Alkynes and Poly(ethylene glycol) Derivatives as Nucleophiles and Catalysts in Substitution Reactions of 1-Chloroanthraquinones

JunPing Fang, Tianbao Lu, Hyunsook Kim, Isaura Delgado, Philippe Geoffroy, Jerry L. Atwood,† and George W. Gokel*

Departments of Chemistry, University of Miami, Coral Gables, Florida 33124, and University of Alabama, Tuscaloosa, Alabama 35487-0336

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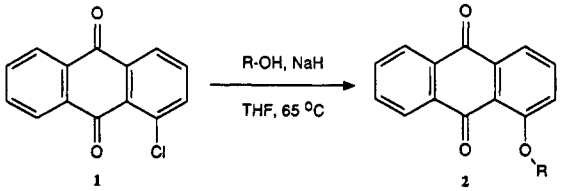
Two synthetically useful approaches to 1-substituted anthraquinone derivatives are reported. Application of these methods afforded the following 1-anthraquinyl ethers: *n*-propyl, *n*-butyl, *n*-octyl, *n*-nonyl, *n*-hexadecyl, isoamyl, allyl, 2-butenyl, (*E*)-2-hexenyl, (*E*)-2-tridecyl, benzyl, phenyl, 4-methylphenyl, 2-butynyl, 2-pentynyl, 2-hexynyl, 3-pentynyl, 3-hexynyl, 3-heptynyl, 3-nonynyl, 4-hexynyl, 4-heptynyl, 5-heptynyl, 5-octynyl, 5-nonynyl, 2-methoxyethyl, 2-(2-methoxyethoxy)ethyl, 2-[2-[2-(octadecyloxy)ethoxy]ethoxy]ethyl, 2-(methylthio)ethyl, 2-(1-piperidino)ethyl, and 2-(1-morpholino)ethyl. The results of about 100 nucleophilic substitution reactions (a number were duplicates) are presented. Most of these reactions involve either a new approach, new products, or both. Included are displacements of chloride by alkanols, alkenols, and alkynols. Of the three, only the latter afford acceptable yields of product, although lower yields are observed as the distance between hydroxyl and triple bond increases. Nucleophiles of the type $RO(CH_2CH_2O)_nOH$ proved remarkably effective. Alkynyl ethers and poly(oxyethylene) ethers also proved to be excellent leaving groups. Both alkynols and oligoethylene glycol monoethers were found to be catalysts for the conversion of 1-chloroanthraquinone into 1-anthraquinyl ethers. In an attempt to understand the mechanism of this reaction, solid-state structures of four anthraquinone derivatives have been obtained. These have poly(ethyleneoxy), morpholino, or alkynyl side arms.

Introduction

Anthraquinones have proved to be important in the development of electrochemically switchable ligands in studies conducted in our[1] and other laboratories,[2] and it is becoming increasingly popular in a variety of related applications.[2-12] Our research program in this area, like others, has been hampered by the lack of synthetic methods[13-20] for the preparation of substituted anthraquinone compounds. The direct displacement of chlorine at the 1-position of anthraquinone is fraught with difficulty. Yields are usually poor, and it is often the case that no product at all is isolated. Vigorous conditions enhance yields some, but even this has proved generally to be an ineffective approach. We report here general methodology for the synthesis of 1-substituted anthraquinone derivatives and two novel, catalytic processes for the replacement of a 1-chloro substituent.[21,22]

Results and Discussion

Substitution of Chloride by Alkoxide Nucleophiles. Yields for nucleophilic substitution by alkoxides on 1-chloroanthraquinone (shown below) have generally been poor despite efforts to improve them.[23] We therefore undertook a survey of reactions, all involving 1-chloroanthraquinone, to determine what nucleophiles might be most successful.



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We have conducted numerous reactions using a standard set of conditions: NaH as base and THF as solvent for 4 h at reflux temperature. By using standard conditions, we hoped to observe trends that might give mechanistic information. Further, under these conditions, normal alkanols afford synthetically unacceptable yields of substi-

* To whom correspondence should be addressed at the University of Miami.
† University of Alabama.

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Table I. Nucleophilic Substitution Reactions of 1-Chloroanthraquinone Using Alkoxide Nucleophiles[a]

nucleophile	% yield	no. of runs
n-C_3H_7OH	16 ± 2	2
n-C_3H_7OH[b]	16	1
n-C_4H_9OH	18 ± 2	2
n-$C_8H_{17}OH$[b]	8	1
n-$C_9H_{19}OH$	7 ± 2	2
n-$C_{16}H_{33}OH$	9, 11, 15[c]	3
n-$C_{16}H_{33}OH$[b]	11	1
CH_2=$CHCH_2OH$	6 ± 2	6
CH_3CH=$CHCH_2OH$[d]	6 ± 1	2
(E)-2-hexenol[e]	6 ± 2	2
$C_6H_5CH_2OH$	22 ± 2	2
CH_3C≡CCH_2OH	71 ± 2[f]	7
CH_3CH_2C≡CCH_2OH	61 ± 7	3
$CH_3(CH_2)_2C$≡CCH_2OH	44 ± 1	2
CH_3C≡$C(CH_2)_2OH$	39 ± 3	2
CH_3CH_2C≡$C(CH_2)_2OH$	32 ± 5	3
$CH_3(CH_2)_2C$≡$C(CH_2)_2OH$	39 ± 3	2
$CH_3(CH_2)_4C$≡$C(CH_2)_2OH$	33 ± 1	2
CH_3C≡$C(CH_2)_3OH$	32 ● 5	2
CH_3CH_2C≡$C(CH_2)_3OH$	31	1
CH_3C≡$C(CH_2)_4OH$	14	1
CH_3CH_2C≡$C(CH_2)_4OH$	27	1
$CH_3(CH_2)_2C$≡$C(CH_2)_4OH$	18 ± 4	3
$CH_3OCH_2CH_2OH$	90 ± 1	2
$CH_3OCH_2CH_2OH$ + KH[g]	52 ± 3	3
$CH_3O(CH_2CH_2O)_2H$	74 ± 1	3
$CH_3O(CH_2CH_2O)_3H$	67 ± 2	2
$C_{18}H_{37}O(CH_2CH_2O)_4H$	80 ± 2	2
$C_{18}H_{37}O(CH_2CH_2O)_4H$	30[h]	1
$CH_3SCH_2CH_2OH$	58 ± 7	3
$(CH_2)_5NCH_2CH_2OH$	64	1
$O(CH_2CH_2)_2NCH_2CH_2OH$	34	1

[a] NaH as base in THF, 4 h at reflux. [b] As in a but DMF as solvent. [c] Reaction time extended to 48 h. [d] E:Z = 10:90. [e] >97% E as judged by HPLC. [f] A wider range of yields for this reaction was obtained in early studies. When these values are included, the average yield is essentially the same (69%) but the variation (±17%) is greater. [g] KH used as base. [h] Na_2CO_3 used as base in CH_3CN.

tution product so improvements would be easy to monitor and assess. The data for all of the direct substitution reactions are presented in Table I. Yields reported are for isolated and fully characterized materials.

