# Electrophilic Additions to Indene and Indenone: Factors Effecting Syn Addition

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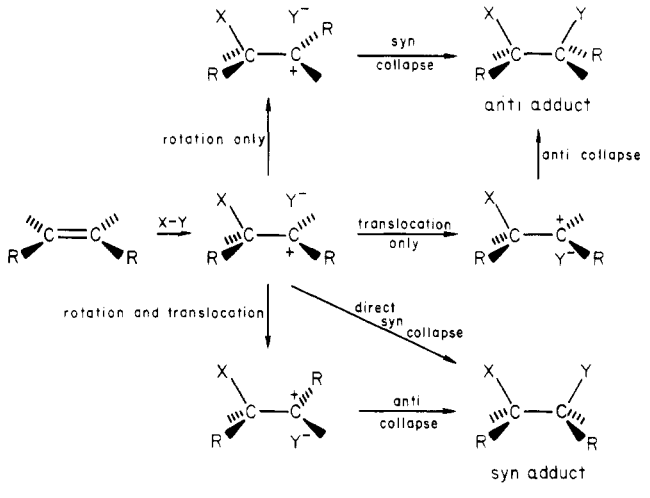
The electrophiles bromine, bromine chloride, chlorine, acetyl hypochlorite, and acetyl hypobromite all yield substantial cis addition product by reaction with indene (1) in aprotic solvents, showing that the direct syn collapse of ion pairs obtained from bromine and similar electrophiles is readily possible. The cis to trans ratios with the halogens (but not with the acyl hypohalites) vary with solvent polarities. In the low-polarity solvents (hydrocarbons and carbon tetrachloride) much more syn addition occurs at high halogen concentration. Syn addition of the above electrophiles to 1 as well as methyl hypobromite and methyl hypochlorite was also observed in methanol and acetic acid, with the exception of bromination in methanol where only the *trans*-dibromide was obtained. Bromine and bromine chloride addition to indenone (**20**) yielded only the *trans*-dihalides, suggesting that a neighboring keto group stabilizes the bridged bromonium ion. Chlorination of **20** was not stereospecific but yielded more *trans*-dichloride than did chlorination of 1.

Although it is well-known that many polar additions of halogen electrophiles to alkenes and dienes take place with exclusive anti stereochemistry, there are also many examples of syn addition, particularly with chlorine electrophiles.[1] The literature shows that syn addition is enhanced by the substitution of groups onto the double bond that stabilize the positive charge and hence diminish the demand for bridging by the halogen. Interpretation of the mechanism of syn addition is a problem, however, since most electrophilic addition studies have been done with acyclic alkenes where the syn adduct can arise either from direct syn collapse of the ion pair or from rotation followed by anti collapse. Scheme I presents some of the possible processes.

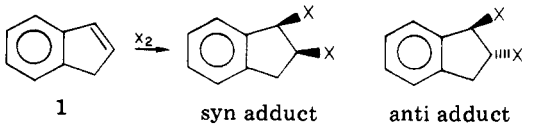
Although the direct collapse of ion pairs involved in the chlorination of alkenes is an accepted fact,[2-5] the literature is not clear concerning the possibility of direct collapse of ion pairs in the bromination of alkenes. In their studies on the bromination of the β-methylstyrenes, Fahey and Schneider[6a] and Rolston and Yates[6b] tentatively accounted for the syn adduct by rotation–translocation followed by anti collapse, presuming that direct syn collapse would be precluded by steric interactions between the two large bromine atoms. Formation of *cis*-1,2-dibromides was reported in two recent studies on the brominations of the cyclic alkenes 1-phenylcyclohexene[7a] and cyclopentadiene.[7b] If these accounts are accurate, the dibromide

**Scheme I**




products must have resulted from direct syn collapse of the intermediate ion pairs. Both studies, however, suffer from experimental difficulties. In the former study, the *cis*-dibromide was unstable, could not be isolated from the many other products, and was not established as a kinetic product. The problems with the more recent study are similar: *cis*-3,4-dibromocyclopentene could not be isolated, and its presence was suggested by rearrangement to the other isomers. The changes in the amounts of the isomers, however, did not confirm the *cis*-dibromide.

It occurred to us that indene (1) would make an ideal system to investigate the extent of direct syn collapse of ion pairs from various electrophiles. Structurally, indene (1) is quite similar to the β-methylstyrenes and so an assessment could be made of the extent of syn collapse of ion pairs vs. rotation and reorientation that had occurred in the earlier studies in these systems. The literature contains one report on the addition of electrophiles to




(1) For reviews of this subject see: (a) G. H. Schmid and D. G. Garratt, "The Chemistry of the Double Bonded Functional Groups", S. Patai, Ed., Wiley, London, 1977, Supplement A; (b) R. C. Fahey, *Top. Stereochem.*, **3**, 286 (1968); (c) P. B. D. de la Mare and R. Bolten, "Electrophilic Additions to Unsaturated Systems", Elsevier, New York, 1966.

(2) P. B. D. de la Mare and R. Koenigsberger, *J. Chem. Soc.*, 5327 (1964).

(3) S. J. Cristol, F. R. Stermitz, and P. S. Ramsey, *J. Am. Chem. Soc.*, **78**, 4939 (1956).

(4) R. C. Fahey and C. Schubert, *J. Am. Chem. Soc.*, **87**, 5172 (1965).

(5) G. E. Heasley, D. C. Hayse, G. R. McClung, D. K. Strickland, V. L. Heasley, P. D. Davis, D. M. Ingle, K. D. Rold, and T. S. Ungermann, *J. Org. Chem.*, **41**, 334 (1976).

(6) (a) R. C. Fahey and H. J. Schneider, *J. Am. Chem. Soc.*, **90**, 4429 (1968); (b) J. H. Rolston and K. Yates, *ibid.*, **91**, 1477 (1969).

