

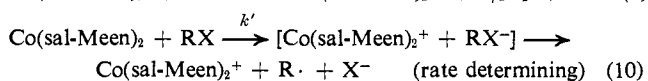
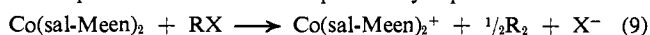
Table I. Kinetic Data in CH₂Cl₂ at 25°

| Cobalt(II) complexes ^a | RX | $kK (= 1/2 k_{exp}), M^{-2} sec^{-1}$ | K, M^{-1} | $k, M^{-1} sec^{-1}$ |
|-----------------------------------|--|---------------------------------------|---------------|--------------------------------|
| Co(salen)(MeIMD) | <i>p</i> -NO ₂ C ₆ H ₄ CH ₂ Cl | $(4.7 \pm 0.5) \times 10^{-1}$ | <0.1 | >4.7 |
| Co(salen)(MeIMD) | <i>p</i> -NO ₂ C ₆ H ₄ CH ₂ Br | 1.4 ± 0.1 | <0.1 | >14 |
| Co(Me ₃ salen)(MeIMD) | <i>p</i> -NO ₂ C ₆ H ₄ CH ₂ Br | 1.0 ± 0.2 | | |
| Co(saloph)(MeIMD) | <i>p</i> -NO ₂ C ₆ H ₄ CH ₂ Cl | $(1.8 \pm 0.3) \times 10^{-1}$ | <0.5 | >0.3 |
| Co(saloph)(IMD) | <i>p</i> -NO ₂ C ₆ H ₄ CH ₂ Cl | 2.7 ± 0.3 | 5.0 ± 0.5 | $(5.4 \pm 0.5) \times 10^{-1}$ |
| Co(saloph)(IMD) | <i>p</i> -NO ₂ C ₆ H ₄ CH ₂ Br | 4.3 ± 0.5 | 5.0 ± 0.5 | $(8.5 \pm 0.5) \times 10^{-1}$ |
| Co(saloph)(BzNH ₂) | <i>p</i> -NO ₂ C ₆ H ₄ CH ₂ Br | 4.0 ± 0.5 | <0.5 | >8 |
| Co(saloph-Cl)(IMD) | <i>p</i> -NO ₂ C ₆ H ₄ CH ₂ Cl | ~1 | ~1 | 1.0 ± 0.2 |
| Co(saloph)(IMD) | <i>o</i> -NO ₂ C ₆ H ₄ CH ₂ Cl | 1.5 ± 0.2 | 5.0 ± 0.5 | $(3.1 \pm 0.3) \times 10^{-1}$ |

^a In addition to those defined in the text, the following abbreviations are used in this table: Me₃salen = *N,N'*-bis(7-methylsalicylidene)-ethylenediamino, saloph = *N,N'*-bis(salicylidene)-*o*-phenylenediamino, saloph-Cl = *N,N'*-bis(salicylidene)-4-chloro-*o*-phenylenediamino, BzNH₂ = benzylamine.

and bromide, $k_{RBr}/k_{RCl} \sim 2$. This is in marked contrast to the reactivity patterns exhibited by those reactions which proceed by the halogen-abstraction mechanism (eq 1-3) for which, typically, $k_{RI}/k_{RBr} \sim k_{RBr}/k_{RCl} \sim 10^3$.^{1,3,10} The latter trend reflects the well-known inverse dependence of reactivity on the carbon-halogen bond dissociation energy, and it is not surprising that this dependence should be much smaller for electron transfer than for atom abstraction. Attention is directed to the parallels between the two alternative mechanisms of reduction of organic halides by five-coordinate cobalt(II) complexes, revealed through these studies, and corresponding alternative mechanisms that have been observed in two other systems, namely (i) the reactions of pyridinyl radicals with halocarbons¹¹ and (ii) the reductions of Co^{III}(NH₃)₅X complexes (X = F, etc.) by Co(CN)₅³⁻, which may occur either through inner-sphere electron transfer (corresponding to X atom abstraction by Co(CN)₅³⁻) or through outer-sphere electron transfer from Co(CN)₆⁴⁻.¹²