The yields observed with simple alkoxides, reported in the preliminary accounts of this work,[21,22] showed more variation in single point experiments than we thought was desirable. We therefore carefully reexamined the substitution by simple alkanols. In previous studies, an apparent yield of zero was obtained at least once for each alkanol although a small but observable quantity of product was obtained in other reactions. In such low-yield cases, both 1-chloroanthraquinone and the nucleophile (if not too water soluble) could be recovered. The yields obtained seem to be somewhat "operator dependent", but we have never observed a yield in any of these reactions in excess of 20%. In any event, yields for the direct replacement of chloride by alkanol under the specified conditions (see Table I) are poor.

Substitution of Chloride by Unsaturated Alkoxides. Olefinic alcohols were found to afford yields of about the same magnitude as the normal alkanols. As in the alkanol case, the yields were poor but highest for the highest melting product. A possible "melting point trend" could be tested experimentally but was not because product yields were too low to be useful in any case.

Changes in Reaction Conditions. A few variations in reaction conditions were examined. These included substituting DMF for THF as solvent while maintaining the temperature at 65 °C, substituting KH for NaH in THF, and use of Na_2CO_3 in CH_3CN. If DMF was used in this reaction at its reflux temperature, extensive decomposition was observed (many spots by TLC). Using n-propanol as nucleophile (refluxing DMF), less than 5% of 1-propoxyanthraquinone was obtained but 19% of 1-aminoanthraquinone (identified by comparison with an authentic sample) was isolated. The replacement of THF by DMF while maintaining temperature and all other variables the same as before in three different alkoxide cases (n-propyl, n-octyl, n-hexadecyl) afforded yields of 1-anthraquinyl ethers as follows: 16%, 8%, and 11%. These values differ little from those reported under corresponding conditions in THF except that the former reactions showed only starting material and product by TLC, but several spots were observed when DMF was used as solvent. Replacement of NaH by KH caused the 90% yield observed when $CH_3OCH_2CH_2OH$ was used as nucleophile to decrease to about half of its previous value. Likewise, the reaction of $C_{18}H_{37}O(CH_2CH_2O)_3H$ with 1 afforded 80% of substitution product when NaH/THF was used but only 30% (single run) when Na_2CO_3 in CH_3CN was the base/solvent combination.

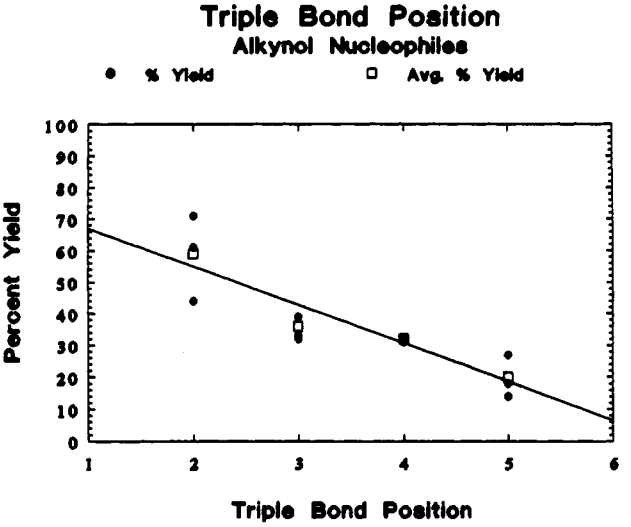


Figure 1.

Substitution of Chloride by Phenoxides. Two substitution reactions of 1-chloroanthraquinone were attempted with phenolic nucleophiles under the same conditions as described above. 1-Phenoxyanthraquinone was obtained from phenol in 66% yield and 4-methylphenol-substituted chloride in 61% yield. Although we have not surveyed a range of phenols, this nucleophile is clearly promising.

Substitution of Chloride by Alkynol Anions. The contrast between saturated or olefinic alcohols and alkynols is dramatic and remarkable. An example of this process in which 2-butynol is the nucleophile is shown below. The alkynol data from Table I are summarized in a plot shown in Figure 1. In the latter, the raw data points appear as filled circles and the open squares are the numerical averages for each position number. The line is calculated for a linear fit through the average of each data set.

Two facts must be considered here. First, the substitution reaction is far more successful for alkynols than for either alkanols or alkenols. Second, the graph strongly suggests that triple-bond position determines the trend rather than the total number of carbon atoms present in the nucleophile. The trend is clear especially when considered in terms of the average yield values. The calculated average yields by position are as follows: 2, 59%; 3, 36%; 4, 32%; and 5, 20%. Note that no data are given for

Table II. Substitution of Alkoxy-Derived Side Arms from the 1-Position of Anthraquinone

nucleofuge	nucleophile	% yield[a]
n-OC_3H_7	1-hexadecanol	20 ± 12 (4)
n-$OC_{16}H_{33}$	1-butanol	9
$OCH_2CH{=}CHCH_3$[b]	1-hexadecanol	51 ± 8 (2)
$OCH_2C{\equiv}CCH_3$	1-nonanol	46
$OCH_2C{\equiv}CCH_3$	1-hexadecanol	43
OEOMe[c]	1-hexadecanol	60 ± 3 (2)
OESMe	1-hexadecanol	49
OESMe	$CH_3CH_2CH_2OH$	68
OEOEOEOMe	$CH_3CH_2CH_2OH$	33, 39, 77
OEOEOEOMe	1-butanol	52 ± 2 (2)
OEOEOEOMe	1-octanol	55 ● 3 (2)
OEOEOEOMe	1-hexadecanol	81 ± 2 (4)
OEOEOEOEOMe	$CH_2{=}CHCH_2OH$	18 (2)
OEOEOEOMe	2-butenol[b]	36 ± 3 (3)
OEOEOEOMe	3-butenol	40 (2)
OEOEOEOMe	(Z)-2-hexenol	44 ± 6 (2)
OEOEOEOMe	(E)-2-tridecenol	25 ± 2 (2)
OEOEOEOMe	$CH_3C{\equiv}CCH_2OH$	38 ± 3 (2)
OEOEOEOMe	$CH_3C{\equiv}C(CH_2)_2OH$	26
OEOEOEOMe	$CH_3CH_2C{\equiv}C(CH_2)_2OH$	46
⟨15N⟩EO[c]	1-hexadecanol	49
⟨15⟩CH_2O	1-hexadecanol	43 ● 3 (2)
⟨18⟩CH_2O	1-hexadecanol	67
$N(CH_2CH_2)_2O$[d]	1-hexadecanol	0

[a] Numbers in parentheses are the number of reactions conducted. [b] E:Z = 10:90. [c] "EO" means $-CH_2CH_2O-$; ⟨00⟩ indicates a crown ether of ⟨00⟩ atoms; ⟨00N⟩ indicates an azacrown ether of 00 atoms. [d] Four products were detected by TLC, but none was isolated.

position 1 since R—C≡C—OH ⇌ R—CH=C=O.

Substitution of Chloride by Poly(ethyleneoxy) Derivatives. Like the triple-bond-containing structures, alkanols having oxygen, nitrogen, or sulfur in the 3-position (i.e., $RXCH_2CH_2OH$, where X = O, N, or S), afforded enhanced yields of nucleophilic substitution product. Thus, $ROCH_2CH_2OH$, $RSCH_2CH_2OH$, and $R_2NCH_2CH_2OH$ displaced chloride from the anthraquinone 1-position in yields of 50–90% (see Table I). Early in this work, we assumed that the increased yields were due to a cation coordination mechanism.[21] The data shown do not confirm this hypothesis.