(7) (a) P. L. Barili, G. Bellucci, F. Marioni, I. Morelli, and V. Scartoni, *J. Org. Chem.*, **38**, 3472 (1973); (b) G. E. Heasley, J. M. Bundy, V. L. Heasley, S. Arnold, A. Gipe, D. McKee, R. Orr, S. L. Rodgers, and D. F. Shellhamer, *J. Org. Chem.*, **43**, 2793 (1978).

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Table I. Percentage of Syn Addition Obtained from Indene and Electrophiles in Aprotic Solvents[a]

| solvent | dielectric const | electrophile: bromine A[b] | bromine B[b] | bromine chloride A[b] | bromine chloride B[b] | chlorine A[b] | chlorine B[b] | acetyl[c] hypobromite | acetyl[c] hypochlorite |
|---|---|---|---|---|---|---|---|---|---|
| *n*-pentane | 1.8 | 14 | | 29 | | | | 15 | 47 |
| *n*-heptane | 1.9 | 12.4 | 6.8 | | | 73.5[d] | 54[d] | | |
| cyclohexane | 2.0 | 17.5 | 10 | 34.5 | 11 | | | | |
| carbon tetrachloride | 2.2 | 15.5 | 8.5 | 41.5 | 14.5 | 73 | 49 | 20 | 43 |
| dichloromethane | 9.1 | 31.5 | 32 | 23 | 20 | 42 | 39 | 19 | 43 |
| 1,2-dichloroethane | 10.4 | 30.5 | 34.5 | 26 | 25 | 50.5 | 49.5 | | |
| acetonitrile | 36.2 | 21 | | 21.5 | | | | 30 | 38 |
| nitromethane | 38.6 | 25 | | 21.5 | | 44.5[e] | 38[e] | 22 | 37 |

[a] Product percentages were reproducible within ±2%. The reaction products, 1,2-disubstituted indans (Y at 1 position and X at 2-position), are identified as follows: from $Br_2$ (X = Br, Y = Br), *trans*-2 and *cis*-3; from BrCl (X = Br, Y = Cl), *trans*-4 and *cis*-5; from $CH_3C(O)OBr$ (X = Br, Y = $OC(O)CH_3$), *trans*-6 and *cis*-7; from $CH_3C(O)OCl$ (X = Cl, Y = $OC(O)CH_3$), *trans*-8 and *cis*-9; from $Cl_2$ (X = Cl, Y = Cl), *trans*-10 and *cis*-11. [b] In A the initial concentration of the electrophile is 0.16 M and in B it is 0.016 M. [c] Reaction conditions were designed so that the initial concentration of 1 was a mole fraction of 0.02 with respect to solvent; the initial concentration of electrophile varies slightly but is close to that in condition A. [d] $Cl_2$ was added as a solution in $CCl_4$. [e] $Cl_2$ was added as a solution in $CH_2Cl_2$.

indene,[8] but the study was limited, and a systematic examination of solvent effects was not undertaken. Furthermore, there was no assurance that the reactions were not occurring by radical mechanisms.

We also proposed to examine the chlorination and bromination of indenone to determine what effect a conjugated electron-withdrawing group would have on the amount of syn addition. We anticipated that the neighboring carbonyl group would strengthen the bridging in the halonium ion and, therefore, lead to a decrease in syn attack.

## Results and Discussion

**Ionic Additions to Indene.** The amounts of syn (vs. anti) addition observed with indene and the electrophilic reagents bromine, bromine chloride, acetyl hypobromite, acetyl hypochlorite, and chlorine in aprotic solvents of varying dielectric constant are shown in Table I.

First, our data show that direct syn collapse of ion pairs from 1 does occur. Steric effects clearly do not prevent the syn attachment of two large bromine atoms since over 30% of the dibromide product is derived by this route in methylene chloride and dichloroethane. Also, the percentage of syn adduct from the bromination of 1 compares favorably with the amount of *syn*-dibromide reported for a number of acyclic alkenes and dienes that yield nonstereospecific products. Table II shows the percentage of *syn*-dibromide obtained from bromination of some representative alkenes. On the basis of our results with indene (1), it is reasonable to conlude that most of the *syn*-dibromide in the case of the acyclic alkenes is formed by direct syn collapse of the intermediate ion pair rather than by carbon–carbon bond rotation followed by anti collapse. Supporting this conclusion is the fact that many pairs of cis–trans alkenes yield comparable amounts of syn adduct whereas if the syn adduct were obtained via the rotation mechanism, we would expect more rotation for the cis alkene and, hence, a larger amount of syn adduct.

Not surprisingly, molecular chlorine and 1 give the largest amount of syn product. At higher chlorine concentration in the less polar solvents, the amount of syn adduct exceeds 70%. Our data suggest that the large amount of syn dichloride reported in the earlier study[4] on the chlorination of the β-methylstyrenes probably results from direct collapse of ion pairs.[9] The proportion of syn adduct with acetyl hypochlorite is consistently greater than that with acetyl hypobromite, probably because of the greater bulk of the bromine atom derived from the latter.

