ation. However, alternative mechanisms cannot be precluded.

Treatment of the spirodienone **10** in methanol with dry HCl gas gave the ketal **13** (71%): mp 107–109°; ir $\lambda_{\max}^{\mathrm{KBr}}$ 5.99 μ; mass spectrum *m/e* 401 (M^+). Room temperature treatment of **13** in THF with an excess of $LiAlH_4$ gave *O*-methylerybidine (**11**, 81%, mp 139–140°, mixture melting point, mixture tlc, and mass spectrum identical with those of a sample prepared by diazomethane methylation of erybidine (**12**)).[16] It is probable that the transformation proceeds *via* reduction of **13** to **14**, fragmentation to a dibenzazonine iminium salt, and reduction to **11**.[17]

Dibenzazonine derivatives related to **11** have been shown to be effective *in vitro* and *in vivo* precursors of the erythrinan alkaloids.[18] In view of the newly discovered facile conversions of the benzylisoquinoline derivative **5** to "neoproerythrinadienone" **10** and thence to dibenzazonine **11**, the chemistry of the neoproerythrine system may have important implications for the biosynthesis of the *Erythrina* alkaloids.

Investigations are in progress to determine possible further implications of nonphenol oxidative coupling for alkaloid biosynthesis.

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Received June 21, 1973

Heteroaromatic Nucleophilic Substitution. Inducing a Change from an Ionic to a Radical-Chain Mechanism with Methoxide Ion

Sir:

A newly emerging area of chemistry is found in radical-anion chain substitution reactions at aromatic and aliphatic carbon atoms.[1–8] We wish to report a novel result. A substitution reaction is changed from an ionic to a radical-chain pathway merely by adding $NaOCH_3$.

4-Bromoisoquinoline (I) reacts with $NaSC_6H_5$ in CH_3OH to give 4-phenylthioisoquinoline (II). But

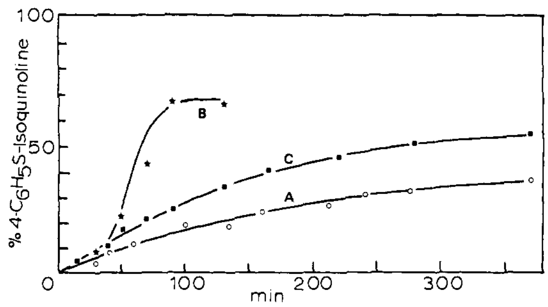
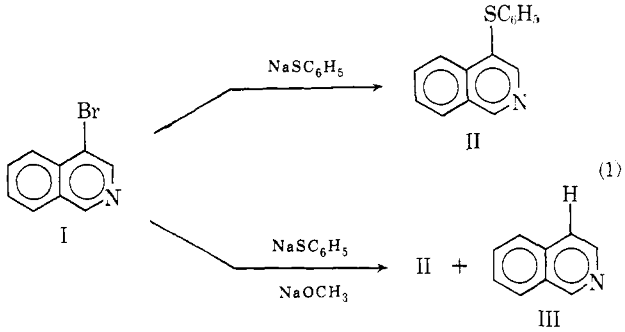


Figure 1. Time-dependent formation of 4-phenylthioisoquinoline from 4-bromoisoquinoline and $NaSC_6H_5$ in methanol at 147°. In all cases the initial concentrations of 4-bromoisoquinoline and $NaSC_6H_5$ are 0.52 and 0.98 *M*, respectively. Curve A shows the rate of formation of the substitution product in the absence of additives. In the case of curve B the additive is 0.98 *M* $NaOCH_3$ while the additives are 0.98 *M* $NaOCH_3$ and 0.2 *M* azobenzene in curve C.

two curious changes result when $NaOCH_3$ is added: (a) The rate of formation of II increases and (b) II as well as isoquinoline (III), a reductive dehalogenation product, are formed,[9] eq 1. Only traces of 4-methoxyisoquinoline are found.[10,11]



The results of three separate experiments summarized in Figure 1 indicate how fast the concentration of II increases with time at 147°. Similar curves (not shown) were constructed to follow the disappearance of I and the formation of III. The initial concentrations of I (0.52 *M*) and $NaSC_6H_5$ (0.98 *M*) are the same in the three experiments. Curve A shows how fast II is formed in the absence of $NaOCH_3$. For example, after 370 min only 38% of II has formed, the remainder being unreacted I. This reaction shows the usual second-order kinetics found for nucleophilic substitution at an aromatic carbon atom ($k = 2.7 \times 10^{-5}$ M^{-1} sec^{-1}). However, the addition of 0.98 *M* $NaOCH_3$ to a second mixture profoundly affects the reaction, curve B. The reaction now is essentially complete after about 90 min; approximately 65% of II and 35% of III have formed. An induction period lasting for about 35 min is readily apparent. Clearly, after this induction period the rate of formation of the substitution product is markedly accelerated.

The experiment which provides insight into the na-

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[9] Reaction mixtures were analyzed by nmr and by glpc. Reported products comprise at least 90% of the mixture at completion. Satisfactory analyses have been obtained for II, mp 60–61°.

[10] It has long been known that I and $NaOCH_3$ give III along with trace amounts of 4-methoxyisoquinoline.[11] We have found the rate of this reductive dehalogenation process to be retarded by radical inhibitors such as azobenzene and azoxybenzene, indicating a radical-chain process.