As the chain length increased (i.e., as n in $(CH_2CH_2O)_n$ was changed from 1 to 3), the expected improvement in cation coordination, and therefore yield, failed to materialize. As alkoxide chain length and product melting point are inversely proportional in this series, it was thought that decreased ease of isolation might be offsetting the expected yield increase. The graph shown below clearly suggests otherwise. Moreover, when the methyl group of $CH_3(OCH_2CH_2)_3OH$ was replaced by $C_{18}H_{37}$, the average yield improved from 67% to 81%.

The presence of nitrogen or sulfur in the 4-position of the nucleophilic alcohol raised substitution yields to the 50–60% range. A mechanism that requires coordination of an alkali metal cation (Na^+ in this case) should show lower yields when S replaces O. It was surprising that when the piperidine ring in $(CH_2)_5NCH_2CH_2OH$ was replaced by morpholine $[O(CH_2CH_2)_2NCH_2CH_2OH]$, the yield approximately halved. Again, these data are not in accord with a simple cation coordination mechanism (Figure 2).

Substitution of Ethyleneoxy-Derived Side Arms at the 1-Position of Anthraquinone. During the attempted preparation of a 1-tris(ethyleneoxy)-8-alkylanthraquinone for use in transport studies[1d] we observed the reaction sequence shown below. In the first case, only 1 equiv of $CH_3(OCH_2CH_2)_3OH$ was used in the hope that one chloride would remain. A 10% yield of disubstituted product

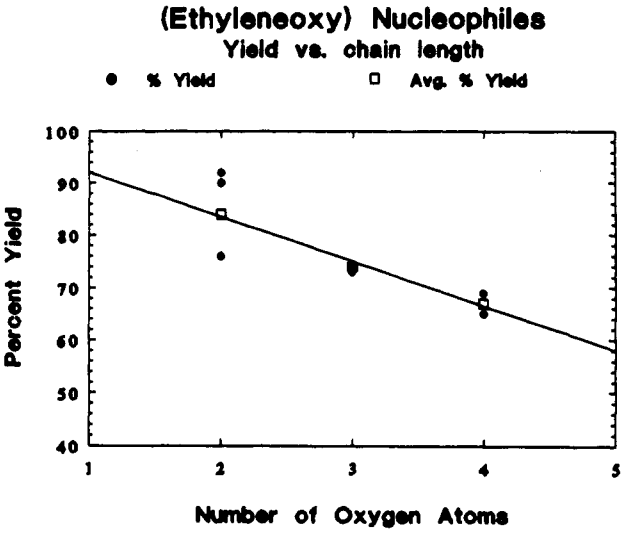
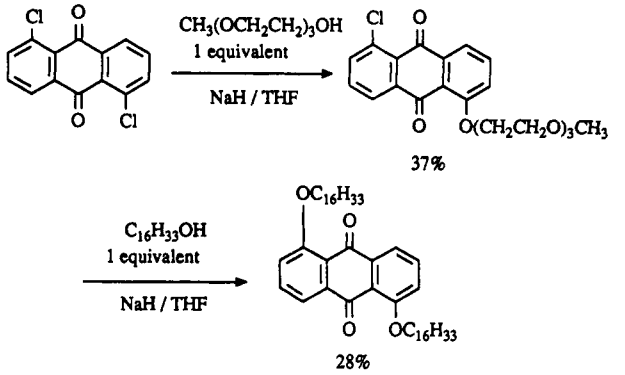
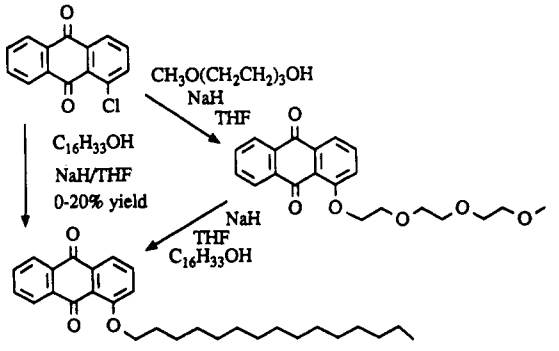


Figure 2.

was obtained as well as 37% of the desired material. The latter was then treated with a single equivalent of hexadecanol. In this case, a 28% (56% of the possible disubstituted product) yield of 1,8-bis(hexadecyloxy)anthraquinone was obtained. This suggested that the ethyleneoxy residue might be a better leaving group than chloride in this case.



From this result, it appeared that an ethyleneoxy-derived sidechain might readily be displaced under circumstances that proved unsuccessful for chloride. We have thus used poly(oxyethylene) alcohols and attempted to use other alcohols as catalysts for this reaction. The sequence involving triethylene glycol monomethyl ether proved successful and is illustrated below.



In this study, most reactions were run more than once and yields are expressed as a simple average and range. In cases where a yield value seemed out of line with other data, the independent data values are recorded although we recognize that (for example) in the group 33, 39, 77, the latter is probably an error. Substitution of simple alkoxide

Table III. Catalysis of 1-Chloroanthraquinone Substitution Reactions[a]

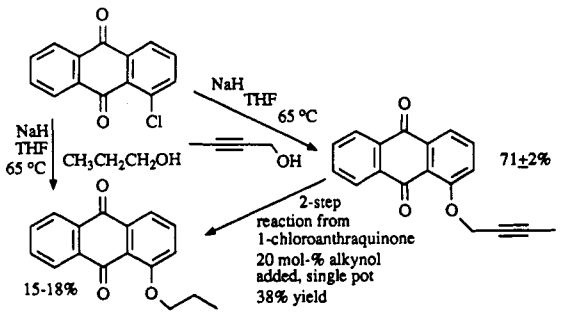
nucleophile	catalyst identity	mol %	% yield
n-C_3H_7OH	MeOEOEOEOMe	20,	21
n-C_3H_7OH	18-crown-6	20	11
n-$C_9H_{19}OH$	18-crown-6	20	13
n-$C_{16}H_{33}OH$	18-crown-6	20	15, 17
n-C_3H_7OH	MeOEOEOEOH	24	37
n-$C_9H_{19}OH$	MeOEOEOEOH	20	58
n-$C_{16}H_{33}OH$	MeOEOH	24	76
n-$C_{16}H_{33}OH$	MeOEOEOH	24	77, 80
n-C_3H_7OH	MeSEOH	24	43
n-$C_9H_{19}OH$	MeSEOH	24	71
n-$C_{16}H_{33}OH$	MeSEOH	24	70
n-C_3H_7OH	$HOEN(CH_2CH_2)_2O$	24	37
n-$C_9H_{19}OH$	$HOEN(CH_2CH_2)_2O$	24	48
n-$C_{16}H_{33}OH$	$HOEN(CH_2CH_2)_2O$	24	48
$(CH_3)_2CHOH$	MeOEOEOEOH	24	0
$C_6H_{11}OH$	MeOEOEOEOH	24	0
$Me_2CHCH_2CH_2OH$	MeOEOEOEOH	24	40
n-C_4H_9OH	$C_{16}H_{33}OH$	20	21
n-C_3H_7OH	$CH_3C{\equiv}CCH_2OH$	20	38
n-$C_9H_{19}OH$	2-butyn-1-ol	20	43
n-$C_{16}H_{33}OH$	2-butyn-1-ol	20	25

[a] NaH as base in THF, 4 h at reflux.

by another alkoxide showed no advantage over replacement of chloride. In contrast, displacement of an alkene ether or alkyne ether afforded 40–60% yields of product. Although alkenols were not as effective as alkynols in substituting chloride, yields from either nucleophile were similar when the nucleofuge was $CH_3(OCH_2CH_2)_3O^-$. Alkanols were the best nucleophiles when $CH_3(OCH_2CH_2)_3O^-$ was the nucleofuge.

