for hemerythrin[11] and protocatechuate-3,4-dioxygenase,[12] the Raman lines of phenolate anion were observed at ~1600, 1500, 1260, and 1170 cm^{-1}. The CO stretching mode of phenolate anion at 1260 cm^{-1} was intense in those complexes whereas it was missing for the present complex. This implies a substantial difference in the interaction mode of phenolate anion for the two types of complexes. An interaction in the parallel plane arrangement may be suggested for the present case. Detailed analysis of the binding mode of the phenolate anion to the flavin coenzyme of OYE as well as the resonance Raman spectra of the OYE complexes of other substituted phenols and their excitation profiles will be reported separately.

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Electron Transfer Processes. 21. The Use of α-Halo Nitroalkanes as Ketone Equivalents in Condensation Reactions

Sir:

The reaction of a variety of enolate-type anions with 2-chloro-2-nitropropane has been demonstrated to proceed by a free radical chain mechanism[1-4] which has been termed $S_{RN}1$ (Scheme I).[5] Only a few examples of secondary enolate anions have been successfully employed. One example is diethyl malonate, which in sodium ethoxide/ethanol gives a 54% yield of 1-nitro-1-methylethyl ethyl malonic ester or a 44% yield of $(CH_3)_2C{=}C(CO_2C_2H_5)$.[6] Other primary or secondary enolate anions, such as cycloalkanone enolate anions, give little or no coupling with 2-chloro-2-nitropropane in sodium ethoxide/ethanol or potassium *tert*-butoxide in *tert*-butyl alcohol, DMF, or Me_2SO solutions even when irradiated. We herein report conditions which allow a wide variety of primary and secondary enolate anions to be condensed with 2-chloro-2-nitropropane by the $S_{RN}1$ process to yield the products of a controlled crossed aldol condensation.

Table I. Reaction of Cyclohexanone Enolate Anion with 2-Chloro-2-nitropropane (Li^+, THF)

mol ratio[a]	temp (°C) and time	reaction products (%)				
		Cl^-	1	2	3	cyclohexylidenyl-cyclohexanone
1:1:1	25°, 15 m	56	9	18	4	trace
1:1:1	20°, 1 h	55	26[b]	20[b]	3	0
1:1:1	45°, 30 m	75	6	16	17	trace
1:1:2	45°, 30 m	96	0	28	~10	18
2:1:2	45°, 30 m	100	6	38	12	12
1:1:1	45°, 1 h	61	5	27	13	trace
1:1:1[c]	45°, 2 h	20	0	0	0	15

[a] Ratio of cyclohexanone:2-chloro-2-nitropropane:lithium diisopropylamide; reactions were generally conducted on a 0.05 mol scale. [b] 46% yield of **1** isolated by distillation of aqueous (basic) hydrosylate. [c] Containing 5.5 mol % of di-*tert*-butyl nitroxide.

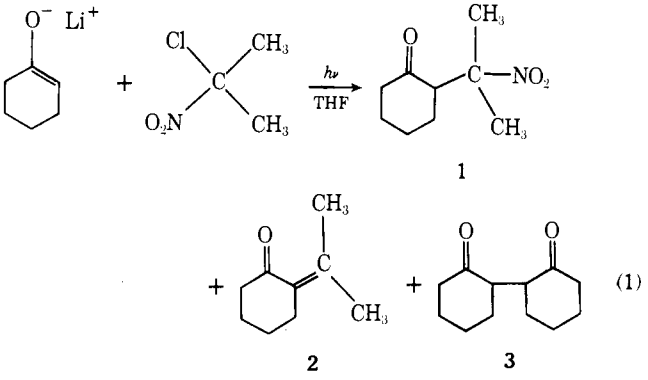
Scheme I. $S_{RN}1$ Mechanism (E^- = Enolate Anion)

$$(CH_3)_2C(Cl)NO_2^-\cdot \rightarrow (CH_3)_2\dot{C}NO_2 + Cl^-$$

$$(CH_3)_2\dot{C}NO_2 + E^- \rightarrow (CH_3)_2C(NO_2)E^-\cdot$$

$$(CH_3)_2C(NO_2)E^-\cdot + (CH_3)_2C(Cl)NO_2 = (CH_3)_2C(Cl)NO_2^-\cdot + (CH_3)_2C(NO_2)E$$

Treatment of cyclohexanone with lithium diisopropylamide in THF followed by the addition of 2-chloro-2-nitropropane gives in 1 h at 10–45 °C a reasonable conversion to **1, 2,** and **3** with only traces of cyclohexylidenylcyclohexanone under the proper conditions (Table I). Yields of **1** plus **2** in the range of 50% are easily achieved. Since the isopropylidene ketone (**2**) is formed from **1** by E2 elimination, the ratio of **1** to **2** depends upon reaction and isolation conditions. Under the best conditions we have observed a ratio of β-nitro ketone/isopropylidene ketone ~5:1 from several ketones. The use of an excess of base in reaction 1 converts **1** to **2** quantitatively, but appreciable amounts of cyclohexylidenylcyclohexanone are now formed. If the reaction product is simply treated with an excess of water and resulting basic solution of water and organic material codistilled, **1** undergoes elimination to yield **2** which is readily isolated in pure form by a redistillation of the organic distillate. Neutralization of the product from reaction 1 followed by solvent extraction and distillation gives **2, 1** (bp 98 °C (0.3 Torr), mp 69–70 °C), and **3** as a higher boiling fraction.