In contrast to the five-coordinate complexes discussed above, six-coordinate cobalt(II) complexes are expected to reduce organic halides only through electron transfer and to exhibit modified stoichiometry, since radical capture by cobalt according to eq 2 or 8 is precluded. These expectations were realized for the high-spin octahedral cobalt(II) complex, bis(*N*-methyl-*N'*-(salicylidene)ethylenediamino)cobalt(II),¹³ (Co(sal-Meen)₂, $\mu = 4.6$ BM at 22°), which was found to react with a variety of nitrobenzyl halides to form the corresponding bibenzyls (R₂) according to the stoichiometry described by eq 9¹⁴ and according to the second-order rate law $-d[\text{Co(sal-Meen)}_2]/dt = k'[\text{Co(sal-Meen)}_2][\text{RX}]$. These results are consistent with the expected mechanism depicted by eq 10 and 11.



(10) This was found to be the case also for those reactions of cobalt(II) Schiff's base complexes with organic halides which proceed through halogen-abstraction mechanisms.⁷

(11) E. M. Kosower and M. Mohammad, *J. Amer. Chem. Soc.*, **90**, 3271 (1968).

(12) J. P. Candlin, J. Halpern, and S. Nakamura, *ibid.*, **85**, 2517 (1963); J. Halpern and S. Nakamura, *Proc. Int. Conf. Coord. Chem.*, *8th*, 1964, 271 (1965); *J. Amer. Chem. Soc.*, **87**, 3002 (1965).

(13) L. Sacconi, M. Ciampolini, and G. P. Speroni, *Inorg. Chem.*, **4**, 1116 (1965).

(14) The stoichiometry was confirmed by isolation and characterization of the products of reaction with *p*-nitrobenzyl bromide and by matching of the spectra of the final reaction solutions with the known spectra of the products.

Table II. Rate Constants for the Reactions of Co(sal-Meen)₂ in CH₂Cl₂ at 25°

| Organic halide | $k', M^{-1} sec^{-1}$ |
|--|---|
| <i>p</i> -NO ₂ C ₆ H ₄ CH ₂ I | $(7.9 \pm 0.4) \times 10^2$ |
| <i>p</i> -NO ₂ C ₆ H ₄ CH ₂ Br | $(6.8 \pm 1.0) \times 10^2$ |
| <i>p</i> -NO ₂ C ₆ H ₄ CH ₂ Cl | $(1.2 \pm 0.1) \times 10^2$ |
| <i>o</i> -NO ₂ C ₆ H ₄ CH ₂ I | $(9.0 \pm 0.6) \times 10^2$ |
| <i>o</i> -NO ₂ C ₆ H ₄ CH ₂ Cl | $(2.2 \pm 0.3) \times 10^2$ |
| <i>m</i> -NO ₂ C ₆ H ₄ CH ₂ I | $(9.2 \pm 0.7) \times 10^{-1}$ |
| <i>m</i> -NO ₂ C ₆ H ₄ CH ₂ Br | $(9.5 \pm 1.0) \times 10^{-2}$ ^a |

^a $2.8 \pm 0.3 M^{-1} sec^{-1}$ in CH₃CN.

The rate constants listed in Table II reveal large decreases in reactivity in going from the *o*- or *p*- to the *m*-nitrobenzyl halides (consistent with the more negative reduction potentials of the latter),⁶ but again only a relatively small dependence on halogen variation. The 30-fold increase in the rate of reaction of *m*-NO₂-C₆H₄CH₂Br in going from CH₂Cl₂ to CH₃CN (*i.e.*, with increasing solvent polarity) is consistent with the proposed electron-transfer mechanism.¹¹

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Nucleophilic Methylene Transfer Reagents. Anions of *N-p*-Toluenesulfonyl Sulfoximines¹

