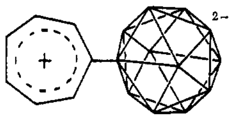
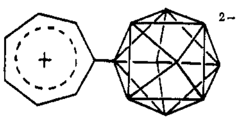


I ($C_7H_6B_{12}H_{11}^-$)



II ($C_7H_6B_{10}H_9^-$)

Slow addition of excess tropenium bromide[4] to an aqueous solution of hydronium dodecahydroclovododecaborate[5] produces a pale yellow solution containing an 86% yield of the hydronium salt of I;[6] concentration of this solution followed by addition of cesium bromide affords a precipitate of 88% cesium tropenylium undecahydroclovododecaborate as yellow needles, no melting point or decomposition below 300°, ultraviolet spectrum (water): $\lambda_{\max}$ 215 mμ (ϵ 33,800), 261.5 (13,000), and 349 (10,300). The salt can be recrystallized from acetonitrile by slow addition of methylene chloride.

Anal. Calcd for $C_7H_{17}B_{12}Cs$: C, 23.10; H, 4.71; B, 35.66. Found:[7] C, 23.23; H, 4.66; B, 35.68.

In our initial paper[1] we tentatively assigned the structure shown for II on the basis of infrared, visible, and ultraviolet spectra; this assignment is now supported by nmr spectra. The ^{11}B nmr spectrum[8] of $B_{10}H_{10}^{2-}$ shows two symmetrical doublets, area ratio 4:1, for the equatorial and apical borons, respectively. The ^{11}B nmr spectrum of II[9] shows a symmetrical doublet for the apical borons and a complex multiplet for the equatorial borons; the equatorial:apical ratio is 4.01:1.00. Thus the boron cage bears a substituent in an equatorial position. The ^1H nmr spectrum of tropenium ion shows a single spike for the seven equivalent protons; the six ring protons of II are divided into a doublet (2 H) and a septuplet (4 H) in a manner characteristic of monosubstituted tropenium ions.[10] The existence of a carbon–boron bond on an equatorial position on the boron cage is consistent with this data.

Examination of a variety of physical properties shows significant electronic interaction between the boron cage and the carbocyclic ring in these ions; this interaction is more extensive in II than in I. Among these properties are: (1) ^{11}B Nmr. In $B_{10}H_{10}^{2-}$ the apical borons appear at 1.4 ppm[11] and the equatorial borons at 28.5 ppm; in II the apical borons are at −13.5 ppm and the equatorial boron multiplet is centered at 18 ppm with the furthest downfield peak at 5 ppm. This strong downfield shift of all boron resonances indicates extensive ground-state deshielding of the cage by electron donation to the ring, with the greatest effect felt by the boron to which the ring is attached. The $B_{12}H_{12}^{2-}$ ion[12] shows a symmetrical doublet at 16.9 ppm, while ion I shows an unsymmetrical doublet at 13.7. Deshielding of the cage by electron donation is significantly less in I than in II. (2) ^1H Nmr. Tropenium ion, $C_7H_7^+$, shows a spike at 0.60 ppm,[13] while the ring protons of II give a doublet at 2.0 ppm (2 H) and a multiplet at 2.71 ppm (4 H). The ring in II thus shows considerable shielding, presumably by electron enrichment from the cage. Ion I shows a similar but smaller shift, with a multiplet at 1.27 ppm (4 H) and a doublet at 1.37 ppm (2 H). (3) $E_{1/2}$. Tropenium ion is reduced at the dropping mercury electrode in an irreversible, one-electron process at −0.3 v,[14,15] and $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ anions are inert to polarographic reduction.[12] We find that ion II is reduced at the dme in 1 *N* KCl in a one-electron, irreversible process at −0.74 v; ion I is reduced in a similar process at −0.69 v. Although we do not know where the electron enters these ions, it is clear that either the ring is more difficult to reduce than tropenium, or the cage is easier to reduce than the free borane anions; either case argues for electron donation from cage to ring. (4) Electronic Spectra. Both ions I and II have spectra whose shape and relative ϵ values[1] are characteristic of substituted tropenium ions.[4] *Z*-Value plots[16] for water–acetone or water–ethanol mixtures give positive slopes for the hypsochromic shift[1] of the long-wavelength band with increasing solvent polarity, indicating internal reduction of dipole in the excitation. (5) Infrared Spectra. It is not possible to discuss the infrared spectra in detail in this space; we wish to note, however, that the B–H stretching frequencies of II are in accord with equatorial substitution, and, while the aromatic C–C region of II strongly resembles that of tropone, this region in I more nearly resembles that of chlorotropenium ion, a species with less substituent–ring interaction.[17]

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[4] H. J. Dauben, Jr., *et al.*, *J. Am. Chem. Soc.*, **79**, 4557 (1957).