(1)

The conversion of an enolate anion into the α-alkylidene ketone, the β-nitro ketone, and the enolate dimer appears to be a general reaction. All of these materials are of interest for further synthetic transformations and are often not readily available. Since a wide variety of α-halo nitroalkanes are readily available and, in fact, can be made from the appropriate ketone,[7-12] this $S_{RN}1$ reaction of primary and secondary en-

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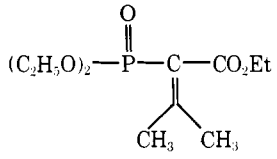
olate anions has wide scope.

Enolates which fail to undergo the normal condensation reaction with ketones can give the aldol condensation product with 2-chloro-2-nitropropane. Thus, the enolate anion from triethyl phosphonoacetate yields **4** in 30% yield.



4

The reaction of cyclohexanone enolate anion with 2-chloro-2-nitropropane clearly follows the $S_{RN}1$ mechanism. In the presence of 5 mol % of di-*tert*-butyl nitroxide products **1–3** are not formed, and the exotherm from 10 to 45 °C is not observed upon the addition of the α-chloro nitroalkane to the enolate solution. Although the initial rate of reaction 1 is quite fast, the reaction slows down and fails to go to completion even with irradiation and long reaction times. Thus the reactions summarized in Table I were accompanied by 20–35% of unreacted starting materials. A side product must be inhibiting the reaction in the later stages. The formation of traces of nitroso compounds which are excellent radical traps ($R\cdot + RNO \rightarrow R_2NO\cdot$, $R_2NO\cdot + R\cdot \rightarrow R_2NOR$) seems to be occurring. In fact, addition of water to the reaction products produces greenish blue solutions.[13]

Cyclopentanone, cyclohexanone, acetophenone, and propiophenone participate in reaction 1 to give products analogous to **1–3** in comparable yields.[14] 4-Methylcyclohexanone yields the 4-methyl derivatives analogous to **1–3**, while 3-methylcyclohexanone undergoes reaction mainly at the 6-position to give pulegone (30%) and 3-methyl-2-isopylidenylcyclohexanone[15] in the ratio of 4:1,[16] Reaction of 2-chloro-2-nitropropane at −25 to 40 °C with the $\Delta^{1(2)}$-enolate ion formed by the methyllithium cleavage of 3-methyl-1-trimethylsiloxycyclohexene[17] for 0.5 h gave 3-methyl-2-isopropylidenylcyclohexanone and pulegone in a ratio of 3:2. The low regioselectivity is apparently a result of proton transfer between the enolate anion and the coupling product **1**. Reaction of 2-octanone demonstrated regioselectivity yielding 3.5 parts of 2-methyl-4-keto-2-decene to one part of 2-methyl-3-acetyl-2-octene.[18]

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Formation of Bis[bis(3,5-di-*tert*-butylcatecholato)oxomolybdenum(VI)] and Related Stable Molybdenum–Catechol Complexes

Sir:

The dianion of catechol is an effective bidentate ligand that forms a variety of complexes with transition metal ions.[1-4] This characteristic as well as the ability of catechol and its derivatives to participate in a wide variety of redox reactions[5] may account for their presence in a multitude of biological systems.[6,7] Such considerations have prompted studies to elucidate the coordination and oxidation–reduction chemistry of catechol complexes and to determine their viability as models for biological processes.[1,2,8] We report here the formation and the properties of the binuclear bis(catechol) complex of oxomolybdenum(VI) and two related catechol complexes of molybdenum(VI) that result from the reaction of molybdenum(VI) with 3,5-di-*tert*-butylcatechol.

Although reactions of molybdenum with various catechols have been studied previously,[9-14] most of these studies have been in aqueous media and, with the exception of the molybdenum carbonyls, have not included the isolation and characterization of stable complexes. When bis(acetylacetonato)-dioxomolybdenum(VI) is combined with 3,5-di-*tert*-butylcatechol in CH_2Cl_2, $CHCl_3$, or benzene, an intense violet-colored solution (λ_{max} 540 nm) is formed. Similarly, a red-brown (λ_{max} 431 nm) solution is obtained when the reagents are combined in methanol, ethanol, or propanol. From either of the above media a complex is isolated with an analytical stoichiometry of two catechols per molybdenum and a molecular weight that is consistent with a binuclear species, **1**.[15] Figure 1 illustrates the absorption spectrum for this complex in acetonitrile. A spectrophotometric titration in methanol confirms the stoichiometry of two catechols per molybdenum. When 1 equiv of tetra-*n*-butylammonium hydroxide (TBAOH)/molybdenum is added to **1**, a bright red-orange solution results (Figure 1) from which an orange species can be isolated, **2**. The latter has an analytical stoichiometry of one

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