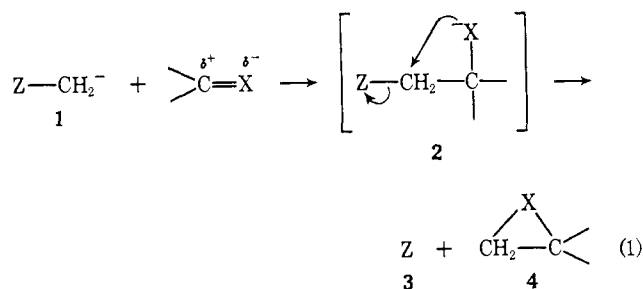
Sir:

A generalized scheme for nucleophilic methylene transfer reactions to electrophilic double bonds is illustrated in eq 1. The success of reagent **1** is dependent on the ability of group Z to stabilize the adjacent carbanion and to function as a leaving group. In typical cases of such reactions both the reagent **1** and leaving group **3** are neutral molecules; examples are sulfonium ylides² and diazoalkanes.³ In this

(1) Part XXVIII in the series "Chemistry of Sulfoxides and Related Compounds." We gratefully acknowledge support by the National Science Foundation (Grant No. GP 8648).

(2) For examples see E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **89**, 1353 (1967); E. J. Corey and M. Jautelat, *ibid.*, **89**, 3912 (1967); C. R. Johnson, E. R. Janiga, and M. Haake, *ibid.*, **90**, 3890 (1968).

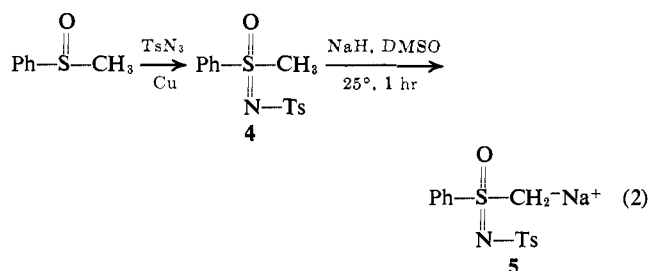
(3) C. D. Gutsche, *Org. React.*, **8**, 364 (1954).



communication we describe a new series of carbanionic reagents—metal salts of *N-p*-toluenesulfonyl sulfoximines—which are exceptionally effective in the transformations of the type described in eq 1.

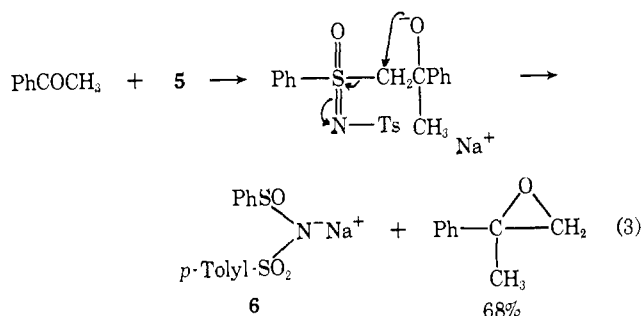
N-Tosylsulfoximines are available from a variety of routes including the reaction of sulfoxides with *p*-toluenesulfonyl azides⁴ or chloramine-T,⁵ the oxidation of *N-p*-toluenesulfonylsulfilimines,⁶ and the reaction of *p*-toluenesulfonyl chloride with free sulfoximines.⁷ These routes allow extensive structural variation to be achieved. Furthermore, the *N*-tosylsulfoximines typically are crystalline materials with unlimited shelf life.

The preparation of the exemplary methylphenyl-*N-p*-toluenesulfonylsulfoximine (4) and the generation of its anion (5) is illustrated in eq 2. Such anions are



generally stable at room temperature. Thus 4 was quantitatively recovered by acidification of a dimethyl sulfoxide (DMSO) solution of 5 after standing for 24 hr at 27°; after 24 hr at 70° only 45% of 4 was recovered.

