

under the conditions required for the reduction.

Registry No. *p*-Tolualdehyde, 104-87-0; decyl aldehyde, 112-31-2; cinnamaldehyde, 104-55-2; 4-phenyl-2-butanone, 2550-26-7; propiophenone, 93-55-0; 2-methylcyclohexanone, 583-60-8; 4-methyl-

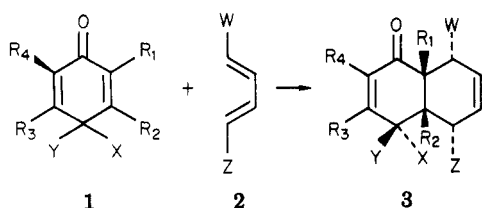
benzenemethanol, 589-18-4; decyl alcohol, 112-30-1; cinnamyl alcohol, 104-54-1; 3-phenyl-1-propanol, 122-97-4; 4-phenyl-2-butanol, 2344-70-9; α -ethylbenzenemethanol, 93-54-9; *cis*-2-methylcyclohexanol, 7443-70-1; *trans*-2-methylcyclohexanol, 7443-52-9; sodium formate, 141-53-7; 1-methyl-2-pyrrolidinone, 872-50-4.

Communications

Selective Reactions of Carbanions with *p*-Quinones. The Aggregate Model

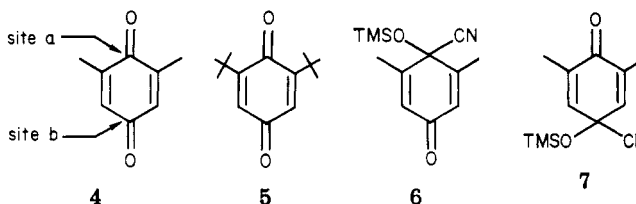
Summary: Additions of carbanions to unsymmetrical *p*-quinones can be achieved at either carbonyl carbon by a judicious choice of reaction conditions.

Sir: Recently, we showed that cross-conjugated cyclohexadienones possessing two different geminal substituents at C4, e.g., 1, undergo "face-selective" Diels-Alder reactions. Thus, the adducts which result, e.g., 3, may contain as many as five asymmetric centers but only one relative stereochemistry.²



In order to apply this methodology to natural product synthesis, easy access to the various substituted cyclohexadienones, depicted by 1, is required.³ Of particular interest here is the availability of quinols (X = OH, Y = alkyl). These compounds are usually prepared by one of three different approaches: (a) exposure of aryl hydroxylamines to strong acid,⁴ (b) oxidation of phenols,⁵⁻⁸ and (c) 1,2-addition of carbanions of *p*-quinones or their synthetic equivalents.^{9,10} Methods a and b often produce complex mixtures of products and are therefore of limited applicability. Method c encompasses a broad spectrum of reactions involving quinones and various organometallic reagents. However, most of these processes lack synthetic utility.⁹ Recently, Fisher and Henderson⁹ reported that reactions of organolithium reagents with *p*-benzoquinones result in the formation of the corresponding quinols in high yield. However, with unsymmetrical quinones these ad-

ditions exhibit low regioselectivity. In this communication we report that additions of carbanions to unsymmetrical *p*-quinones can be achieved at either carbonyl carbon by a judicious choice of the reaction conditions.



The basic principles that were used to achieve regioselective 1,2-additions of carbanions to *p*-quinones are as follows. If the carbanion in question is made sufficiently bulky by varying its counterion, its degree of aggregation, and/or its degree of solvation, steric factors should dominate the transition state, resulting in regioselective addition to the less hindered carbonyl carbon (site b). By contrast, if the carbanion in question is relatively small and only weakly solvated, electronic factors should dominate the transition state, resulting in regioselective addition to the more electrophilic carbonyl carbon (site a).