Table II. Percentages of 1,2-*syn*-Dibromide Formed from Various Alkenes

| reactants | % *syn*-1,2-dibromide[a] |
|---|---|
| *cis*-$C_6H_5CH{=}CHCH_3$, $Br_2$, $CCl_4$ | 17[6a] |
| *trans*-$C_6H_5CH{=}CHCH_3$, $Br_2$, $CCl_4$ | 12[6a] |
| *cis*-$C_6H_5CH{=}CHCH_3$, $Br_2$, $CH_2Cl_2$ | 26,[6a] 29.8[6b] |
| *trans*-$C_6H_5CH{=}CHCH_3$, $Br_2$, $CH_2Cl_2$ | 12[6a] |
| *cis,cis*-$CH_3CH{=}CHCH{=}CHCH_3$, $Br_2$, $CCl_4$ | 21[12] |
| *cis,cis*-$CH_3CH{=}CHCH{=}CHCH_3$, $Br_2$, $CH_2Cl_2$ | 21[12] |
| *trans,trans*-$CH_3CH{=}CHCH{=}CHCH_3$, $Br_2$, $CCl_4$ | 21[12] |
| *trans,trans*-$CH_3CH{=}CHCH{=}CHCH_3$, $Br_2$, $CH_2Cl_2$ | 15[12] |
| (*Z*)-$C_2H_5OCH{=}CHCH_3$, $Br_2$, $CCl_4$ | 29[13] |
| (*E*)-$C_2H_5OCH{=}CHCH_3$, $Br_2$, $CCl_4$ | 32[13] |
| (*Z*)-$C_6H_5OCH{=}CHCH_3$, $Br_2$, $CCl_4$ | 5[13] |
| (*E*)-$C_6H_5OCH{=}CHCH_3$, $Br_2$, $CCl_4$ | 14[13] |
| (*Z*)-$C_6H_5CH_2OCH{=}CHCH_3$, $Br_2$, $CCl_4$ | 26[13] |
| (*E*)-$C_6H_5CH_2OCH{=}CHCH_3$, $Br_2$, $CCl_4$ | 35[13] |

[a] *syn*-Dibromide is defined as the percentage of *threo*-dibromide from a trans alkene and *erythro*-dibromide from a cis alkene.

Before proceeding to discuss the effects of solvents on the proportion of syn addition, we need to call attention to the surprising effect of halogen electrophile concentration on the syn/anti ratio in some of the solvents. In carbon tetrachloride and the alkane solvents, we observed that the percentage of syn addition was strikingly greater at the higher halogen concentration (0.16 M compared to 0.016 M).[10] This is especially evident with bromine

(8) R. A. Austin and C. P. Lillya, *J. Org. Chem.*, 34, 1327 (1969).

(9) Fahey and Schubert[4] state that chlorination of *cis*- and *trans*-β-methylstyrene gives different ratios of erythro and threo dichlorides, indicating that nonidentical ion pairs are involved in chlorination of the two alkenes. Recently, we reexamined these reactions under ionic conditions and found that the ratio of erythro and threo dichlorides is the same from either isomeric β-methylstyrene. Our results suggest that some reorientation–rotation (Scheme I) of ion pairs as well as direct collapse must occur for formation of identical products from the cis and trans alkenes.

(10) The degree of stereoselectivity observed in bromination of methyl *trans*-cinnamates[11] was also found to depend markedly upon bromine concentration, in the same general manner as we report here.

Table III. Reactions of Indene with Electrophiles in Methanol and Acetic Acid

| entry | reaction conditions[a] | 1/EY[d] | dihalo adducts,[b,c] % syn | dihalo adducts,[b,c] % anti | dihalo adducts,[b,c] % % syn | halomethoxy (acetoxy) adducts,[b,c] % syn | halomethoxy (acetoxy) adducts,[b,c] % anti | halomethoxy (acetoxy) adducts,[b,c] % % syn |
|---|---|---|---|---|---|---|---|---|
| 1 | 1 (5%), MeOH (95%), $Br_2$ | 0.80 | 0.8 | 44.7 | 1.8 | 0.8 | 53.7 | 1.5 |
| 2 | 1, MeOH, $Br_2$ | 0.25 | | 2.5 | <1 | | 97.5 | <1 |
| 3 | 1, MeOH, $Br_2$, 0.1 M NaBr | 0.25 | | 15.5 | <1 | | 84.5 | <1 |
| 4 | 1, MeOH, MeOBr[e] | 0.50 | | | | 4.0 | 96 | 4 |
| 5 | 1, HOAc, $Br_2$ | 1.0 | 23.9 | 64.6 | 27 | | 11.5 | 5 |
| 6 | 1, MeOH, $Cl_2$[e] | 0.50 | 15.7 | 8.8 | 64 | 16.6 | 58.9 | 22 |
| 7 | 1, MeOH, MeOCl[f] | 0.50 | | | | 27 | 73 | 27 |
| 8 | 1, HOAc, $Cl_2$[e] | 1.0 | 55.4 | 27.3 | 67 | 6.7 | 10.6 | 39 |
| 9 | 1, HOAc, AcOBr[e] | 1.0 | | | | 21 | 79 | 21 |
| 10 | 1, HOAc, AcOCl[e] | 1.0 | | | | 49 | 59 | 41 |

[a] Unless otherwise noted, the reaction conditions are as follows: concentration of indene, 2 mol % with respect to the methanol or acetic acid; temperature 0–3 °C. [b] Dihalides and halomethoxy (acetoxy) products together equal 100% of the identified products. [c] Products are identified as follows: bromoacetoxy products, 6 and 7; chloroacetoxy products, 8 and 9; 2-bromo-1-methoxyindans, *trans*-12 and *cis*-13; 2-chloro-1-methoxyindans, *trans*-14 and *cis*-15. [d] Mole ratio of indene to the electrophile. [e] Ca. 1 M solution in $CCl_4$. [f] MeOCl as a 1 M solution in $CH_2Cl_2$.

chloride. We suspect that this change is caused by a larger number of halogens in the product-forming step at higher halogen concentration.[14] Another possibility is that at higher halogen concentration some species of halogen telomer (e.g., $Br_4$) is the direct halogenating agent.

Now consider some of the trends that develop with changes in solvent polarity. Reactions of acetyl hypobromite, acetyl hypochlorite, and chlorine at the lower concentration do not exhibit a significant solvent effect. Hoffman and Bishop have observed a similar lack of solvent effect in the stereoselectivity of addition of *p*-nitrobenzenesulfonyl peroxide to *cis*- and *trans*-stilbene.[18] They concluded that their results were consistent with the formation of a nonbridged cation in intimate association with an anion which collapsed without solvent separation. We suggest a similar explanation for our results.

