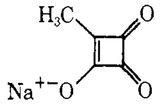
fragment ions, loss of CO, C_2H_3O, C_2O_2, and C_3O_2, similar to that observed for other oxocarbons.[5]

Anal. Calcd for $C_6H_6O_3$: C, 57.14; H, 4.80; mol wt, 126. Found: C, 57.11; H, 4.71; mol wt, 129 ($CHCl_3$); *m*/*e*, 126.

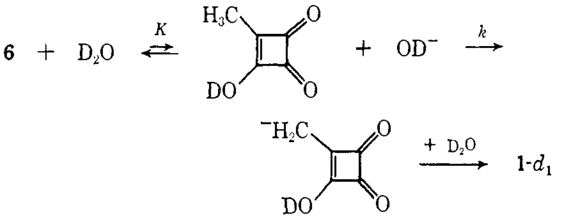
The p*K* of **1** was found to be 0.69 ± 0.03 by measurement of the pH of 0.147, 0.207, and 0.433 *M* aqueous solutions. In comparison, phenylhydroxycyclobutenedione (p*K* = 0.37) is about twice as strong an acid as **1**. This result is consistent with the relative stabilizing effects of the two groups.

Neutralization of **1** afforded the crystalline salt **6**



6

(>90%); mp ≥270°; ν_{max} (Nujol) 1790, 1700, 1580, and 1065 cm^{-1}; nmr (D_2O, $(CH_2OH)_2$) τ 7.97 (s). When dissolved in a solution of deuterium oxide–sodium deuterioxide, **6** rapidly underwent H/D exchange as evidenced by a decrease in the methyl resonance at τ 7.97. The pseudo-first-order rate constant for exchange divided by the deuterioxide ion concentration is approximately 3×10^{-3} M^{-1} sec^{-1} (31°).[6] A mechanism involving a hydrolysis step prior to exchange requires exchange to proceed independent of added deuterioxide concentration (eq 1). In contrast



(1)

$$\text{rate}_{(\text{H/D ex})} = kK[\mathbf{6}]$$
$$= k_{\text{obsd}}[\mathbf{6}]$$
$$K = K_w/K_a$$

the mechanism shown in eq 2 demands the presence of

$$\mathbf{6} + OD^- \xrightarrow{k} \mathbf{3} + D_2O \longrightarrow \mathbf{6}\text{-}d_1 + OD^- \qquad (2)$$

$$\text{rate}_{(\text{H/D ex})} = k[\mathbf{6}][OD^-]$$
$$= k_{\text{obsd}}[\mathbf{6}]$$

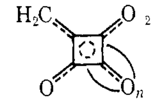
added base. The kinetic data shown in Table I allow a distinction between these two possibilities. These data demonstrate the requirement of added base for exchange and an independence of the calculated second-order rate constant (k_{obsd}/[NaOD]) on the added deuterioxide concentration. The observed first-order dependence on deuterioxide ion (Table I) requires the exchange process to proceed through a dianion intermediate (eq 2). Although the structure of the dianion may be subject to question, **3** is probably a reasonable representation.[7]

Table I[a,b]

[**6**][c]	$k_{obsd} \times 10^4$,[d] sec^{-1}	[NaOD][e]	$k_{obsd} \times 10^3$/[NaOD], M^{-1} sec^{-1}
Ca. 0.9	No exchange[6]	0.00	
0.7	1.27	0.038	3.3
1.1	3.89	0.138	2.8
0.9	5.25	0.186	2.8
0.9	7.90	0.249	3.2

[a] Temperature, 31°. [b] Rates were measured by nmr integration of the methyl resonance of **6** as a function of time. [c] Moles/liter. [d] k_{obsd}'s are pseudo-first-order rate constants obtained from single runs carried out to approximately three half-lives by plotting ln [**6**] as a function of time. [e] Added sodium deuterioxide.

The facile exchange observed in **6** suggests that H/D exchange might serve as a delicate probe in determining the relative stabilities of the π systems in the similar three-, five-, and six-membered ring analogs (**7**, *n* = 0, 2, 3) and other related systems.[2e] Unfortunately these compounds are not yet available.