Catalytic Displacements of 1-Substituted Anthraquinones. When we discovered that poly(ethyleneoxy) alcohols could displace chloride in high yield from anthraquinone and that they could themselves be displaced by various nucleophiles, the possibility of catalytic displacement suggested itself. This notion proved successful when 1.2 equiv of n-hexadecanol was used as nucleophile (ROH) and 20–24 mol % of diethylene glycol monomethyl ether was used as catalyst. Thus, 1-(hexadecyloxy)-anthraquinone was isolated in 78 ± 2% yield compared to 10% yield in the absence of any catalyst. Note that this yield is indistinguishable from that obtained when $HO(CH_2CH_2O)_3CH_3$ was the nucleophile (see Table I). The data for catalytic substitution reactions are summarized in Table III.

The observation that alkynols are good nucleophiles for substitution of 1-chloroanthraquinone was surprising, but its catalytic activity is even more remarkable. The sequence is illustrated below for the best case, i.e., a 2-butynol.

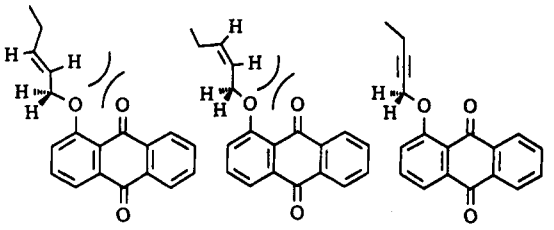


Observations and Speculation Concerning the Substitution Mechanism. When we began the studies described herein, the two possibilities that seemed most likely were a mechanism involving coordination and one involving electron transfer. EPR evidence failed to confirm the latter. The electron-transfer mechanism was therefore discarded.[21]

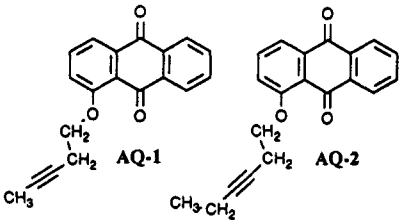
The basic facts of substitution are as follows: (i) Saturated alkoxides and olefinic alkoxides are very poor nucleophiles for the 1-chloroanthraquinone substitution reaction. (ii) Oxyanions derived from alkynols or alkoxyalkanols are good to excellent nucleophiles in this reaction. (iii) Triple-bond position is critical to the success of alkynol substitutions. (iv) The advantage of triple bonds and alkoxy substitution is also felt when either one is a leaving group replacing chloride. In such cases, even the poor nucleophiles (in this case) such as anions derived from alkanols and alkenols substitute at the anthraquinone 1-position. (v) Only two phenols were studied as nucleophiles, but in both cases reaction with 1-chloroanthraquinone proved successful.

A solid-state structure[21] in which an anthraquinone bis(podand) coordinated two cations suggested a coordination mechanism. The complement of this coordination/substitution mechanism is that the poly(oxyethylene) chain could do the same thing in reverse when it was the nucleofuge. Indeed, this mechanism may operate in the poly(ethylene glycol) case but it cannot operate when the nucleophiles contain no oxygen except hydroxyl. The contrast between the alkanols and alkenols on the one hand and the alkynols on the other is impossible to rationalize in terms of coordination as suggested for the ethylene glycol derivatives. This is also true, however, for the simple $-OCH_2CH_2OCH_3$ and $-OCH_2CH_2SCH_3$ derivatives. It is also difficult to see how a cation–coordination mechanism is relevant to the alkenes and alkynes.

Two differences between alkynols and both alkanols and alkenols are obvious. The linear C—C≡C—C unit is inherently rigid. It also has a relatively small steric demand. The difference in A values of ethyl, ethenyl, and ethynyl are, respectively, 1.7_5, 1.7_0, and 0.4_5. In the structure below are illustrated representations of 1-anthraquinone ethers in which the substituents are (E)-alkenyl, (Z)-alkenyl, and alkynyl. Of the three, the latter appears to be the least sterically congested.



In an effort to resolve this problem, we obtained solid-state structures of two anthraquinone derivatives: 3-pentynyl 1-anthraquinyl ether (**AQ-1**) and 3-hexynyl 1-anthraquinyl ether (**AQ-2**). Unfortunately, suitable crystals of the corresponding 2-butynyl ether could not be obtained. Structural drawings (based on the crystal structures, see Experimental Section) of these two compounds are shown below in a fashion intended to illustrate the arrangement of atoms in the solid state.



As expected from an examination of CPK atomic models, no unusual or potentially coordinating feature is apparent in **AQ-1** or **AQ-2**. Despite our efforts to do so, no Na^+ complex of these or any other alkynyl anthraquinyl ether was obtained.

It now seems unlikely that the coordination mechanism postulated for the (ethyleneoxy) nucleophiles is general. If such a mechanism is responsible for the high yields observed with poly(ethylene glycol) derivatives, we expect coordination to improve with chain length. This, in turn, should improve yields. The chain-length dependence of yields for ethyleneoxy derivatives clearly contradicts this (see Figure 2), although the slope is obviously shallow. Crude yields in several cases were checked by HPLC to show that the trend was not related to difficulty of isolation.

It is also interesting to note that when a catalytic reaction was attempted using *n*-propanol (NaH, THF, reflux) and 20 mol % of 18-crown-6, only 11% of 1-propoxyanthraquinone was isolated. Under comparable conditions, 20 mol % of added 2-[2-(2-methoxyethoxy)ethoxy]ethanol gave 1-propoxyanthraquinone in 37% yield, about the same as for alkyne catalysis. Likewise, $CH_3SCH_2CH_2OH$ afforded 43% of this product.

We thus conclude that both steric factors and coordination play a role in the present transformations. When poly(ethyleneoxy) or other coordinating side arms are present, substitution is dominated by their proximity. When no such coordination is possible, steric effects play an important role. The lack of steric bulk in the alkynes along with some small electronic effect (alkoxide anion stabilization due to proximate sp-hybridized orbitals) favor these species as nucleophiles and nucleofuges over either alkanols or alkenols. Why alkanols and alkenols should be more effective nucleophiles in the catalytic reaction, however, remains a mystery.

Finally, the two results with phenolic nucleophiles are striking. Even benzyl alcohol gave significantly (3-fold) better yields of substitution product than the other unsaturated alcohols (Table II). The benzene ring is of substantial size but does not coordinate alkali metal cations to any significant extent. Why phenols should be such excellent nucleophiles in this reaction also remains elusive.

Conclusions

A recent review of anthraquinone anthracycline synthesis includes a section on "nucleophilic additions to anthraquinones"[16] but no mention is made of anything akin to the present displacement process. Recent additions of sidechains to anthraquinone derivatives have involved displacement of fluoride (obtained from aminoanthraquinone by diazotization followed by the Schiemann reaction)[17] or by attack on a 2-halomethyl group.[6] The dearth of relevant examples suggests the need for direct substitution processes.