[5] Prepared from a sample of the triethylammonium salt generously furnished by J. L. Boone.

[6] At least 1 mole of cycloheptatriene per mole of I can be recovered from the reaction, in accord with our proposed route for the formation of such compounds.[1]

[7] Analysis by Schwarzkopf Microanalytical Laboratory.

[8] W. N. Lipscomb, M. F. Hawthorne, and A. R. Pitochelli, *J. Am. Chem. Soc.*, **81**, 5833 (1959).

[9] We are indebted to R. E. Williams for the ^{11}B nmr spectra of these ions.

[10] H. J. Dauben, Jr., and K. M. Harmon (unpublished work) have determined the ^1H nmr spectra of a number of substituted tropenium ions.

[11] All ^{11}B chemical shifts are in part per million relative to boron trifluoride etherate = 0. Spectra are in acetonitrile.

[12] E. L. Muetterties, *et al.*, *Inorg. Chem.*, **3**, 444 (1964).

[13] All ^1H chemical shifts are in parts per million relative to tetramethylsilane = 10 (τ). Spectra are in acetonitrile.

[14] P. Zuman, J. Chodkowski, and F. Santavy, *Collection Czech. Chem. Commun.*, **26**, 380 (1961).

[15] Half-wave potentials are relative to the saturated calomel electrode.

[16] E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1858).

[17] Full details will be presented in a paper now in preparation for this journal.

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Facile Reduction of Alkyl Halides with Chromium(II) Complexes. Alkylchromium Species as Intermediates

Sir:

Simple chromous salts are readily accessible and have proven to be versatile reducing agents for a variety of organic compounds, including organic halides.[1] Among halides, the application of this reagent has been limited to the rather reactive allylic and benzylic halides, as well as α-halo carbonyl and cyano compounds, etc.[2] The inertness of chromous ion toward most alkyl halides has restricted its synthetic utility.

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[1] (a) J. K. Kochi and D. D. Davis, *J. Am. Chem. Soc.*, **86**, 5264 (1964); (b) L. H. Slaugh and J. H. Raley, *Tetrahedron*, **20**, 1005 (1964).

[2] C. E. Castro and W. C. Kray, Jr., *J. Am. Chem. Soc.*, **85**, 2768 (1963).

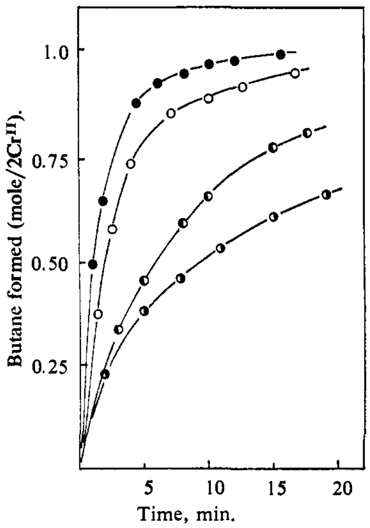

Figure 1. Reduction of *n*-butyl bromide with Cr^{II}(en) complex in DMF at 25°. Cr^{II}:en: ◑, 1.0; ●, 2.0; ○, 2.5; ◐, 3.0.

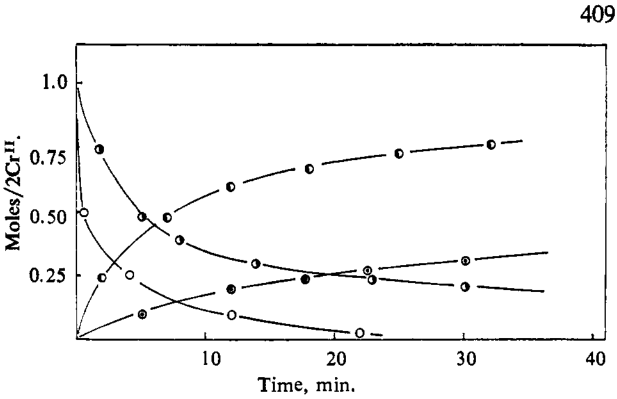

Figure 2. Reduction of alkyl halide by Cr^{II}(en) and concomitant formation of alkane: ○, *t*-butyl chloride; ◑, *sec*-butyl chloride; ⊙, isobutane (from *t*-butyl chloride); ◐, butane (from *sec*-butyl chloride).