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Acknowledgments. We thank the Research Corporation for partial financial support of this work and Professor R. Winter for stimulating discussions.

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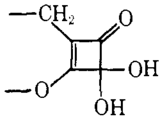
[5] S. Skujins, J. Delderfield, and G. A. Webb, *Tetrahedron*, **24**, 4805 (1968).

[6] **1** could be recovered in excess of 80% after complete exchange. The methyl group was found to contain 2.8 D/molecule (mass spectroscopy). No exchange could be detected in the absence of added base.

[7] In a very similar system, 3-hydroxy-2,4-dimethylcyclobutenone (pK_a 2.8),[8] no appreciable base-catalyzed H/D exchange was observed (K_2CO_3, D_2O) in the methyl group.[9] This suggests intermediates such as i are not involved in the exchange process.



i

[8] R. B. Woodward and G. Small, Jr., *J. Amer. Chem. Soc.*, **72**, 1297 (1950).

[9] D. Farnum, T. Heybey, and B. Webster, *ibid.*, **86**, 673 (1964).

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Photochromic Indigoids. II.[1] Absorption Spectra and Quantum Yields for the Photoisomerization of Selenoindigo

Sir:

As part of an investigation of the photochemical cis–trans isomerization of indigoid dyes, we have examined selenoindigo (**1**), which has been reported by Pummerer and Marondel[2] to undergo photoisomerization. A recent communication[3] of the absorption spectra and quantum yields for the photoisomerization of *trans*- and *cis*-oxindigo (**2**) prompts us to report our results for **1**.

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[1] Paper I in this series: J. Blanc and D. L. Ross, *J. Phys. Chem.*, 72, 2817 (1968).

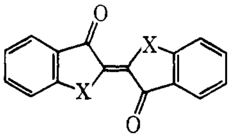
[2] R. Pummerer and G. Marondel, *Chem. Ber.*, **93**, 2834 (1960).

[3] H. Güsten, *Chem. Commun.*, 133 (1969).

Table I

Compound	λ_{max}, nm (ϵ)	Φ_T	Φ_C	Solvent	Ref
trans-**1**	562 (14,950 ± 290)[a]	0.0250 ± 0.0015[b]		Toluene	This work
cis-**1**	485 (9,780 ± 100)[c]		0.275 ± 0.015[d]	Toluene	This work
trans-**3**	542 (17,800 ± 700)	0.027 ± 0.002		Toluene	1
cis-**3**	485 (13,700 ± 130)		0.25 ± 0.02	Toluene	1
trans-**2**	413 (13,800)[e]	0.63		Benzene	3
cis-**2**	396 (13,100)[e]		0.35	Benzene	3
trans-**4**	644 (23,100)	0.004–0.08		Benzene	5
cis-**4**	588 (8,300)			Benzene	5

[a] ϵ_{cis} at this wavelength is 1830 ± 300. [b] Φ_C measured at 562 is 0.25 ± 0.03. [c] ϵ_{trans} at this wavelength is 1870 ± 140. [d] Φ_T measured at 485 is 0.027 ± 0.005. [e] In hexane.



1, X = Se
2, X = O
3, X = S
4, X = NCH_3

As has been observed for the majority of photoisomerizable indigoids[1,4,5] (but *not* for oxindigo[3]), *trans*-selenoindigo shows a red fluorescence at about 620 nm (but only having about 10% of the intensity of the corresponding fluorescence of *trans*-thioindigo, **3**) upon irradiation in its principal visible absorption band. We were thus able to utilize the procedures described in ref 1 to determine the absorption spectra of the cis and trans isomers without the need of physically separating them.