We have described here a survey of nucleophilic displacement reactions using 1-chloroanthraquinone as substrate. Alkanols and alkenols are poor nucleophiles but alkynols are better and ethyleneoxy derivatives are good. Phenols are also good nucleophiles in this reaction, although a limited data set supports that assertion. When the leaving group is either an alkynol or ethyleneoxy derivative, yields are much improved compared to chloride. The overall process may be made catalytic by using either in addition to the desired nucleophile. The reactions presented here are thus an important addition to known synthetic access in the anthraquinone system. Unfortunately, we have not been able to propose a unified mechanism to account for these successful and useful reactions.

Experimental Section

^1H NMR were recorded at either 60 or 400 MHz as approximately 10% by weight solutions in $CDCl_3$ and are reported in ppm (δ) downfield from internal Me_4Si. ^{13}C NMR were recorded at 20 or 100 MHz as noted above. Infrared spectra were recorded in KBr unless otherwise noted and were calibrated against the 1601 cm^{-1} band of polystyrene. Melting points were determined on a solid block device in open capillaries and are uncorrected. Thin-layer chromatographic (TLC) analyses were performed on aluminum oxide 60 F-254 neutral (type E) with a 0.2-mm layer thickness or on silica gel 60 F-254 with a 0.2-mm layer thickness. Preparative chromatography columns were packed with activated aluminum oxide (MCB 80-325 mesh, chromatographic grade, AX 611) or with Kieselgel 60 (70–230 mesh). Chromatotron chromatography was performed on 2-mm thick circular plates prepared from Kieselgel 60 PF-254.

All reactions were conducted under dry N_2 unless otherwise noted. All reagents were the best grade commercially available and were distilled, recrystallized, or used without further purification, as appropriate. Molecular distillation temperatures refer to the oven temperature of a Kugelrohr apparatus. Combustion analyses were performed by Atlantic Microlab, Inc., Atlanta, GA, and are reported as percents.

General Procedure of 1-Chloroanthraquinone Displacement. NaH (0.25 g, 60% in oil dispersion) was washed with hexane (distilled, dried over molecular sieves). As much hexane as possible was removed after stirring for ~15 min. THF (25 mL, dried over KOH, distilled from CaH_2 just before use) was added, and stirring and heating commenced. Then 5.12 mmol of alcohol, which was dissolved in THF (25 mL), was added dropwise and was brought to reflux. After 30 min, 1-chloroanthraquinone (4.12 mmol) in THF (100 mL) was added dropwise. The reaction mixture was stirred for 4 h under reflux temperature then cooled to room temperature and concentrated in vacuo. The residue was dissolved in CH_2Cl_2 and washed successively with water and brine. The organic phase was dried with $MgSO_4$, filtered, and concentrated. Column chromatography was followed using CH_2Cl_2 as eluting solvent. Occasionally, methanol or hexane was used to adjust the polarity of the eluting solvent. Normally, yellow crystals of the anthraquinone derivative were obtained after crystallization from ethanol.

Anthraquinone derivatives are described below. Since a compound might be obtained by more than one procedure, the reader is directed to the tables to determine the best synthesis.

1-Propoxyanthraquinone. Yield: 17 ± 2% (two runs). Mp: 150–151 °C. ^1H NMR: δ 1.0 (t, CH_3); 2.0 (q, CH_2); 4.1 (t, CH_2); 7.2–8.4 (m, 7 H). IR: 2950, 2880, 1675, 1580, 1440, 1320, 1260, 1230, 1060 cm^{-1}. Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.31. Found: C, 76.60; H, 5.35.

1-*n*-Butoxyanthraquinone. Yield: 18 ± 2% (two runs). Mp: 116–116.5 °C. ^1H NMR: δ 1.0 (t, CH_3); 1.9 (m, 4 H); 4.2 (t, CH_2); 7.2–8.3 (m, 7 H). IR: 2950, 2870, 1670, 1590, 1440, 1320, 1260, 1230, 1070 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.04; H, 5.76.

1-(*n*-Octyloxy)anthraquinone. Yield: 5%. Mp: 93–94 °C. ^1H NMR: δ 1.0 (t, CH_3); 1.5 (s, 14 H); 4.1 (t, CH_2); 7.2–8.3 (m, 7 H). IR: 2940, 2860, 1650, 1570, 1440, 1320, 1250, 1060 cm^{-1}. Anal. Calcd for $C_{22}H_{24}O_3$: C, 78.53; H, 7.20. Found: C, 78.41; H, 7.18.

1-(*n*-Nonyloxy)anthraquinone. Yield: 7 ± 2% (two runs). Mp: 88.5–89 °C. ^1H NMR: δ 1.0 (t, CH_3); 1.5 (s, 14 H); 4.1 (t, CH_2); 7.2–8.3 (m, 7 H). IR: 2920, 2860, 1670, 1580, 1430, 1310, 1250 cm^{-1}. Anal. Calcd for $C_{23}H_{26}O_3$: C, 78.83; H, 7.48. Found: C, 78.96; H, 7.49.

1-(*n*-Hexadecyloxy)anthraquinone. Yield: 10 ± 1% (two runs). Mp: 88.5–89 °C. ^1H NMR: δ 1.0 (t, CH_3); 1.3 (s, 28 H); 4.1 (t, CH_3); 7.2–8.3 (m, 7 H). IR: 2940, 2870, 1670, 1580, 1440, 1320, 1260, 1230, 1070 cm^{-1}. Anal. Calcd for $C_{30}H_{40}O_3$: C, 80.30; H, 9.00. Found: C, 80.31; H, 9.00.

1-(Isoamyloxy)anthraquinone. Yield: 40%. Mp: 92–93 °C. ^1H NMR: δ 1.0 (d, 6 H); 1.3 (s, 1 H); 1.9 (m, 2 H); 4.2 (t, 2 H); 7.2–8.3 (m, 7 H). IR: 2850, 1660, 1580, 1430, 1310, 1260 cm^{-1}. Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.44; H, 6.17.

1-(Allyloxy)anthraquinone. Yield: 6 ± 2% (six runs). Mp: 141–142 °C. ^{1}H NMR: δ 4.78 (d, 2 H); 5.40–6.15 (m, 3 H); 7.33–8.29 (m, 7 H). IR: 1660, 1590, 1310, 1280, 1275, 710 cm^{-1}. Anal. Calcd for $C_{17}H_{12}O_3$: C, 77.25; H, 4.59. Found: C, 77.02; H, 4.66.

1-(2-Butenyloxy)anthraquinone.[24] Yield: 6 ± 1% (two runs). Mp: 105–106 °C. ^{1}H NMR: δ 1.8 (m, CH_3); 4.7 (m, 2 H); 5.8–6.1 (m, CH=CH); 7.2–8.3 (m, 7 H). IR: 2940, 2870, 1670, 1590, 1440, 1320, 1265, 1230, 1070, 1020 cm^{-1}. Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.67; H, 5.08. Found: C, 77.59; H, 5.13.