The reactions of indene with bromine, bromine chloride, and chlorine led to more complex results. For bromine and bromine chloride at the lower concentration, there is a fairly regular trend from a lesser amount of syn addition in the least polar solvents to a greater amount in the more polar solvents. The results suggest that a bridged bromonium ion may be involved in the least polar solvents and that anti collapse on this bridged ion takes place at a rate that is competitive with ring opening of the bridged ion to give a carbocation.

As has been noted, more syn addition is observed with bromine, bromine chloride, and chlorine in the least polar solvents at high halogen concentration than at low halogen concentration. This effect is not observed in the more polar solvents. Furthermore, bromine chloride and chlorine give more syn product in the low-polarity solvents (alkanes, carbon tetrachloride) than in the high-polarity solvents (methylene chloride through nitromethane). Somehow the combination of low solvent polarity and higher halogen concentration favors the partial intervention by a mechanism that avoids a bridged bromonium ion and at the same time provides an intermediate in which syn collapse is favored. Perhaps the coordination of two or more halogens permits a concerted mechanism as shown in Scheme II.[19]

Scheme II

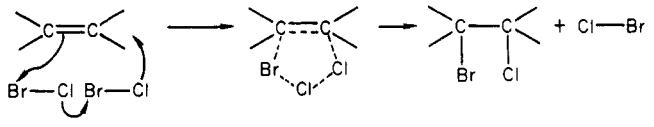



Table IV. Radical Additions to Indene

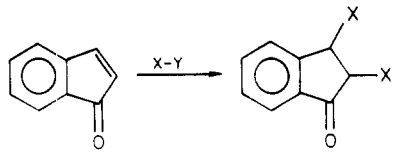
| reaction conditions[a] | % syn adduct[b] | reaction conditions[a] | % syn adduct[b] |
|---|---|---|---|
| 1, MeOCl, UV | 22 | 1, $NCl_3$, UV | 27.5 |
| 1, MeOBr, UV | 19 | 1, $C_6H_5ICl_2$, UV | 5.9 |

[a] Reactions were done at 0–5 °C under sunlamp irradiation and were complete within a few minutes. Solutions of MeOCl and MeOBr (ca. 1 M) in methylene chloride were added to neat 1 in sufficient amounts to consume 25–50% of 1. A solution of $NCl_3$ (ca. 1 M) in methylene chloride and solid iodobenzene dichloride were added to dilute solutions of 1 in methylene chloride in amounts equal to 75% of 1. [b] Addition products are identified as follows: from $CH_3OCl$, 1-chloro-2-methoxyindans *trans*-16 and *cis*-17; from $CH_3OBr$, 1-bromo-2-methoxyindans *trans*-18 and *cis*-19; from $C_6H_5ICl_2$ and $NCl_3$, 10 and 11.

Data for additions of several electrophiles to indene in the protic solvents, methanol, and acetic acid are shown in Table III. In these nucleophilic solvents, products can arise from attack on the cationic intermediate either by the counterion of the electrophile or by the solvent. To a considerable extent, the results in protic solvents resemble those in the aprotic solvents. Syn addition of chlorine is even more pronounced in methanol and acetic acid than in the aprotic solvents. Direct syn collapse of

(11) M. A. Wilson and P. D. Woodgate, *J. Chem. Soc., Perkin Trans. 2*, 141 (1976).
(12) G. E. Heasley, V. L. Heasley, S. L. Manatt, H. A. Day, R. V. Hodges, P. A. Kroon, D. A. Redfield, T. L. Rold, and D. E. Williamson, *J. Org. Chem.*, **38**, 4109 (1973).
(13) G. Dana, O. Convert, and C. Perrin, *J. Org. Chem.*, **40**, 2133 (1975).
(14) The kinetics of bromination in tetrachloroethane[15] are reported to be second order in bromine even at a bromine concentration of $2 \times 10^{-4}$ M. Therefore, we assume that a minimum of two bromine molecules are involved in mechanisms occurring in the less polar solvents. Data on the kinetic orders in the more polar aprotic solvents are not available. Previous studies[16] have found that kinetics of chlorination exhibit only a first-order dependence upon chlorine. However, these results were primarily obtained in acetic acid, and, apparently, the kinetic order in aprotic solvents with reactive alkenes has not been established. Since the $Cl_3^-$ ion has been reported to be more stable than $Br_3^-$ in aprotic solvents,[17] the possibility of catalysis by a second chlorine molecule cannot be discounted.
(15) A. Modro, G. H. Schmid, and K. Yates, *J. Org. Chem.*, **42**, 3673 (1977).
(16) E.g., see ref. 1a, p 755.
(17) Victor Gutmann, Ed., "Halogen Chemistry", Vol. I, Academic Press, 1967, London and New York, p 253.
(18) R. V. Hoffman and R. D. Bishop, *Tetrahedron Lett.*, 33 (1976).
(19) To account for similar concentration effects, Wilson and Woodgate[11] have proposed an ion-pair mechanism in which coordination by two or more additional halogen molecules serves to eliminate bridging by halogen.

Scheme III



20 1a, X = Br; Y = Br; 100% trans
b, X = Br; Y = Cl; 100% trans
c, X = Cl; Y = Cl; 87% trans, 13% cis

the chloride ion without significant reorientation must occur.

Bromination in methanol, however, stands out by itself. Unlike bromination in acetic acid which gave 27% *syn*-dibromide, only a trace of *syn*-dibromide was produced in methanol. It seems highly unlikely that this result means that a tightly bridged bromonium ion is an intermediate in methanol but not in the other polar solvents. A much more likely explanation is that bromination in methanol leads directly to a solvent-separated ion pair and that the dibromide product arises from attack by a solvent-separated bromide ion.[20] Steric factors must dictate a strong preference for anti attack on this solvated ion. The fact that large amounts of syn addition occur in other solvents suggests that tightly associated ion pairs are the product-forming intermediates in these solvents. Evidence favoring solvent-separated ion pairs in the methanol bromination is suggested by the fact that the ratio of dibromide formation to methoxy bromide formation was highly variable, depending upon the concentration of alkene, the ratio of indene to bromine, and the concentration of added bromide (see entries 1–3, Table III).