The results are shown in Figure 1.[6] With this compound, the maximum value of the ratio[9] [trans] before irradiation/[trans] after irradiation obtainable on irradiation at 562 nm is 1.75, a fact reflected in the accuracy reported in Table I for the extinction coefficients of the cis isomer. At the photostationary state achieved on irradiating **1** in toluene at 562 nm, the solution contained 57% of the trans isomer, as compared with **3**, which gives 41% trans when irradiated at 542 nm in the same solvent. The published spectra of Pummerer and Marondel[2] for selenoindigo in chloroform suggest that, at the photostationary state in this solvent, the mixture is more cis rich than can be obtained in toluene. We have confirmed this finding and believe it to be due to a lowering of the value of the quantum yield for cis-to-trans photoisomerization on going to chloroform as the solvent. A degree of photodegradation of this dye was observed after prolonged irradiation.

Substitution of selenium for sulfur has resulted in a bathochromic shift of 20 nm for the trans isomer and a lowering of the extinction coefficient, both in qualitative agreement with the calculations of Klessinger and Lüttke.[10] The apparent insensitivity of the wavelength of maximum absorption of the cis isomer to this change in heteroatom is surprising.

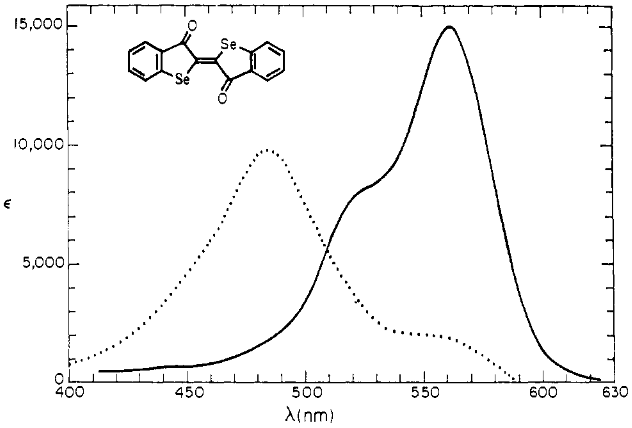


Figure 1. Calculated absorption spectra of *trans*- (—) and *cis*- (······) selenoindigo in toluene.

The relatively weak long-wavelength absorption, seen at about 560 nm in the case of *cis*-selenoindigo, is a feature we have observed in the spectra of a number of *cis*-indigoids (compare, for example, *cis*-thioindigo and *cis*-*N*,*N'*-diacetylindigo reported in ref 1). It is possible that this absorption represents a weak 0–0 transition.[11] We have found no wavelength dependence of the quantum yield for cis-to-trans photoisomerization over regions of the spectrum which include these long-wavelength absorptions.

Quantum yields for the photochemical trans-to-cis (Φ_T) and cis-to-trans (Φ_C) isomerizations were determined by the method of "initial slopes" described by Lippert and Lüder,[13] and are also reported in the table. Included in the table are some corresponding values which have been reported for several other symmetrical indigoids having different heteroatoms. The coincidence of the values of both Φ_T and Φ_C for **1** and **3** is remarkable, especially in light of the considerable differ-

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(4) D. A. Rogers, J. D. Margerum, and G. M. Wyman, *J. Amer. Chem. Soc.*, **79**, 2464 (1957).

(5) C. R. Giuliano, L. D. Hess, and J. D. Margerum, *ibid.*, **90**, 587 (1968).

(6) Selenoindigo was prepared by cyclization and oxidation of *o*-carboxyphenylselenoglycolic acid, which was synthesized by the method of Lesser and Weiss[7] from diselenodisalicylic acid, made as described by Ruwet and Renson.[8] An analytical sample had mp 337–340° after several recrystallizations from dimethylformamide. The photochemical measurements were made using the procedures and instrumentation described in ref 1 on 6.79 × 10^{-5} *M* solutions in toluene.

(7) R. Lesser and R. Weiss, *Ber.*, **45**, 1835 (1912).

(8) A. Ruwet and M. Renson, *Bull. Soc. Chim. Belg.*, **75**, 157 (1966).

(9) *Cf.* eq 3 in ref 1.

(10) M. Klessinger and W. Lüttke, *Tetrahedron, Suppl.*, **2**, 315 (1963).

(11) If these long-wavelength absorptions (at *ca.* 540 nm for *cis*-**3** and *ca.* 560 nm for *cis*-**1** are assumed to be the 0–0 transitions, then the transition energy for *cis*-selenoindigo can be said to have shifted to a lower value as compared with that of *cis*-thioindigo. This result is what would have been expected both from theoretical calculations[12] and the shift oserved for the trans isomers.