1-((*E*)-2-Hexenyloxy)anthraquinone. Yield: 6 ± 2% (two runs). Mp: 108–109 °C. ^{1}H NMR: δ 1.0 (t, CH_3); 1.4 (q, CH_2); 2.1 (q, CH=CH); 4.7 (m, CH_2); 7.2–8.3 (m, 7 H). IR: 2940, 2870, 1670, 1590, 1440, 1320, 1265, 1230, 1050 cm^{-1}. Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 4.49. Found: C, 80.17; H, 4.52.

1-((*E*)-2-Tridecyloxy)anthraquinone. Yield: 5 ± 1% (two runs). Mp: 90–91 °C. ^{1}H NMR: δ 1.0 (t, CH_3); 1.2–1.4 (m, 16 H); 2.1–2.2 (q, CH_2); 4.7 (t, CH_2); 5.8–6.1 (m, CH=CH); 7.3–8.3 (m, 7 H). IR: 2940, 2870, 1670, 1600, 1450, 1320, 1270, 1235, 1100, 1050 cm^{-1}. Anal. Calcd for $C_{27}H_{32}O_3$: C, 80.15; H, 7.99. Found: C, 80.14; H, 8.03.

1-(Benzyloxy)anthraquinone. Yield: 22 ± 2% (two runs). Mp: 177–178 °C. ^{1}H NMR: δ 5.4 (s, CH_2); 7.3–8.2 (m, 12 H). IR: 3080, 1670, 1590, 1440, 1320, 1265, 1235, 1050, 1020 cm^{-1}. Anal. Calcd for $C_{21}H_{14}O_3$: C, 80.24; H, 4.49. Found: C, 80.03; H, 4.47.

1-Phenoxyanthraquinone. Yield: 66%. Mp: 141–142 °C. ^{1}H NMR: δ 7.1–8.4 (m, 12 H). IR: 1640, 1580, 1430, 1310, 1240, 1210 cm^{-1}. Anal. Calcd for $C_{20}H_{12}O_3$: C, 79.99; H, 4.03. Found: C, 79.90; H, 4.08.

1-(4-Methylphenoxy)anthraquinone. Yield: 61%. Mp: 136–137 °C. ^{1}H NMR: δ 2.3 (s, CH_3); 7.0–8.3 (m, 11 H). IR: 1670, 1590, 1440, 1320, 1260, 1210, 1010 cm^{-1}. Anal. Calcd for $C_{21}H_{14}O_3$: C, 80.24; H, 4.49. Found: C, 80.17; H, 4.52.

1-(2-Butynyloxy)anthraquinone. Yield: 71 ± 2% (seven runs). Mp: 194–195 °C. ^{1}H NMR: δ 1.6 (t, CH_3); 4.7 (s, CH_2); 7.2–7.8 (m, 7 H). IR: 2940, 2860, 2260, 1690, 1600, 1460, 1440, 1335, 1290, 1250, 1070 cm^{-1}. Anal. Calcd for $C_{18}H_{12}O_3$: C, 78.24; H, 4.39. Found: C, 78.02; H, 4.35.

1-(2-Pentynyloxy)anthraquinone. Yield: 61 ± 7% (three runs). Mp: 121–122 °C. ^{1}H NMR: δ 1.0 (t, CH_3); 2.1 (q, CH_2); 7.0–8.4 (m, 7 H). IR: 2940, 2870, 2260, 1650, 1565, 1420, 1300, 1235, 1210, 1040 cm^{-1}. Anal. Calcd for $C_{19}H_{14}O_3$: C, 78.60; H, 4.87. Found: C, 78.50; H, 4.87.

1-(2-Hexynyloxy)anthraquinone. Yield: 44 ± 1% (two runs). Mp: 101–102 °C. ^{1}H NMR: δ 1.0 (t, CH_3); 1.2–1.8 (q, CH_2); 2.1 (t, CH_2); 4.7 (t, CH_2); 7.2–8.4 (m, 7 H). IR: 2940, 2870, 2280, 1650, 1565, 1420, 1280, 1240, 1210, 1040, 1000 cm^{-1}. Anal. Calcd for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30. Found: C, 78.95; H, 5.34.

1-(3-Pentynyloxy)anthraquinone. Yield: 39 ± 3% (two runs). Mp: 171–172 °C. ^{1}H NMR: δ 1.6 (t, CH_3); 2.5–3.1 (m, 2 H); 4.5 (t, CH_2); 7.2–8.4 (m, 7 H). IR: 2940, 2870, 2250, 1675, 1590, 1450, 1335, 1290, 1250, 1080 cm^{-1}. Anal. Calcd for $C_{19}H_{14}O_3$: C, 78.61; H, 4.86. Found: C, 78.47; H, 4.90.

1-(3-Hexynyloxy)anthraquinone. Yield: 32 ± 5% (three runs). Mp: 137–138 °C. ^{1}H NMR: δ 1.0 (t, CH_3); 2.0–2.3 (m, 2 H); 2.5–3.0 (m, 2 H); 4.2 (t, CH_2); 7.1–8.2 (m, 7 H). IR: 2940, 2870, 1650, 1565, 1440, 1300, 1230, 1160, 1050 cm^{-1}. Anal. Calcd for $C_{20}H_{16}O_3$: C, 78.92; H, 5.31. Found: C, 79.01; H, 5.33.

1-(3-Heptynyloxy)anthraquinone. Yield: 39 ± 3% (two runs). Mp: 121–122 °C. ^{1}H NMR: δ 1.0 (t, CH_3); 1.3–1.7 (q, 2 H); 2.1 (t, 2 H); 2.8 (m, 2 H); 4.2 (t, CH_2); 7.1–8.3 (m, 7 H). IR: 2940, 2870, 1650, 1560, 1420, 1285, 1240, 1210, 1030 cm^{-1}. Anal. Calcd for $C_{21}H_{18}O_3$: C, 79.23; H, 5.70. Found: C, 79.11; H, 5.73.

1-(3-Nonynyloxy)anthraquinone. Yield: 33 ± 1% (two runs). Mp: 109.5–110 °C. ^{1}H NMR: 0.9 (t, CH_3); 1.4 (m, 6 H); 2.1 (m, 2 H); 2.8 (m, 2 H); 4.2 (t, CH_2); 7.2–8.4 (m, 7 H). IR: 2940, 2870, 1650, 1575, 1430, 1300, 1250, 1230, 1050 cm^{-1}. Anal. Calcd for $C_{23}H_{22}O_3$: C, 79.74; H, 6.40. Found: C, 79.55; H, 6.48.

1-(4-Hexynyloxy)anthraquinone. Yield: 32 ± 5% (two runs). Mp: 152.5–153 °C. ^{1}H NMR: 1.5–2.5 (m, 7 H); 4.2 (t, CH_2); 7.2–8.2 (m, 7 H). IR: 2910, 1850, 1640, 1550, 1420, 1290, 1235, 1205, 1040 cm^{-1}. Anal. Calcd for $C_{20}H_{16}O_3$: C, 78.92; H, 5.30. Found: C, 78.93; H, 5.34.

1-(4-Heptynyloxy)anthraquinone. Yield: 31%. Mp: 118.5–119.5 °C. ^{1}H NMR: δ 1.0 (t, CH_3); 1.6–2.7 (m, 6 H); 4.2 (t, CH_2); 7.1–8.4 (m, 7 H). IR: 2900, 2870, 1650, 1565, 1420, 1290, 1240, 1210, 1040 cm^{-1}. Anal. Calcd for $C_{21}H_{18}O_3$: C, 79.22; H, 5.70. Found: C, 79.24; H, 5.71.

