	2.6458	2.2554	.3904
$S^0 = 3.61 \times 10^3$ cc./mole, $\mu = 5.41$ *D.*			
endo-3-Bromo-*exo*-2-norbornyl 2′,4′-dinitrophenyl sulfide			
0.99	2.3081	2.2443	0.0638
3.06	2.3868	2.2464	.1404
4.89	2.4533	2.2487	.2046
6.72	2.5221	2.2509	.2712
8.67	2.5953	2.2540	.3413
$S^0 = 3.59 \times 10^3$ cc./mole, $\mu = 5.40$ *D.*			

to contain the nortricyclyl chloride if any were present. The infrared spectrum showed no trace of any of the prominent bands of nortricyclyl chloride.[19] A very small amount of *anti*-7-*exo*-2-dichloronorbornane was found. The bulk of the material was a viscous black oil which would not distill.

Dipole Moment Measurements.—All compounds were recrystallized to constant melting point. The solvent was thiophene-free benzene which was dried just prior to use by azeotropic distillation of a trace of water. All data were taken at 25° and collected in Table II. In all cases the plot of $e - n^2$ *vs.* concentration gave a line with no detectable curvature.

The dipole moments were derived from the dielectric constants and refractive indices of benzene solutions by the Guggenheim method of initial slopes.[20] Values of the dielectric constants were obtained using a heterodyne beat apparatus similar to that of Smyth and Lewis.[21]

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[21] C. P. Smyth and G. L. Lewis, *J. Chem. Phys.*, **7**, 1085 (1939).

NEWARK, DELAWARE

[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

The Chemistry of Derivatives of 2-Benzaltetralone. II. Absorption Spectra and Stereostructure

BY ALFRED HASSNER[1a] AND NORMAN H. CROMWELL[1b]

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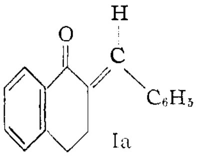
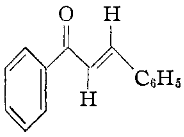
trans-2-Benzal-4,4-dimethyl-1-tetralone (Ib) and its endocyclic unsaturated isomer IXb were synthesized in good yields and characterized by their chemical properties and absorption spectra. The structure of 2-benzal-4,4-dimethyl-1-tetralone oxide (VIIb) obtained by alkaline epoxidation of Ib was verified by synthesis through a Darzens condensation. The advantage of 80% sulfuric acid in the condensation of *o*-nitrobenzaldehyde with 1-tetralone and 1-indanone was demonstrated. Analogies between 2-benzal-1-tetralones, 2-benzal-1-indanone and chalcones are pointed out and a discussion is presented of the effect of conjugation, α-bromo substitution and 4-*gem*-dimethyl substitution in 1-tetralones in terms of conformational analysis, ultraviolet and infrared absorption characteristics.

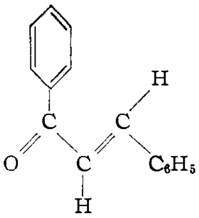
In connection with our study of the chemical behavior of cyclic aromatic ketones[2,3] we have synthesized and examined the stereostructure and absorption spectra of several 2-substituted tetralones and indanones. The 2-benzal-1-tetralones are structurally related to the chalcones in the open chain series, the chemistry of which has been the subject of several investigations.[4] For the cyclic ketones, however, the conformation of the ring and of the substituents are additional aspects to be considered. Moreover, in these exocyclic α,β-unsaturated ketones there exists a fixed *s-cis* conformation of the C=C with respect to the C=O bond, while in the open chain chalcone types the *s*-conformation is labile.[5]



s-cis-trans



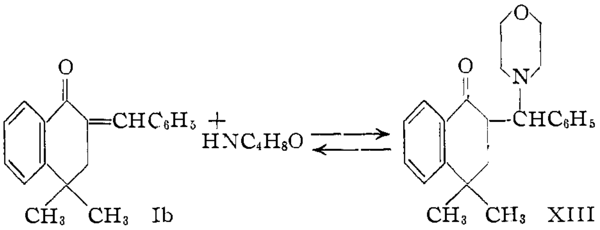
s-cis-trans-chalcone



s-trans-trans

As in the case of 2-benzal-1-tetralone (Ia),[2] the 4,4-dimethyl analog Ib was obtained from a base-catalyzed condensation of the corresponding 1-tetralone with benzaldehyde. Only one of the two possible stereoisomers of 2-benzal-4,4-dimethyl-1-tetralone (Ib) was isolated (presumably the *trans* form). It showed the same chemical inertness against acids and bases as did 2-benzal-1-tetralone (Ia).[2]

A careful study of the reactivity of Ib with morpholine revealed the existence of the equilibrium



The morpholinoketone XIII was formed in yields of about 10% when 2-benzal-4,4-dimethyl-1-tetralone (Ib) was allowed to stand for one day with three molar equivalents of morpholine. The equilibrium outlined above may be approached from either side. Thus 2-[α-(N-morpholino)-benzyl]-4,4-dimethyl-1-tetralone (XIII) was converted back to Ib in 40% yield upon standing with excess morpholine alone or in benzene solution. This facile change probably involves a quasi six-membered ring with the morpholine serving as a proton transfer agent to give this α,β-unsaturated ketone with a fixed *s-cis* conformation.

The preparations of 2-(*o*-nitrobenzal)-1-tetralone (Xa) and 2-(*o*-nitrobenzal)-1-indanone (Xc) were accomplished in high yields by employing 80% sulfuric acid or a sulfuric–acetic acid mixture as the condensing agent. With boiling acetic anhydride the synthesis of pure Xc[6] was accomplished in 36% yield while with 80% sulfuric acid as the solvent-catalyst the yield was 73%.

Selective hydrogenation of 2-benzal-4,4-dimethyl-1-tetralone (Ib) over platinum oxide af-

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[2] A. Hassner, N. H. Cromwell and S. J. Davis, THIS JOURNAL, **79**, 230 (1957).

[3] N. H. Cromwell, H. H. Eby and D. B. Capps, *ibid.*, **73**, 1230 (1951).

[4] For example see N. H. Cromwell, *Chem. Revs.*, **38**, 83 (1946).

[5] (a) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955); (b) E. A. Braude and C. J. Timmons, *ibid.*, 3766 (1955).

[6] G. Singh and J. N. Ray, *J. Indian Chem. Soc.*, **7**, 638 (1930), failed to effect the reaction of 1-indanone with *o*-nitrobenzaldehyde in the presence of bases but obtained low yields of 2-(*o*-nitrobenzal)-1-indanone (Xc) by using boiling acetic anhydride.