(12) M. Klessinger, *Tetrahedron*, **22**, 3355 (1966).

(13) E. Lippert and W. Lüder, *J. Phys. Chem.*, **66**, 2430 (1962).

ence between these values and those reported for oxindigo.

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Reduction of Organic Halides by Cobalt(II) Schiff's Base Complexes. Evidence for an Electron-Transfer Mechanism

Sir:

Previous work[1-3] in this laboratory has demonstrated that the reductions of organic halides (RX) by certain low-spin cobalt(II) complexes (L_5Co^{II}, notably Co(CN)$_5^{3-}$ and Co(DH)$_2$B, where DH$_2$ = dimethylglyoxime and B = pyridine, triphenylphosphine, etc.) proceed according to the stoichiometry and mechanism depicted by

$$\mathrm{L_5Co^{II} + RX \longrightarrow L_5Co^{III}X + R\cdot} \quad \text{(rate determining)} \tag{1}$$

$$\mathrm{L_5Co^{II} + R\cdot \longrightarrow L_5Co^{III}R} \tag{2}$$

$$\overline{\mathrm{2L_5Co^{II} + RX \longrightarrow L_5Co^{III}X + L_5Co^{III}R}} \tag{3}$$

In this communication, we report the discovery and characterization of another class of reactions between cobalt(II) complexes and organic halides, which proceeds by a different and previously unrecognized mechanism involving "outer-sphere" electron transfer rather than halogen abstraction. Both types of reactions may yield organocobalt products.

The new class of processes that we wish to describe is exemplified by the reaction between *N,N'*-bis(salicylidene)ethylenediamino-1-methylimidazolecobalt(II) [Co(salen)(MeIMD)] and *p*-nitrobenzyl bromide (RX), which was found to proceed quantitatively in CH_2Cl_2 solution in the presence of excess MeIMD, in accord with the stoichiometry described by eq 4. The stoichiometry was established by isolation and full characterization (elemental, spectral, and nmr analysis) of the products [Co(salen)(MeIMD)$_2^+$ isolated as its bromide salt] and by quantitative matching of the spectrum of the final reaction solution with the known spectra of the products.

$$\mathrm{2Co(salen)(MeIMD) + RX + MeIMD \longrightarrow} \\ \mathrm{Co(salen)(MeIMD)_2^+ + Co(salen)(MeIMD)R + X^-} \tag{4}$$

Kinetic measurements in which the reactions were followed spectrally and in which the initial solution composition was varied over the concentration ranges 1.2×10^{-4}–1.2×10^{-3} *M* Co(salen)(MeIMD), 0.4–3.0 *M* MeIMD,[4] and 1.4×10^{-3}–1.1×10^{-1} *M* RX, yielded the third-order rate law corresponding to eq 5 with $k_{\mathrm{exp}} = 2.8 \pm 0.2\ M^{-2}\ \mathrm{sec}^{-1}$ at 25° in CH_2Cl_2. We interpret these observations in terms of the mechanism depicted by eq 6–8, in which the rate-determining step is an outer-sphere electron transfer between Co(salen)(MeIMD)$_2$ and RX. According to this interpretation $k_{\mathrm{exp}} = 2kK$.

$$-\mathrm{d[Co(salen)(MeIMD)]}/\mathrm{d}t = \\ k_{\mathrm{exp}}\mathrm{[Co(salen)(MeIMD)][RX][MeIMD]} \tag{5}$$

$$\mathrm{Co(salen)(MeIMD) + MeIMD \overset{K}{\rightleftarrows} Co(salen)(MeIMD)_2} \\ \text{(rapid equilibrium)} \tag{6}$$

$$\mathrm{Co(salen)(MeIMD)_2 + RX \xrightarrow{k}} \\ \mathrm{[Co(salen)(MeIMD)_2^+ + RX^-] \longrightarrow} \\ \mathrm{Co(salen)(MeIMD)_2^+ + R\cdot + X^-} \quad \text{(rate determining)} \tag{7}$$

$$\mathrm{Co(salen)(MeIMD) + R\cdot \longrightarrow} \\ \mathrm{Co(salen)(MeIMD)R} \quad \text{(rapid)} \tag{8}$$