1-(5-Heptynyloxy)anthraquinone. Yield: 14%. Mp: 104–104.5 °C. ^{1}H NMR: δ 1.6–2.4 (m, 9 H); 4.2 (t, CH_2); 7.2–8.4 (m, 7 H). IR (KBr): 2940, 2870, 1650, 1585, 1440, 1310, 1260, 1240, 1060, 1000 cm^{-1}. Anal. Calcd for $C_{21}H_{18}O_3$: C, 79.23; H, 5.70. Found: C, 78.93; H, 5.49.

1-(5-Octynyloxy)anthraquinone. Yield: 27%. Mp: 101.5–102.5 °C. ^{1}H NMR: δ 1.0 (t, CH_3); 1.5–2.0 (m, 8 H); 4.2 (t, CH_2); 7.2–8.3 (m, 7 H). IR: 2940, 2870, 1640, 1560, 1420, 1300, 1240, 1040 cm^{-1}. Anal. Calcd for $C_{22}H_{20}O_3$: C, 79.50; H, 6.06. Found: C, 79.28; H, 6.01.

1-(5-Nonynyloxy)anthraquinone. Yield: 18 ± 4% (three runs). Mp: 94–95 °C. ^{1}H NMR: δ 1.0 (t, CH_3); 1.4–2.4 (m, 10 H); 4.2 (t, CH_2); 7.2–8.3 (m, 7 H). IR: 2940, 2870, 1640, 1560, 1420, 1300, 1240, 1040 cm^{-1}. Anal. Calcd for $C_{23}H_{22}O_3$: C, 79.74; H, 6.40. Found: C, 79.47; H, 6.47.

1-(2-Methoxyethoxy)anthraquinone.[16] Yield: 91 ± 1% (three runs). Mp: 146–147 °C. ^{1}H NMR: 3.5 (t, CH_3); 3.8 (q, CH_2); 4.3 (q, CH_2); 7.2–8.3 (m, 7 H). IR: 2940, 2870, 1690, 1600, 1460, 1320, 1280, 1240, 1140, 1070, 1040, 1010 cm^{-1}.

1-[2-(2-Methoxyethoxy)ethoxy]anthraquinone. Yield: 74 ± 1% (three runs). Mp: 70–71 °C. ^{1}H NMR: δ 3.3–4.4 (m, 11 H); 7.2–8.3 (m, 7 H). IR: 2940, 2870, 1670, 1590, 1450, 1320, 1275, 1240, 1140, 1070, 1040, 1000 cm^{-1}. Anal. Calcd for $C_{19}H_{18}O_5$: C, 69.92; H, 5.57. Found: C, 69.83; H, 5.60.

1-[2-[2-[2-(Octadecyloxy)ethoxy]ethoxy]ethoxy]anthraquinone. Yield: 80 ± 2% (two runs). Mp: 72–73 °C. ^{1}H NMR: 0.8–1.7 (m, 35 H); 3.2–4.4 (m, 20 H); 7.2–8.3 (m, 7 H). IR: 2940, 2870, 1690, 1600, 1460, 1450, 1320, 1270, 1250, 1140, 1100 cm^{-1}. Anal. Calcd for $C_{40}H_{60}O_7$: C, 73.57; H, 9.28. Found: C, 73.41; H, 9.31.

1-[2-(Methylthio)ethoxy]anthraquinone. Yield: 58%. Mp: 111–112 °C. ^{1}H NMR: 2.3 (s, 3 H); 3.1 (t, 2 H); 4.4 (t, 2 H); 7.3–8.3 (m, 7 H). IR: 1630, 1570, 1430, 1310, 1240, 1190 cm^{-1}. Anal. Calcd for $C_{17}H_{14}SO_3$: C, 68.44; H, 4.73. Found: C, 68.28; H, 4.76.

1-(2-Piperidinoethoxy)anthraquinone. Yield: 64%. Mp: 76–77 °C. ^{1}H NMR: 1.7 (m, 6 H); 2.7 (m, 4 H); 3.0 (t, 2 H); 4.3 (t, 2 H); 7.2–8.2 (m, 7 H). IR: 1630, 1580, 1420, 1310, 1230, 1150 cm^{-1}. Anal. Calcd for $C_{21}H_{21}NO_3$: C, 75.20; H, 6.31; N, 4.18. Found: C, 75.51; H, 6.34; N, 4.13.

1-(2-Morpholinoethoxy)anthraquinone. Yield: 34%. Mp: 123–124 °C. ^{1}H NMR: 2.4–3.1 (m, 6 H); 3.8 (m, 4 H); 4.3 (t, 2 H); 7.3–8.3 (m, 7 H). IR: 2930, 2830, 1670, 1580, 1440, 1320, 1270, 1100 cm^{-1}. Anal. Calcd for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68; N, 4.15. Found: C, 70.92; H, 5.74; N, 4.13.

General Procedure for Catalytic Displacement of 1-Chloroanthraquinone. The procedure was exactly the same as the preceding procedure with the exception that a solution of the alcohol and 20 mol % of the chosen catalyst in THF (50 μL) was added dropwise.

Solid-State Structure Analyses. Samples suitable for single-crystal X-ray analysis were grown by slow cooling of a warm saturated solution, by evaporation of a saturated solution, or by vapor diffusion. Details are included in the supplementary material.

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Registry No. 1, 82-44-0; 2 (R = C_3H_7), 81386-67-6; 2 (R = $C_{16}H_{33}$), 126156-70-5; 2 (R = (*E*)-2-butenyl), 136863-69-9; 2 (R = (*Z*)-2-butenyl), 136892-83-6; 2 (R = $CH_3C{\equiv}CCH_2$), 136863-70-2; 2 (R = OEOMe), 126156-71-6; 2 (R = OESMe), 136863-71-3; 2 (R = OEOEOEOMe), 104779-01-3; 2 (R = C_4H_9), 136863-72-4; 2 (R = C_8H_{17}), 127696-14-4; 2 (R = C_9H_{19}), 126156-72-7; 2 (R = $CH_2{=}CHCH_2$), 64302-83-6; 2 (R = (*E*)-2-hexenyl), 136863-73-5; 2 (R = $C_6H_5CH_2$), 79352-68-4; 2 (R = $CH_3CH_2C{\equiv}CCH_2$), 136863-74-6; 2 (R = $CH_3(CH_2)_2C{\equiv}CCH_2$), 136863-75-7; 2 (R = $CH_3(CH_2)_2C{\equiv}C(CH_2)_2$), 136863-76-8; 2 (R = $CH_3(CH_2)_4C{\equiv}C(CH_2)_2$), 136863-77-9; 2 (R = $CH_3C{\equiv}C(CH_2)_3$), 136863-78-0; 2 (R = $CH_3CH_2C{\equiv}C(CH_2)_3$), 136863-79-1; 2 (R = $CH_3C{\equiv}C(CH_2)_4$),