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ture of the beneficial effect of $NaOCH_3$ on the substitution reaction is summarized by curve C. The initial concentrations of I, $NaSC_6H_5$, and $NaOCH_3$ are the same as those giving rise to curve B. Now, 0.2 *M* azobenzene is present as well, and the $NaOCH_3$ promoted reaction is inhibited. Inhibition is not complete because the formation of II still is faster than in the absence of $NaOCH_3$, curve A. Similarly, the formation of III also is inhibited. A control experiment involving a mixture of $NaSC_6H_5$, $NaOCH_3$, and azobenzene but not I shows that these materials do not react. A second control indicates that 0.3 *M* azobenzene does not influence the rate of formation of II in the absence of $NaOCH_3$.

The formation of II in the absence of $NaOCH_3$ very likely proceeds by the well-known ionic route involving attack of $C_6H_5S^-$ on I to give an intermediate σ complex.[12] A new pathway must be followed in the presence of $NaOCH_3$. The induction period and the rate retarding effect of a material known to be a good electron acceptor[13–15] strongly suggests that substitution in the presence of $NaOCH_3$ involves electron transfer and a radical chain mechanism.

We speculate that the propagation steps of the chain reaction may involve the formation of the radical anion of I which then eliminates bromide ion to give the 4-isoquinolyl radical (Ar·), eq 2. This radical may react with $C_6H_5S^-$ to give the radical anion of II, eq 3, which then donates an electron to I to give II and to continue the chain, eq 4. The 4-isoquinolyl radical also can abstract a hydrogen atom from CH_3OH or CH_3O^- to give III, eq 5. The radical ion $\dot{C}H_2O^-$ formed by the reduction process can also continue the chain, eq 6.[16] Such an electron transfer scheme is not unprecedented.[1,17,18] The identity of initiation and termination steps is unknown.

$$\mathrm{I}\cdot^- \longrightarrow \mathrm{Br}^- + \mathrm{Ar}\cdot \qquad (2)$$

$$\mathrm{Ar}\cdot + C_6H_5S^- \longrightarrow \mathrm{II}\cdot^- \qquad (3)$$

$$\mathrm{II}\cdot^- + \mathrm{I} \longrightarrow \mathrm{II} + \mathrm{I}\cdot^- \qquad (4)$$

$$\mathrm{Ar}\cdot + CH_3O^- \longrightarrow \mathrm{III} + \dot{C}H_2O^- \qquad (5)$$

$$\mathrm{I} + \dot{C}H_2O^- \longrightarrow CH_2{=}O + \mathrm{I}\cdot^- \qquad (6)$$

Our results have significant implications. Thus, it is a common practice when studying substitution reactions involving $R'S^-$ nucleophiles in ROH solvent to suppress the concentration of RO^-. This is done to avoid the possibility of a competing substitution reaction involving RO^-. In our case the addition of RO^- brings about an entirely new mechanism of substitution. It seems likely that a similar change in mechanism may be observed in other instances as well. Indeed, it may prove rewarding to deliberately add RO^-. Certainly, the suppression of RO^- should not always be the rule.

Acknowledgment. This work was kindly supported by the National Science Foundation.

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Received July 2, 1973

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Oxygen Quenching of Charge-Transfer Excited States of Ruthenium(II) Complexes. Evidence for Singlet Oxygen Production

Sir:

Ground-state oxygen is a good energy-transfer quencher of organic triplets[1,2] and a good catalytic deactivator of organic singlet states.[3] Little is known, however, about the excited-state interactions of metal complexes and oxygen. Oxygen efficiently quenches doublet states of Cr(III) complexes,[4] and Co(II) and Ni(II) complexes efficiently deactivate singlet oxygen;[5] the mechanisms remain uncertain. Because d–d and charge-transfer (CT) excited states of metal complexes have no direct organic counterpart and since spin–orbit coupling is much greater in complexes than in organics, different rules may well apply. We report here evidence for the efficient production of singlet oxygen on deactivation of CT-triplet states of ruthenium(II) complexes.

$Ru(bipy)_3Cl_2$ (G. Frederick Smith), $Ru(bipy)_2(CN)_2$,[6] $Ru(phen)_3(ClO_4)_3$, $Ru(phen)_2(CN)_2$[7] (bipy = 2,2′-bipyridine; phen = 1,10-phenanthroline), and Fisher Rose Bengal were used as sensitizers. Aldrich 2,3-dimethyl-2-butene (TME) and 1,3-cyclohexadiene (CHD) were used as oxygen scavengers.

Stern–Volmer quenching constants, K_{sv}'s, were computed from $[(\phi_0/\phi) - 1]/[O_2]$ and $[(\tau_0/\tau) - 1]/[O_2]$; ϕ's and τ's represent emission intensities and mean lifetimes, respectively. K_{sv}'s and bimolecular quenching constants, k_2's, are summarized in Table I.

That O_2 quenching involved more than just catalytic deactivation of the complexes was demonstrated by

Table I. Oxygen Quenching of Metal Complexes at ~21°

Complex–solvent	K_{sv}, M^{-1} ϕ method[a]	 τ method[b]	$k_2 \times 10^9$,[c] M^{-1} sec^{-1}
$Ru(phen)_2(CN)_2$–H_2O	3900	3900	5.5
$Ru(phen)_2(CN)_2$–CH_3OH	8500	9900	5.0
$Ru(phen)_3{}^{2+}$–H_2O	4900		4.7
$Ru(phen)_3{}^{2+}$–CH_3OH	1010		3.2
$Ru(bipy)_2(CN_2)$–H_2O	1180		4.5
$Ru(bipy)_2(CN)_2$–CH_3OH	1910		4.5
$Ru(bipy)_3{}^{2+}$–H_2O	2060	1890	3.3
$Ru(bipy)_3{}^{2+}$–CH_3OH	1380	1470	1.7

[a] ±5%. [b] ±10%. [c] Calculated from K_{sv} by ϕ method.

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