**Radical Reactions.** The results of several radical additions[23] to indene are presented in Table IV. The stereochemistry of the radical additions should provide some clue to the importance of steric factors in the addition to indene. The three reagents methyl hypochlorite, methyl hypobromite, and trichloramine all yield predominately the trans product in the range of 70–80%. Iodobenzene dichloride on the other hand gives 94% of the *trans*-dichloride. This is probably due to the great bulk of the iodobenzene dichloride molecule. Its strong bias for trans attack has been observed in radical reactions with other alkenes.[24a]

**Addition to Indenone (20).** Addition of bromine and bromine chloride to indenone gave products with only *trans* stereochemistry (**1a–c**, Scheme III). The data show that chlorine addition to **20** also occurs with much higher stereoselectivity than that for indene itself, suggesting that partial bridging is involved in this intermediate chloronium ion.

The increase in stereoselectivity in going from indene to indenone would not have been predicted from earlier investigations. The stereoselectivities observed previously in the additions of bromine and acetyl hypobromite to cinnamate esters[11] and the β-methylstyrenes[6] are very similar. The electron-withdrawing capacity of a ketone carbonyl is much greater than that of an ester carbonyl, and, perhaps, this accounts for the increased stereoselectivity with indenone.

The bromonium ion from the addition of bromine chloride to indenone was opened exclusively at the benzylic (β) carbon as shown in Scheme III. We speculated that the carbonyl group might increase the reactivity at the α carbon if the ring-opening had $S_N2$ character, but apparently no rate enhancement occurred. There are at least two possible reasons for the lack of rate enhancement. One involves the fact that the C–Br bond is bent back and too distant from the p orbital to overlap, as we have discussed previously.[25] Also, the requirement for alignment of the X–C–Br bond and the p orbital, as reported by Bartlett and Trachtenberg,[26] cannot be met because of the steric orientation of the bonds.

## Experimental Section

**Reaction Conditions.** Commercially available indene was distilled prior to use. The preparation and use of several of the electrophilic reagents has been described previously: acetyl hypobromite,[27] acetyl hypochlorite,[27] methyl hypochlorite,[24b] methyl hypobromite,[24c] trichloramine,[24a] iodobenzene dichloride,[24a] and bromine chloride.[7b]

The reaction conditions chosen were those which had been found in previous[24c,27-29] studies with these electrophiles to prevent radical reactions. The results reported in Table I were obtained by adding neat indene (usually in slight excess) quickly to well-stirred solutions of the electrophile in the appropriate solvent at ice temperature (0–3 °C). Reactions were protected from light. In chlorinations the solvent was saturated with oxygen prior to addition of the chlorine.[30] In a typical "concentrated" bromination, 0.3 mL (2.6 mmol) of indene was added to a solution of 0.11 mL (2.1 mmol) of bromine in 8.1 mL of carbon tetrachloride. In "dilute" reactions the same quantities were used, but the volume of solvent was increased tenfold. Reactions with other electrophiles were done on a similar scale. Bromine chloride was used as an ~1 M carbon tetrachloride solution. Carbon tetrachloride solutions of acetyl hypobromite (ca. 0.5 M) and acetyl hypochlorite (ca. 1 M) were also used.

Reactions that were carried out in methanol or acetic acid were subjected to water workup to remove the solvents before product analysis was attempted.

We carried out experiments which showed that the reaction products were unaffected for short periods of time by conditions of the reaction. For example, the ratio of the *cis*- and *trans*-dibromides of 1 was not changed by a brief period of standing with excess bromine. Mixtures of dibromides and other products of varying compositions showed no tendency to undergo change in the solvents used for NMR analysis.[31]

(20) Previous investigators[21] have concluded that the dichloride formed from chlorination of alkenes in methanol arises mainly from associated ion pairs. On the other hand, a study of salt effects in the bromination of styrenes[22] in acetic acid showed that dibromide was formed by attack from solvent-separated bromine ion.

(21) (a) G. E. Heasley, W. E. Emery III, R. Hinton, D. F. Shellhamer, V. L. Heasley, and S. L. Rogers, *J. Org. Chem.*, **43**, 361 (1978); (b) J. H. Rolston and K. Yates, *J. Am. Chem. Soc.*, **91**, 1477 (1969).

(22) J. H. Rolston and K. Yates, *J. Am. Chem. Soc.*, **91**, 1469 (1969).

(23) Previous studies[24] with these electrophiles established that the reaction conditions described in Table IV assure radical conditions. This is readily confirmed for the hypohalites where the products were found to be anti-Markovnikov adducts.

(24) For $NCl_3$ and $C_6H_5ICl_2$: (a) V. L. Heasley, K. D. Rold, D. B. McKee, and G. E. Heasley, *J. Org. Chem.*, **41**, 1287 (1976). For MeOCl: (b) G. E. Heasley, V. M. McCully, R. T. Wiegman, V. L. Heasley, and R. A. Skidgel, *ibid.*, **41**, 644 (1976). For MeOBr: (c) V. L. Heasley, C. L. Frye, G. E. Heasley, K. A. Martin, D. A. Redfield, and P. S. Wilday, *Tetrahedron Lett.*, 1573 (1970).

(25) We recently reported that the carbonyl group did not increase the rate of attack at the α carbon in the addition of bromine chloride to methyl acrylate and the methyl crotonates: V. L. Heasley, D. W. Spaite, D. F. Shellhamer, and G. E. Heasley, *J. Org. Chem.*, **44**, 2608 (1979).