We have found that complexing the Cr^{II} ion with ligands such as ethylenediamine (en) greatly enhances its ability to reduce even primary alkyl halides to alkanes. For example, *n*-butyl bromide is reduced by this reagent to *n*-butane according to eq 1 in 20–30

$$RBr + 2Cr^{II}(en) \xrightarrow{SH} RH + Cr^{III}(en) + Cr^{III}Br(en) \quad (1)$$

min at room temperature in aqueous dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) solutions.[3,4] The reduction is quantitative, and proceeds at optimum rate at various molar ratios of Cr^{II}:en as shown in Figure 1. The reaction proceeds equally well in a variety of other solvents such as ethanol, acetonitrile, tetrahydrofuran, ethylene glycol, glycol ethers, etc., in which the Cr^{II} complex has differing solubilities. In addition to en, other β-amines such as N,N,N′,N′-tetramethylethylenediamine, diethylenetriamine, and related oligopolyethylenimines have been successfully used.

The reactivity of alkyl halides toward $Cr(en)^{+2}$ decreases in the order: tertiary > secondary > primary and iodides > bromides > chlorides. Thus, *t*-butyl bromide reacts four times faster than *sec*-butyl or isopropyl bromide, which react five times faster than *n*-butyl, isobutyl, neopentyl, or *n*-propyl bromide. *n*-Butyl iodide is 20 times more reactive than *n*-butyl bromide. *n*-Butyl chloride, which is the least reactive of the halides, requires more than 12 hr at room temperature for complete reduction.

However, *n*-butyl chloride as well as other primary chlorides can be easily reduced with a *chromium(II)–ethanolamine* complex.[5] Thus, *n*-butyl chloride is reduced completely to *n*-butane by this reagent at room temperature within 2 hr. Other halides are reduced correspondingly rapidly. Di- and triethanolamine as well as N-alkyl- and N,N-dialkylethanolamines and trishydroxymethylaminomethane show similar behavior as ligands. The facility with which these chromous–β-hydroxyamine complexes reduce halides is not as sensitively attenuated by employing excess ligand, unlike the di- and polyamines cited earlier. Contrariwise, the rate of reduction increases monotonically with ethanolamine, and ratios of ligand:Cr^{II} as high as 30 have been employed. This reagent will reduce water;[6] the rate of hydrogen evolution similarly increases with ethanolamine concentration.

It is possible to detect *alkylchromium species* as transient intermediates in both of these reductions. Thus, the addition of *t*-butyl chloride, bromide, or iodide to the Cr^{II}(en) complex in DMF is accompanied by a rapid color change from blue to orange. A new species with a prominent band ($\epsilon \sim 3000$) at 3970 A can be detected in the visible spectrum; it decays to Cr^{III}(en) with the liberation of isobutane. A similar absorption band (3860 A) can be detected with the same series of *sec*-butyl halides. The corresponding band (3820 A)[7] from *n*-butyl iodide is never large, since the rate of formation of the alkylchromium complex is comparable to its hydrolysis.

The formation of an alkylchromium intermediate can be related to the kinetics of the disappearance of alkyl halide and appearance of alkane. As shown in Figure 2, *t*-butyl chloride is consumed by Cr^{II}(en) at a much faster rate than isobutane is formed. The discrepancy is less with *sec*-butyl chloride, and, in the case of *n*-butyl chloride, butane is formed at very nearly the same rate that *n*-butyl chloride is consumed. The discrepancy in rates of loss of alkyl halide and production of alkane is directly related to the rate of protonolysis of the alkylchromium intermediate. The highest instantaneous concentrations of these alkylchromium species are attainable with tertiary halides, since their hydrolytic stabilities decrease, in the order tertiary > secondary > primary.[8]

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[3] The nature of the Cr^{III} products has been inferred from earlier studies (*vide infra*).

[4] In water the formation constants of $Cr^{II}(en)_n^{+2}$ are: $\log K_1 = 5.15$, $\log K_2 = 4.04$ (R. L. Pecsok and J. Bjerrum, *Acta Chem. Scand.*, **11**, 1418 (1957)).