Some precedents exist for both the steric and electronic models. For example, Grignard reagents are reported to attack exclusively the less-hindered carbonyl group of extremely hindered quinones, such as 5, to produce the corresponding quinols in good yield.¹¹ On the other hand, Evans et al. have previously shown that 4 reacts with trimethylsilyl cyanide to form 6 and 7 in a 94:6 ratio, presumably because the relatively small nucleophile, cyanide ion, preferentially attacks the more electrophilic carbonyl carbon.¹²

In order to test our hypothesis, the following experiments were carried out. Addition of 1 equiv of methylmagnesium bromide to a THF solution of 4 at -78°C results in the formation of 8 and 9 in 62% and 10% isolated yields, respectively.¹³ No trace of 10 is observed. This highly selective, 1,2-addition presumably occurs because methylmagnesium bromide in THF is a relatively large and heavily solvated carbanion, which reacts in accord with the steric model discussed earlier.¹⁴ By contrast,

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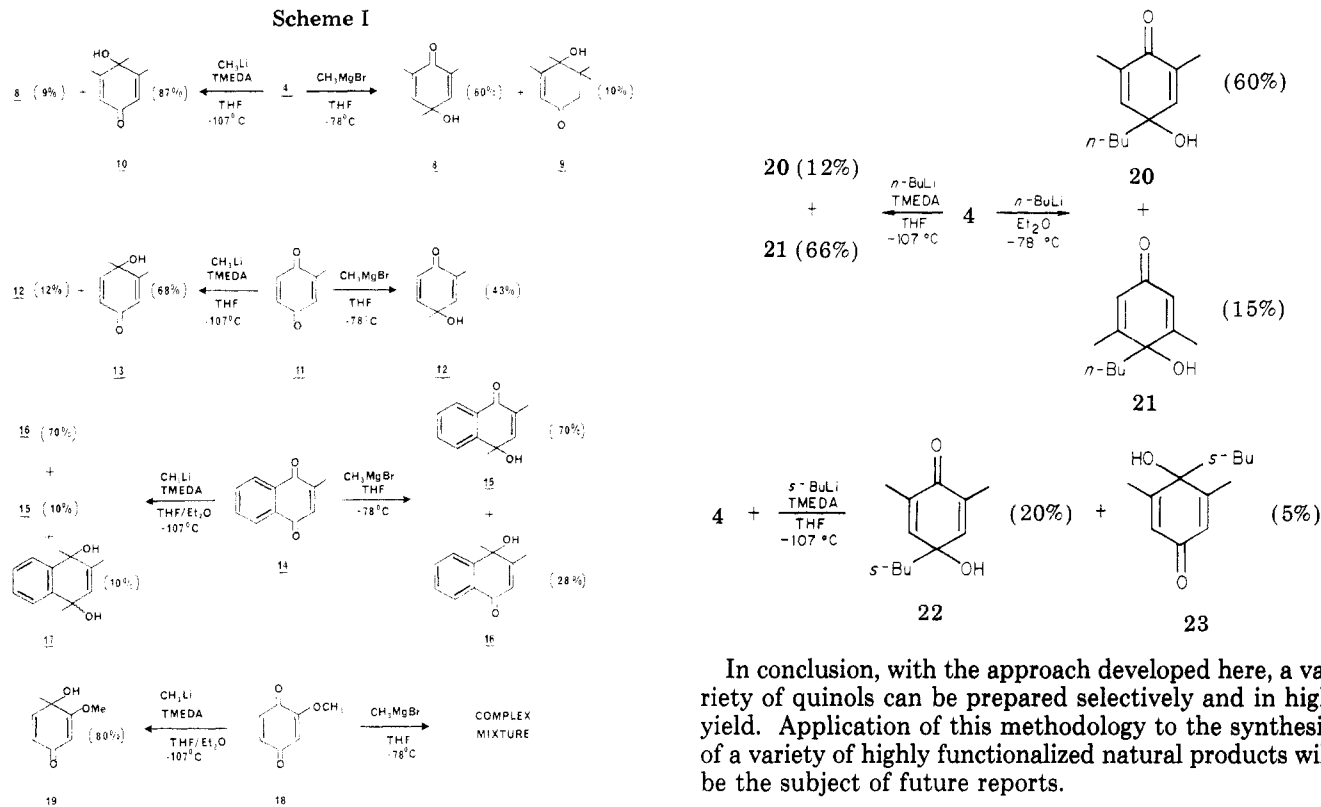
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(13) The double addition product 9 is presumably produced by an initial Michael addition at C2 (or C6) followed by a subsequent 1,2-addition at C1.