(26) P. D. Bartlett and E. N. Trachtenberg, *J. Am. Chem. Soc.*, **80**, 5808 (1958).

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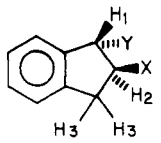
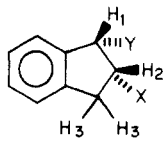
(29) V. L. Heasley and S. K. Taylor, *J. Org. Chem.*, **34**, 2779 (1969).

(30) Oxygen is effective in inhibiting radical reactions of chlorine with alkenes.[28] In previous studies we found that dilution alone was sufficient to prevent radical reactions of bromine with reactive alkenes.[29] We also used a radical scavenger, ethylbenzene,[29] to show that bromination of indene under the conditions described for Table I did not contain a radical component. Bromination of indene (mole fraction of 0.02) in $CCl_4$ in the presence of a tenfold excess of ethylbenzene gave no α-bromoethylbenzene whereas bromination at high indene concentration under sunlamp irradiation (indene and ethylbenzene in equimolar amounts with no solvent) gave α-bromoethylbenzene in significant amounts.

Table V. Data for Analysis of Products




| substituents | compd | NMR[a] ($H_1$[b]) | VPC[c] | compd | NMR[a] ($H_1$[b]) | VPC[c] |
|---|---|---|---|---|---|---|
| X = Br, Y = Br | 2 | 5.52 (5.38) | 15.6 | 3 | 5.30 (4.93) | 24 |
| X = Br, Y = Cl | 4 | 5.33 (5.23) | 10.0 | 5 | 5.12 (4.75) | 15.6 |
| X = Br, Y = OAc | 6 | 6.23 | | 7 | 5.88 | |
| X = Cl, Y = OAc | 8 | 6.17 | | 9 | 6.00 | |
| X = Cl, Y = Cl | 10 | 5.23 (5.07) | 6.6 | 11 | 5.18 (4.80) | 10.0 |
| X = Br, Y = $OCH_3$ | 12 | 4.85 | 11.7 | 13 | | 14.9 |
| X = Cl, Y = $OCH_3$ | 14 | 4.77 | 7.3 | 15 | 4.58 | 9.6 |
| X = $OCH_3$, Y = Cl | 16 | 5.08 | 8.2 | 17 | 5.25 | 10.2 |
| X = $OCH_3$, Y = Br | 18 | 5.27 (5.18) | 12.5 | 19 | 5.30 (5.08) | 16.7 |

[a] In parts per million downfield from $Me_4Si$ in $CCl_4$ ($\delta$ values in parentheses were obtained in benzene). Spectra obtained with a Varian T60A spectrometer. [b] Additional NMR data (see also ref 8): **4**, $J_{1,2}$ = 2.3 Hz; **5**, $J_{1,2}$ = 4.9 Hz; **6**, $J_{2,3}$ = 3.6 Hz; **7**, $J_{1,2}$ = 5.6 Hz; **12**, $\delta$ 4.58 (d, 1, $H_1$, $J_{1,2}$ = 3.6 Hz), 4.53 (ddd, 1, $H_2$, $J_{1,2}$ = 3.6, $J_{2,3}$ = 5.2, $J_{2,3'}$ = 6.0 Hz), 3.05 (dd, 1, $H_3$, $J_{2,3}$ = 5.2, $J_{3,3'}$ = 17 Hz), 3.58 (dd, 1, $H_{3'}$, $J_{2,3'}$ = 6.0, $J_{3,3'}$ = 17 Hz), 3.48 (s, 3, $CH_3O$), 6.97-7.48 (m, 4, Ar H); **15**, $\delta$ 4.43-4.73 (m, 2, $H_1$, $H_2$), 3.07-3.35 (m, 2, $H_3$, $H_4$), 3.45 (s, 3, $CH_3O$), 7.05-7.40 (m, 4, Ar H); **16**, $\delta$ 5.08 (d, 1, $H_1$, $J_{1,2}$ = 3.6 Hz), 4.18 (ddd, 1, $H_2$, $J_{1,2}$ = 3.6, $J_{2,3}$ = 5.0, $J_{2,3'}$ = 6.5 Hz), 3.32 (dd, 1, $H_{3'}$, $J_{2,3'}$ = 6.5, $J_{3,3'}$ = 16 Hz), 2.78 (dd, 1, $H_3$, $J_{2,3}$ = 5.0, $J_{3,3'}$ = 16 Hz), 3.47 (s, 3, $CH_3O$), 7.07-7.42 (m, 4, Ar H); **17**, $\delta$ 5.25 (d, 1, $H_1$, $J_{1,2}$ = 5.0 Hz), 4.05 (dt, 1, $H_2$, $J_{1,2}$ = 5.0, $J_{2,3}$ = 7.5 Hz), 3.03 (d, 2, $H_3$, $J_{2,3}$ = 7.5 Hz), 3.47 (s, 3, $CH_3O$), 7.08-7.48 (m, 4, Ar H); **18**, $\delta$ 5.27 (d, 1, $H_1$, $J_{1,2}$ = 2.5 Hz), 4.33 (ddd, 1, $H_2$, $J_{1,2}$ = 2.5 Hz, $J_{2,3}$ = 3.8 Hz, $J_{2,3'}$ = 6.0 Hz), 3.35 (dd, 1, $H_{3'}$, $J_{2,3'}$ = 6.0, $J_{3,3'}$ = 15.5 Hz), 2.83 (dd, 1, $H_3$, $J_{2,3}$ = 3.8, $J_{3,3'}$ = 15.5 Hz), 3.45 (s, 3, $CH_3O$), 7.07-7.42 (m, 4, Ar H); **19**, $J_{1,2}$ = 4.2 Hz, 3.45 [$CH_3O(CCl_4)$], 3.15 [$CH_3O$ (benzene)]. [c] VPC retention times in minutes. Conditions are as follows: 6 ft × 6 mm (o.d.) glass column, 2.5% SE-30 on Chromosorb W-AW-DMCS, 100 °C.