[5] The formation constants for chromium(II)–ethanolamine complexes are under investigation.

[6] In this respect the chromium(II)–ethanolamine complex resembles $Co^{II}(CN)_5^{-3}$ (N. K. King and M. E. Winfield, *J. Am. Chem. Soc.*, **80**, 2060 (1958)); J. Kwiatek, *et al.*, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963 p 210. See also K. D. Kopple, G. F. Svatos, and H. Taube, *Nature*, **189**, 393 (1961), for studies of Cr^{II} in aqueous alkaline solutions of polyamines.

[7] Alkylchromium–ethanolamine complexes absorb at lower energies (*t*-butyl, 4300 A; *sec*-butyl, 4140 A; *n*-butyl, 4100 A).

[8] For example, at 5×10^{-3} *M*, one-half the *t*-butylchromium–ethylenediamine species hydrolyzes in 12 min in aqueous DMSO at room temperature.

The formation of simple alkylchromium species is reminiscent of benzylchromium reported earlier[1a,9] and recently isolated as the pyridine complex.[10] The stabilities of these organochromium complexes are: benzyl > tertiary > secondary > primary. *t*-Butylchromium complex without its nitrogen-containing ligands can also be detected spectroscopically (4260 A) in the reaction between *t*-butyl iodide and chromous perchlorate in DMF. By analogy with benzylchromium, we postulate that these alkylchromium species are of the type $RCrL_n^{+2}$(L = en, ethanolamine, etc.).

Further studies on the use and identification of these chromium(II)-amine complexes as potent reducing agents, and characterization of the attendant chromium(III) species, are in progress.

[9] F. A. L. Anet and E. LeBlanc, *J. Am. Chem. Soc.*, 79, 2649 (1957); J. K. Kochi and D. B. Buchanan, *ibid.*, **87**, 853 (1965).

[10] R. P. A. Sneeden and H. P. Throndsen, *Chem. Commun.*, 509 (1965); *cf.* R. G. Coombes, *et al.*, *ibid.*, 251 (1965); *J. Chem. Soc.*, 7029 (1965).

[11] We wish to thank the National Science Foundation for generous support of this research.

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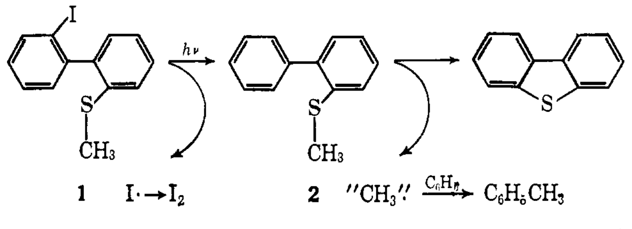
Radical Reactions of Organic Sulfides. II.[1] Behavior of the 2-(2′-Methylthio)biphenylyl Radical[2]

Sir:

The role of the sulfur atom in free-radical reactions of organic sulfides and disufides has been investigated previously because of the possible importance of octet expansion by sulfur. Various lines of evidence indicate that radicals are stabilized by an adjacent sulfur atom.[3] Bentrude and Martin[4] have presented striking kinetic evidence of anchimeric assistance by sulfides in homolytic perester decompositions. Radical displacements on the sulfur of disulfides have been recognized for some time[5] and have recently been studied in detail by Pryor and Guard.[6] We wish to report chemical evidence for the involvement of neighboring sulfur in the reactions of the 2-(2′-methylthio)biphenylyl radical (**2**). The general behavior of this radical constitutes the first example of a radical displacement[7] on the sulfur atom of a sulfide.

Photolysis of benzene solutions (10^{-3} to 10^{-2} *M*) of 2-iodo-2′-methylthiobiphenyl[8] (**1**) in a Vycor vessel with an external mercury resonance lamp[10] for 45–60 hr gives dibenzothiophene[11] in quantitative yields, toluene[11] (37–45%), and iodine (82%). Photolysis of **1** in a better hydrogen donor solvent, cyclohexane, is equally successful, giving dibenzothiophene in quantitative yield and iodine (65–70%). These observations are readily accommodated by a simple homolytic dissociation of the carbon–iodine bond of **1**, followed by rapid reaction of the carbon radical with the neighboring sulfide group.[12]



Several observations support the key role of the 2-(2′-methylthio)biphenylyl radical (**2**) in the ring closure to dibenzothiophene. Wolf and Kharasch[13] and others[14] have examined the photolyses of aryl iodides. These studies clearly indicate the formation of aryl radicals by dissociation of the carbon–iodine bond and therefore provide analogy for the production of radical **2**. More cogent is the fact that the 2-(2′-methylthio)biphenyl radical can be partially diverted by hydrogen transfer. Photolysis of **1** for 50 hr in *n*-butylthiol as solvent still gives dibenzothiophene as the major product (*ca.* 90%). Vapor phase chromatography of the reaction mixture, however, shows the product of hydrogen transfer to the radical, 2-thiomethylbiphenyl,[11] dibenzothiophene, and starting material in relative areas of 6:86:8.