The reaction of 5 with acetophenone is shown in eq 3. The highly stabilized anion 6 is extruded in the



ring-closing step. Products were usually obtained by quenching with water and extraction with an appropriate solvent. The sodium salt of *N*-benzenesulfonyl-*p*-toluenesulfonamide (6) and related salts (see below) remain in the aqueous layer. Acidification of the aqueous phase and extraction provided the relatively

(4) H. Kwart and A. A. Kahn, *J. Amer. Chem. Soc.*, **89**, 1950 (1967).

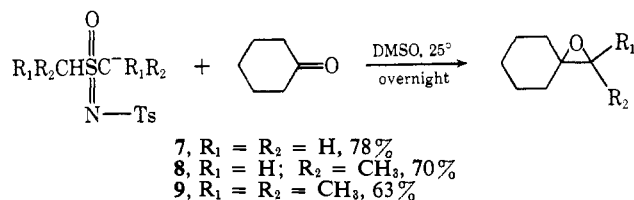
(5) D. Carr, T. P. Seden, and R. W. Turnec, *Tetrahedron Lett.*, 477 (1969).

(6) D. R. Rayner, D. M. von Schniltz, J. Day, and D. J. Cram, *J. Amer. Chem. Soc.*, **90**, 2721 (1968).

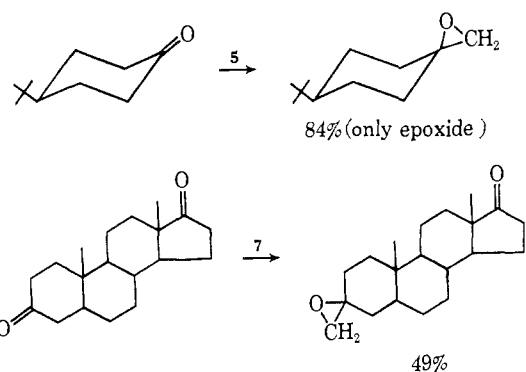
(7) H. R. Bentley and J. K. Whitehead, *J. Chem. Soc.*, 2081 (1950); C. R. Johnson and J. J. Rigau, *J. Org. Chem.*, **33**, 4340 (1968).

unstable *N*-benzenesulfonyl-*p*-toluenesulfonamide; ν 3400 (NH), 1360 and 1160 (SO₂), and 1095 cm⁻¹ (SO).

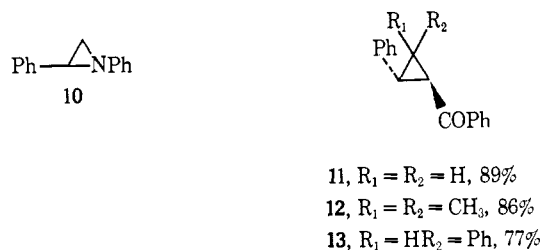
For simplicity of preparation and manipulation these reagents appear to be distinctly superior to any previously described for the preparation of substituted oxiranes from ketones. The anions derived from dimethyl *N-p*-toluenesulfonylsulfoximine,⁸ diethyl *N-p*-toluenesulfonylsulfoximine, and diisopropyl-*N-p*-toluenesulfonylsulfoximine reacted with cyclohexanone as follows. Selective and stereoselective syntheses of



oxiranes can be achieved with these reagents, e.g.



These nucleophilic methylene transfer reactions are not restricted to aldehydes and ketones. Reaction of 5 or 7 with benzalaniline gave aziridine 10 in 86% yield.



These reagents are also useful for the preparation of substituted cyclopropanes from electrophilic olefins. From the appropriate reagents and benzalacetophenone, cyclopropanes 11, 12, and 13 were prepared.

As in the case of oxosulfonium ylides derived from salts of sulfoximines,⁹ optically active oxiranes and cyclopropanes might also be accessible with optically active reagents in this series. We are continuing our investigation of reactions of these reagents with electrophilic double bonds, as well as with acylating and alkylating substrates.

(8) Available from Columbia Organic Chemicals Co., Inc., Columbia, S. C.

(9) C. R. Johnson and C. W. Schroeck, *J. Amer. Chem. Soc.*, **90**, 6852 (1968).

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