Whether or not a radical anion intermediate (RX$^-$) of finite lifetime is formed is not established by our observations. However, evidence for such a species (which dissociates into R· and X$^-$) has previously been advanced in studies on the alkylation of various anions with *p*-nitrobenzyl halides[5] and on the electrochemical reduction of nitrobenzyl halides.[6]

The above reaction pattern appears to be conditioned by the strongly electron-accepting nitro group and has thus far been observed only for nitrobenzyl halides. Other benzyl halides, including, *p*-cyanobenzyl halides, were found to react more slowly with Co(salen)(MeIMD) and related cobalt(II) complexes by the "conventional" halogen-abstraction mechanism (eq 1–3) rather than by electron transfer. Even with *p*-nitrobenzyl halides, the electron-transfer mechanism was found to be favored only for certain ligand bases, notably imidazole (IMD) and MeIMD; with pyridine and substituted pyridines, the alternative abstraction mechanism was observed.[7,8] Kinetic data for several reactions which exhibited electron-transfer mechanisms are summarized in Table I. In a few cases *K* was sufficiently large that formation of the six-coordinate complex (Co(saloph)(IMD)$_2$, etc.) could be detected and the value of *K* determined from the dependence of k_{exp} on the free-ligand (IMD, etc.) concentration. For these reactions the individual values of *k* and *K* are listed; in other cases only limiting values can be given.

The variation in rates among the reactions in Table I is relatively small. A particularly striking feature is the very small reactivity difference between the chloride

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(1) J. Halpern and J. P. Maher, *J. Amer. Chem. Soc.*, **86**, 2311 (1964); **87**, 5361 (1965).

(2) P. W. Schneider, P. F. Phelan, and J. Halpern, *ibid.*, **91**, 77 (1969).

(3) P. B. Chock and J. Halpern, *ibid.*, **91**, 582 (1969).

(4) The dissociation constant of Co(salen)(MeIMD) to Co(salen) + MeIMD was determined spectrophotometrically to be 3.8×10^{-2} *M*. Thus, over the MeIMD concentration range cited, the cobalt(II) was present virtually entirely as Co(salen)(MeIMD). The kinetic behavior described by eq 5 persisted to lower MeIMD concentrations (down to 0.02 *M*), provided that the necessary correction for the dissociation of Co(salen)(MeIMD) was applied.

(5) R. C. Kerber, G. W. Urry, and N. Kornblum, *J. Amer. Chem. Soc.*, **87**, 4520 (1965); N. Kornblum, R. E. Michel, and R. C. Kerber, *ibid.*, **88**, 5660 (1966); G. A. Russell and W. C. Danen, *ibid.*, **90**, 347 (1968).

(6) J. G. Lawless, D. E. Bartak, and M. D. Hawley, *ibid.*, **91**, 7121 (1969).

(7) L. G. Marzilli, P. A. Marzilli, and J. Halpern, submitted for publication.

(8) The magnetic behavior of cobalt(II) Schiff's base compounds is complex and not well understood.[9] The five-coordinate complexes (Co(salen)(MeIMD), etc.) exhibit temperature-dependent magnetic moments, characteristic of high-spin–low-spin equilibria, with values ranging from 2 to 3.5 BM at room temperature and approaching the limiting low-spin value of ~1.9 BM at low temperatures. MeIMD, which favors the high-spin form, is also among the most effective ligands in favoring the electron-transfer mechanism of reaction with *p*-nitrobenzyl halides. This is not unexpected since the equilibrium for formation of the six-coordinate species (eq 5) should be more favorable for high-spin complexes. A detailed account of magnetic studies on these complexes will be published elsewhere.

(9) A. Earnshaw, P. C. Hewlett, E. A. King, and L. F. Larkworthy, *J. Chem. Soc. A*, 241 (1968).