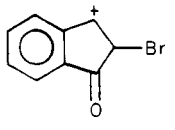
**Analysis and Product Identification.** The NMR measurement of the $H_1$ absorption was used to analyze mixtures of the dibromides, the dichlorides, the bromo chlorides, the halo esters (**6–9**), the methoxy chlorides (**14** and **15**), and the methoxy bromides (**18** and **19**). The use of benzene as solvent greatly improved the separation of the $H_1$ absorptions for mixtures of the dibromides, dichlorides, and bromochlorides. Mixtures of **16** and **17** were analyzed by VPC, and mixtures of dichlorides with methoxy chlorides were analyzed by a combination of NMR and VPC. Mixtures of dichlorides and dibromides were also separated by VPC and gave results in good agreement with those obtained by NMR. The NMR and VPC data used for analysis are summarized in Table V.

Compounds for which NMR data has been previously reported[8] are **2**, **3**, **8–11**, and **14**. Structures for **12** and **15–18** were assigned on the basis of NMR spectra obtained from pure samples isolated by preparative VPC (10 ft × 9 mm glass column, 5% Silicone DC-550 on Chromosorb W-AW, 100 °C). The *cis*-methoxy bromide **19** decomposed when preparative VPC collection was attempted. The presence of **19** in the mixture with **18** was confirmed by an NMR analysis in benzene where absorptions for the $C_1$ proton and the methoxyl protons were distinct from those of **18**. The bromo chlorides **4** and **5** and the bromo acetates **6** and **7** were identified in mixtures on the basis of characteristic NMR absorptions which could be assigned to the $H_1$ protons in those compounds (the dibromides, dichlorides, and chloro acetates serve as excellent model compounds for prediction of the expected absorptions). The *cis*-methoxy bromide **13** was formed in such small amounts that we did not attempt to collect it by preparative VPC, nor were we able to identify it by its NMR absorptions (in mixture with large amounts of **12**). We observed a peak in the VPC analysis of the products from the reaction of **1** with bromine and with methyl hypobromite in methanol which we assigned to **13**.

**Reactions of Indenone (20).** Indenone was prepared by the method described by Hansen and Undheim[32] except that $CCl_4$ was used as the solvent instead of ether. The crude indenone crystals were dissolved in $CCl_4$ and the concentration of **20** was found by NMR with *p*-methylanisole as an internal standard. Solutions of the halogens in $CCl_4$ were added to stirred $CCl_4$ solutions of **20** (ca. a mole fraction of 0.02) at 25 °C in sufficient amount to consume 40% of **20**. The products were analyzed directly by NMR after removal of the solvent under vacuum.

The product from bromination showed evidence of a single dibromide with NMR absorptions ($CCl_4$) at $\delta$ 4.17 (d, $H_2$, $J_{2,3}$ = 2.2 Hz) and 5.55 (d, $H_3$, $J_{2,3}$ = 2.2 Hz), in good agreement with the values reported for *trans*-2,3-dibromoindanone.[33]

The product from reaction of **20** with bromine chloride showed evidence of only a single product which was assigned the structure *trans*-2-bromo-3-chloroindanone. NMR absorptions were observed at $\delta$ 4.60 (d, $H_2$, $J_{2,3}$ = 2.8 Hz) and 5.47 (d, $H_3$, $J_{2,3}$ = 2.8 Hz). Evidence that the compound is 2-bromo-3-chloroindanone (Markovnikov adduct) rather than 3-bromo-2-chloroindanone (anti-Markovnikov adduct) is the following. (1) Treatment of the product with silver nitrate yielded a precipitate, readily soluble in ammonia, showing that labile chlorine rather than labile bromine was attached to the benzylic carbon atom. (2) Mass spectrometry of the bromine chloride adduct showed, among other ions, an isotope cluster with *m/e* 208 and 210, assigned structure **21**. This same isotope cluster was observed in the mass spectrum




**21**

of the dibromide above. The bromo chloride compound did not exhibit the isotope cluster of *m/e* 165 and 167 (obtained from the dichloride below) which would have been expected if chlorine were in the benzylic (3-carbon) position.

The product from chlorination of **20** showed evidence of two dichlorides in its NMR. The minor product was assigned the cis structure on the basis of the larger coupling constant which it exhibited (in line with this established difference between cis- and trans-disubstituted indanes, compounds in this paper and ref 8). NMR data follows: *trans*-2,3-dichloroindanone, $\delta$ 4.50 (d, $H_2$, $J_{2,3}$ = 3.6 Hz), 5.32 (d, $H_3$, $J_{2,3}$ = 3.6 Hz); *cis*-2,3-dichloroindanone, 4.75 (d, $H_2$, $J_{2,3}$ = 6.0 Hz), 5.62 (d, $H_3$, $J_{2,3}$ = 6.0 Hz).

(31) The thermal equilibration of the cis and trans dibromides of indene is slow. Two samples (A, ≥99% *trans* dibromide, and B, 70% trans, 30% cis) had not fully equilibrated after being heated at 70 °C in $CCl_4$ for over 1 month (sample A then contained 7% *cis*-dibromide and sample B 15% *cis*-dibromide).

(32) P. E. Hansen and K. Undheim, *J. Chem. Soc., Perkin Trans. 1*, 305 (1975).