(14) An alternative and complementary argument involves selective activation of the less hindered carbonyl group by complexation with magnesium bromide, which is present as a consequence of the Schlenk equilibrium. Selective Lewis acid complexation with 4 has been previously observed. See: Dickinson, R. A.; Kubela, R.; MacAlpine, G. A.; Stojanc, Z.; Valenta, Z. *Can. J. Chem.* **1972**, *50*, 2377.

Scheme I



addition of 1 equiv of methyl lithium, containing 6 equiv of tetramethylethylenediamine (TMEDA) in THF at -107°C , produces 8 and 10 in 9% and 87% isolated yields, respectively. Under these conditions the methyl carbanion is in a nonaggregated, weakly solvated state and reacts in accord with the electronic model discussed above. Thus, by altering the nature of the methyl carbanion, one can effect an almost total reversal of the regioselectivity of the process.

Similar reversals can also be achieved with the other quinones (see Scheme I).^{15,16} This is especially noteworthy for the additions of methyl carbanions to 11, where both the steric and electronic differences between the two carbonyl carbons are quite small. When electronic differences between the carbonyl carbons are very large, as is the case in 18, only monoadditions to the more electrophilic carbonyl carbon can be achieved, irrespective of the conditions employed. Attempts to force 18 to react in accord with the steric model resulted only in the formation of complex mixtures, consisting primarily of hydroquinones.

These reversals of regioselectivity are not simply limited to methyl carbanions. For example, 4 reacts with *n*-butyllithium in ether at -78°C to produce 20 and 21 in a 4:1 ratio. However, by carrying out the reaction in THF in the presence of TMEDA at -107°C , the ratio of 20 to 21 becomes 1:5.5.

When the steric requirements of the carbanion become very large, selective attack at the more electrophilic carbonyl carbon is no longer possible. Thus, addition of *sec*-butyllithium to 4 in THF/TMEDA at -107°C results in a 4:1 mixture of 22 and 23, respectively.

(15) All new materials exhibited satisfactory combustion analysis and/or precise mass measurements.

(16) Cases involving intermediate degrees of solvation and/or aggregation result in poor regioselectivity (vide infra): 4 + CH₃Li (Et₂O, -78°C) → 8 (55%) + 9 (42%) and 11 + CH₃Li (Et₂O, -78°C) → 12 (42%) + 13 (36%).

In conclusion, with the approach developed here, a variety of quinols can be prepared selectively and in high yield. Application of this methodology to the synthesis of a variety of highly functionalized natural products will be the subject of future reports.

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Registry No. 4, 527-61-7; 8, 16404-66-3; 9, 52103-92-1; 10, 55776-84-6; 11, 553-97-9; 12, 51770-93-5; 13, 55153-54-3; 14, 58-27-5; 15, 78127-78-3; 16, 78127-79-4; 17, 78127-80-7; 18, 2880-58-2; 19, 78127-81-8; 20, 78127-82-9; 21, 78127-83-0; 22, 78127-84-1; 23, 78127-85-2.

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Electron Transfer Induced Decomposition of Diazoacetophenone

Summary: Triarylamine radical cations are shown to induce the decomposition of diazoacetophenone by a second-order rate process directly related to their redox potentials.

Sir: Interest in electron-transfer processes of organic reactions is increasing as the scope and extent of these phenomena become appreciated. Recently, a number of papers have appeared describing experimental observations of organic reactions which occur by electron-transfer mechanisms.^{1,2} Several subsequent papers have dealt with the theoretical and mechanistic interpretation of these data.^{1,2,3}

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