136863-80-4; **2** (R = $CH_3CH_2C{\equiv}C(CH_2)_4$), 136863-81-5; **2** (R = $CH_3(CH_2)_2C{\equiv}C(CH_2)_4$), 136863-82-6; **2** (R = $CH_3OCH_2CH_2O(CH_2)_2$), 104779-00-2; **2** (R = $C_{18}H_{37}O(CH_2CH_2O)_3(CH_3)_2$), 136863-83-7; **2** (R = $(CH_2)_5N(CH_2O_2)$, 102475-03-6; **2** (R = $O(CH_2CH_2)_2N)CH_2)_2$), 102237-91-2; **2** (R = 3-butenyl), 127696-13-3; **2** (R = (*Z*)-2-hexenyl), 136863-84-8; **2** (R = (*E*)-2-tridecenyl), 136863-85-9; **2** (R = $CH_2CH_2CHMe_2$), 126156-74-9; **2** (R = ⟨15⟩CH_2), 104084-69-7; **2** (R = ⟨18⟩CH_2), 118921-90-7; **2** (R = 4-MeC_6H_4), 125507-32-6; **2** (R = Ph), 17613-65-9; AQ-1, 136863-86-0; AQ-2, 136863-87-1; $CH_3(CH_2)_2C{\equiv}C(CH_2)_4OH$, 68274-96-4; $C_{18}H_{37}O(CH_2CH_2O)_3H$, 4439-32-1; *n*-$C_3H_7OH$, 71-23-8; *n*-$C_4H_9OH$, 71-36-3; *n*-$C_8H_{17}OH$, 111-87-5; *n*-$C_9H_{19}OH$, 143-08-8; *n*-$C_{16}H_{33}OH$, 36653-82-4; $CH_2{=}CHCH_2OH$, 107-18-6; (*E*)-$CH_3CH{=}CHCH_2OH$, 504-61-0; (*Z*)-$CH_3CH{=}CHCH_2OH$, 4088-60-2; $C_6H_5CH_2OH$, 100-51-6; $CH_3C{\equiv}CH_2OH$, 764-01-2; $CH_3CH_2C{\equiv}CCH_2OH$, 6261-22-9; $CH_3(CH_2)_2C{\equiv}CCH_2OH$, 764-60-3; $CH_3C{\equiv}C(CH_2)_2OH$, 10229-10-4; $CH_3CH_2C{\equiv}C(CH_2)_2OH$, 1002-28-4; $CH_3(CH_2)_2C{\equiv}C(CH_2)_2OH$, 14916-79-1; $CH_3(CH_2)_4C{\equiv}C(CH_2)_2OH$, 31333-13-8; $CH_3C{\equiv}C(CH_2)_3OH$, 928-93-8; $CH_3CH_2C{\equiv}C(CH_2)_3OH$, 42397-24-0; $CH_3C{\equiv}C(CH_2)_4OH$, 58944-42-6; $CH_3CH_2C{\equiv}C(CH_2)_4OH$, 41547-21-1; $CH_3OCH_2CH_2OH$, 109-86-4; MeOEOEOH, 111-77-3; MeOEOEOEOH, 112-35-6; MeSEOH, 5271-38-5; $(CH_2)_5NCH_2CH_2OH$, 3040-44-6; $O(CH_2CH_2)_2NCH_2CH_2OH$, 622-40-2; $Me_2CHCH_2CH_2OH$, 123-51-3; $(CH_3)_2CHOH$, 67-63-0; $C_6H_{11}OH$, 108-93-0; MeOEOEOEOMe, 112-49-2; 18-crown-6, 17455-13-9; phenol, 108-95-2; 4-methylphenol, 106-44-5; (*E*)-2-hexanol, 928-95-0; 1,5-dichloroanthraquinone, 82-46-2; (*Z*)-2-hexenol, 928-94-9; (*E*)-2-tridecenol, 74962-98-4; 1,5-bis(hexadecyloxy)anthraquinone, 136892-84-7; 3-butenol, 627-27-0; 1-chloro-5-[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]anthraquinone, 136863-88-2.

Supplementary Material Available: Solid-state experimental and supplementary references, ORTEP plots and details, and ^1H NMR spectra (65 pages). Ordering information is given on any current masthead page.

Regioselectivity of Rhodium(II)-Catalyzed Decomposition of 1-Alkyl-1-(diazoacetyl)alkenes. Synthesis of 2-Alkyl-2-cyclopentenones and 2-Alkylidenecyclopentanones

Paolo Ceccherelli, Massimo Curini,* Maria Carla Marcotullio, and Ornelio Rosati

Istituto de Chimica Organica, Facoltà di Farmacia, Università degli Studi, 06100 Perugia, Italy

Ernest Wenkert*

Department of Chemistry (0506), University of California—San Diego, La Jolla, California 92093

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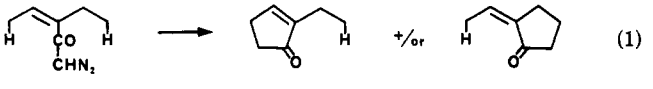
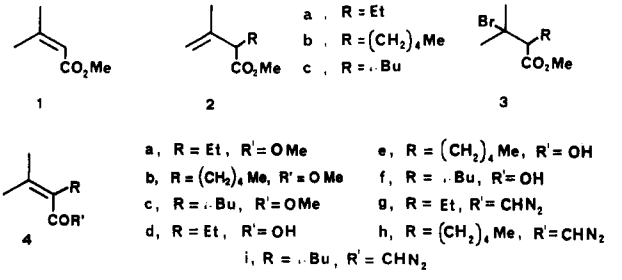
The synthesis of 1-alkyl-1-(diazoacetyl)alkenes and their dirhodium tetraacetate catalyzed transformation into 2-cyclopentenones and 2-alkylidenecyclopentanones are described. The competitive, intramolecular carbon–hydrogen insertion at two γ centers is discussed.

Recently there was introduced a new cyclopentenone synthesis based on rhodium(II)-catalyzed, intramolecular γ-carbon–hydrogen insertion of diazomethyl ketones derived from α,β-unsaturated acids.[1] Whereas the reaction revealed interesting features of stereochemistry (in some of the cases studied), it was unidirectional in view of the rigidity of the substrates and the proximity of the carbenoid carbon to only one γ-carbon center. It now became of interest to investigate the chemical behavior of diazomethyl ketones derived from α-alkyl α,β-unsaturated acids, thus exposing two γ-carbon sites to the carbenoid center and raising the question of regioselectivity of the reaction (eq 1). Nine cases, representing every combination of γ-methyl, γ-methylene, and γ-methine examples, were submitted to scrutiny.



(1)

Preparation of α,β-Unsaturated Acids. Alkylation of methyl senecioate (**1**)[2] with ethyl iodide, *n*-pentyl iodide, and isobutyl bromide under the influence of lithium diisopropylamide (LDA) furnished esters **2a**, **2b**, and **2c**, respectively. Treatment of the esters with hydrogen bromide in chloroform afforded bromo esters **3a**, **3b**, and **3c**, respectively, whose dehydrohalogenation with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in benzene[3] gave esters **4a**, **4b**, and **4c**, respectively. Finally, demethylation of these esters with trimethylsilyl iodide in carbon tetrachloride[4] yielded acids **4d**, **4e**, and **4f**, respectively.



The remaining α,β-unsaturated acids were prepared in a different manner, as follows. Triethyl α-phosphonobutyrate (**5a**),[5] triethyl α-phosphonohexanoate (**5b**), and methyl α-(diethoxyphosphinyl)isocaproate (**5c**) were obtained from their α-bromo ester equivalents and trialkyl

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