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**Registry No.** 1, 95-13-6; 2, 19598-15-3; 3, 19598-04-0; 4, 20245-19-6; 5, 74947-77-6; 6, 5837-70-7; 7, 74984-78-4; 8, 19598-12-0; 9, 19598-02-8; 10, 19598-14-2; 11, 19598-03-9; 12, 5927-94-6; 13, 74947-78-7; 14, 19598-11-9; 15, 74947-79-8; 16, 74947-80-1; 17, 74947-81-2; 18, 74947-82-3; 19, 74947-83-4; 20, 480-90-0; acetyl hypobromite, 4254-22-2; acetyl hypochlorite, 758-11-2; methyl hypochlorite, 593-78-2; methyl hypobromite, 28078-73-1; trichloramine, 10025-85-1; iodobenzene dichloride, 932-72-9; bromine chloride, 13863-41-7; chlorine, 7782-50-5; bromine, 7726-95-6; *trans*-2,3-dibromoindanone, 40774-43-4; *trans*-2-bromo-3-chloroindanone, 74947-84-5; *trans*-2,3-dichloroindanone, 74947-85-6; *cis*-2,3-dichloroindanone, 74947-86-7.

# Desulfurization of Organic Trisulfides by Tris(dialkylamino)phosphines. Mechanistic Aspects[1]

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Tris(dialkylamino)phosphines effect a rapid desulfurization of trisulfides to disulfides under mild conditions. The reaction mechanism involves a bimolecular process, proceeding by the rate-determining formation of a phosphonium salt intermediate. The central sulfur atom of a diaryl trisulfide is removed in the process, while a dialkyl trisulfide loses a terminal sulfur atom to the aminophosphine.

A wide variety of organosulfur compounds have been desulfurized by trivalent phosphorus compounds[2] as represented by the general expression given in eq 1. There

$$RSX + R'_3P \rightarrow RX + R'_3P{=}S \qquad (1)$$

X = SR, $SS_xR$, SH, S(O)R, $SO_2R$, $SSO_2R$, S(C=O)OR, S(C=O)R, S(C=S)R, $N[(C{=}O)R]_2$, OR, $CH_2(C{=}O)R$, CN, Cl

R′ = RO, $R_2N$, R

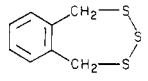
are several reports in the literature of the selective desulfurization of trisulfides (1) to disulfides by the action

$$R{-}S{-}\underset{1}{S}{-}S{-}R$$

of triphenylphosphine.[3e,i,4] The first studies to determine which sulfur atom (central or terminal) in a trisulfide is removed by a tertiary phosphine were performed by Safe and Taylor.[4e,f] Two epitrithiodioxopiperazines, thiodehydrogliotoxin and sporidesmin E, were shown to lose their central sulfur atoms (radiochemically labeled with

Table I. Desulfurization of Trisulfides by Tris(dialkylamino)phosphines

$$RSSSR' + R''_3P \longrightarrow RSSR' + R''_3P{=}S$$

| trisulfide R and R′ | R″ | % yield RSSR′ [a] |
|---|---|---|
| 4-$CH_3C_6H_4$ | $Et_2N$ | 88 |
| 4-$CH_3OC_6H_4$ | $Et_2N$ | 62 |
| $C_6H_5$ | $Et_2N$ | 92 |
| $C_6H_5CH_2$ | $Et_2N$ | 94 |
| | $Me_2N$ | 100[b,c] |
| | morpholino | 100[b,d] |
| $C_6H_5CHCH_3$ | $Me_2N$ | 100[c,e] |
| | morpholino | 75[f] |
|  | $Me_2N$ | 77 |
| R = $C_6H_5CH_2$, R′ = $(CH_3)_2CH$ | $Et_2N$ | 96 |
| R = $C_6H_5CH_2$, R′ = $CH_3(CH_2)_2$ | $Et_2N$ | 100[b] |
| $CH_3(CH_2)_2$ | $Et_2N$ | 80 |
| | $Me_2N$ | 100[b] |
| | morpholino | 100[b,g] |
| $CH_3(CH_2)_4$ | $Et_2N$ | 71 |
| $CH_3OC(O)CH_2$ | $Et_2N$ | 91 |
| $CH_3(CH_2)_5CHCH_3$ | $Me_2N$ | 60[h] |
| $(CH_3)_3C$ | $Me_2N$ | 0[i] |

[a] Yield as isolated by silica gel column chromatography unless otherwise noted. Reaction conditions were 2-3 h at room temperature in anhydrous diethyl ether or benzene with a 0-10% excess of $R''_3P$, unless otherwise noted. [b] Quantitative by GC analysis. [c] Quantitative by NMR analysis. [d] Reaction solvent was 2:1 $Et_2O$-$CH_3CN$ or $CH_3CN$. [e] Reaction conditions were ca. 2 days at room temperature in acetonitrile-$d_3$ to 9 days at room temperature in cyclohexane-$d_{12}$. [f] Percentage conversion by NMR after 10 days at 65 °C in $CD_3CN$. [g] Reaction conditions were 3 h at reflux in acetonitrile. [h] Percentage conversion by GC and NMR after 7 days at room temperature in benzene. [i] No reaction detected by GC, even after 40 min of reflux in acetonitrile with a five-fold excess of $(Me_2N)_3P$.

(1) Organic Sulfur Chemistry. Part 38. For Part 37, see D. N. Harpp and A. Granata, *J. Org. Chem.*, 45, 271 (1980).

(2) The following is not an exhaustive review of desulfurization reactions but provides leading references for most types of ionic desulfurization reactions: X = SR,[3a-d] $SS_xR$,[3d-f] SH,[3c,g] S(O)R,[3d,h] $SO_2R$,[3d,i] $SSO_2R$,[3j] S(C=O)OR,[1] S(C=O)R,[3k] S(C=S)R,[3l] $N[(C{=}O)R]_2$,[3d,m] OR,[3n] $CH_2(C{=}O)R$,[3o] CN,[3o] Cl.[3p] See also: R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry", Academic Press, New York, 1965, p 172; A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus", Elsevier, New York, 1967, p 95; J. I. G. Cadogan and R. K. Mackie, *Chem. Soc. Rev.*, 3, 87 (1974).

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