Two further observations demonstrate that the formation of dibenzothiophene is a nonphotochemical, free-radical process. Reaction of **1** with 2 equiv of tri-*n*-butyltin hydride in refluxing toluene in the dark for 4.5 hr gives essentially quantitative conversion to dibenzothiophene. The rate of this reaction is markedly decreased by the presence of 7 mole % of a radical scavenger, trinitrobenzene. Since it is likely that the reaction of **1** with tri-*n*-butyltin hydride involves a radical chain mechanism,[15] radical **2** is implicated as a thermal precursor of dibenzothiophene. In addition 2-iodo-2′-methoxybiphenyl[16] was photolyzed in cyclohexane under conditions identical with those used for quantitative conversion of **1** to dibenzothiophene. Straightforward radical chemistry obtains, giving iodine (75%) and hydrogen transfer product, 2-methoxybiphenyl[11] (64%). The ratio of quantum yields for the initial production of iodine in cyclohexane from 2-iodo-2′-methoxybiphenyl and 2-iodo-2′-methylthiobiphenyl ($\phi_{I_2}{}^{OMe}/\phi_{I_2}{}^{SMe}$) is approximately 1.1. The similarity

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[1] Part I: J. A. Kampmeier, R. P. Geer, A. J. Meskin, and R. M. D'Silva, *J. Am. Chem. Soc.*, **88**, 1257 (1966).

[2] This work was supported by Public Health Service Research Grant CA-06535 from the National Cancer Institute.

[3] C. C. Price and J. Zomlefer, *J. Am. Chem. Soc.*, 72, 14 (1950); C. E. Scott and C. C. Price, *ibid.*, **81**, 2672 (1959); R. F. Bridger and G. A. Russell, *ibid.*, **85**, 3754 (1963); G. Sosnovsky, *J. Org. Chem.*, **26**, 281 (1961).

[4] W. G. Bentrude and J. C. Martin, *ibid.*, **84**, 1561 (1962).

[5] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 332.

[6] W. A. Pryor and H. Guard, *J. Am. Chem. Soc.*, **86**, 1150 (1964).

[7] Displacement is used in a stoichiometric sense, without mechanistic implication.

[8] Compound **1**, mp 88.5–89.0°, is obtained in 49–64% yield by the thermal decomposition of dibenziodolium *t*-butyl mercaptide[9] in refluxing benzene containing a 20-fold excess of dimethyl disulfide. The corresponding sulfone, mp 150.5–152°, was prepared by the oxidation of **1** with hydrogen peroxide. Satisfactory analytical and spectral data were obtained for both compounds.

[9] J. W. Greidanus, W. J. Rebel, and R. B. Sandin, *J. Am. Chem. Soc.*, **84**, 1504 (1962).

[10] Hanovia SC 2537, Hanovia Chemical and Manufacturing Co., Newark, N. J.

[11] Most analyses were made by vpc. Materials were identified by both isolation and coinjection with authentic samples.

[12] The detailed nature of the methyl fragment and the route to toluene are not established by these experiments.

[13] W. Wolf and N. Kharasch, *J. Org. Chem.*, 30, 2493 (1965).

[14] J. M. Blair, D. Bryce-Smith, and B. W. Pengilly, *J. Chem. Soc.*, 3174 (1959); J. M. Blair and D. Bryce-Smith, *ibid.*, 1788 (1960).

[15] L. W. Menapace and H. G. Kuivila, *J. Am. Chem. Soc.*, **86**, 3047 (1964); H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 47 (1964); D. H. Lorenz, P. Shapiro, A. Stern, and E. I. Becker, *J. Org. Chem.*, **28**, 2332 (1963).

[16] R. C. Fuson and R. L. Albright, *J. Am. Chem. Soc.*, **81**, 487 (1959).