bromine that can be manipulated conveniently, precisely, and safely.

The high stability of Dabco·$2Br_2$, however, is accompanied by a low solubility in a variety of solvents and a low reactivity of its bromine. This undoubtedly accounts for the fact that this complex has not been explored as a new reagent with general application in chemical synthesis. We have found, however, that, if Dabco·$2Br_2$ is employed with additional Dabco the reactivity of the bromine is enhanced, perhaps as a result of conversion of Dabco·$2Br_2$ into a more soluble species, or one that contains a more active form of bromine.[4] Thus, we are able to report our preliminary results for the oxidation of alcohols by Dabco·$2Br_2$ in Table I. Table I reflects the optimum conditions for oxidations found thus far (see supplementary material).

The alcohol oxidations were planned on the assumed stoichiometries of eq 1 or 2 illustrated by the oxidation of benzyl alcohol.

$$2C_6H_5CH_2OH + \text{Dabco}\cdot 2Br_2 + 3\text{Dabco} = 2C_6H_5CHO + 4\text{Dabco}\cdot HBr \quad (1)$$

$$2C_6H_5CH_2OH + \text{Dabco}\cdot 2Br_2 + \text{Dabco} = 2C_6H_5CHO + 2\text{Dabco}\cdot 2HBr \quad (2)$$

For these exploratory studies the oxidations were carried out with 100% excess alcohol. Thus, with Dabco·$2Br_2$ as the limiting agent, an equimolar mixture of unreacted alcohol and product aldehyde or ketone should be obtained for a 100% yield. A material balance was calculated as the percent of the starting alcohol accounted for as product or unreacted alcohol. Generally, the material balance is very good which means that few competing reactions are occurring. Thus, in spite of the slow rates, the reaction yields mainly one product. This is particularly important in deciphering the mechanism of these reactions and other oxidations of alcohols by active bromine.[5] The oxidation of secondary alcohols by bromine in the presence of silver salts gives ketones and/or tetrahydrofurans depending on the reaction conditions.[6] In our studies, no GLC product peaks other than the expected aldehyde or ketone were observed; however, we have not yet rigorously determined that small yields of other products are observable under our conditions of analysis. The very low yields of aldehydes from the primary alcohols suggest that Dabco·$2Br_2$ with added Dabco can be used as a selective oxidizing agent for secondary and benzylic -OH groups.[7,8]

Materials. All alcohols, solvents, and bromine were analytical reagents or spectroquality materials and were used without further purification. Dabco, obtained as a gift from The Chemical Additives Division of Air Products and Chemicals, Inc., was purified by distillation with benzene to remove water, precipitation of Dabco by addition of hexane to the dry benzene residue, followed by recrystallization two or three times from dry benzene/hexane. Dabco·$2Br_2$ was prepared in stock quantities by adding a solution of 10 mL of Br_2 (5% excess) in 200 mL of CCl_4 dropwise over a period of 1–2 h to a vigorously stirred solution of 10.4 g of Dabco in 200 ml of CCl_4. After the mixture stirred for 30 min, the complex was collected in a sintered-glass funnel, washed twice with CCl_4, and placed on a watch glass to dry for 24 h. The complex is very insoluble in a variety of common solvents and cannot be recrystallized. No special precautions are necessary to handle or store the complex.

General Procedure. To a mixture of 0.5 mmol of Dabco·$2Br_2$ and 1.5 mmol of Dabco was added 2.0 mmol of alcohol and 2.0 mL of solvent. The reaction flask was fitted with a serum cap for low temperature runs and a reflux condenser with $CaCl_2$ drying tube for high temperature runs. The flask was wrapped with aluminum foil to keep out light. Under constant magnetic stirring at the temperature indicated by Table I, the reaction was allowed to proceed until the yellow color of the solid complex changed to the white color of the solid Dabco hydrobromide.[9] Then, at room temperature the reaction mixture was filtered through a sintered-glass funnel to collect the Dabco hydrobromide solid which was washed with solvent. To the filtrate was added an internal standard (1.0 mmol of chlorobenzene or bromobenzene) and solvent to afford a 10-ml total volume. This solution was then analyzed by GLC for unreacted alcohol and product ketone or aldehyde by the usual procedure which involves relative peak areas, an internal standard, and a standard solution.

Acknowledgment. Financial support from Research Corporation, The Dreyfus Foundation, and National Science Foundation is gratefully appreciated.

Supplementary Material Available. Thirteen additional entries to Table I including results for other solvents (C_6H_6, $CHCl_3$, CCl_4, CH_3OH) and additional reactions in CH_3CN and CH_2Cl_2 at different temperatures and molar ratios of reactants (1 page). Ordering information is given on any current masthead page.

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Larry K. Blair,* Jonathon Baldwin
William C. Smith, Jr.
Department of Chemistry, Berea College
Berea, Kentucky 40404

Received January 5, 1977

Acidities of Anilines and Toluenes

Summary: The p*K*s in dimethyl sulfoxide solution of *p*-CN, *p*-$PhSO_2$, *p*-PhCO, *p*-F_3CSO_2, and *p*-NO_2 toluenes have been found to plot linearly against the p*K*s of the corresponding anilines; from these data, and the Hammett ρ for meta-substituted anilines (ρ = 5.67), it is estimated that ρ for substituted toluenes is ~12 and that the p*K* for toluene in a dipolar aprotic solvent is ~42.

Sir: Acidity data are sparse for anilines and toluenes, two fundamental classes of very weak organic acids. Absolute acidities for a number of meta- and para-substituted anilines have been measured potentiometrically in dimethyl sulfoxide (Me_2SO),[1,2] and by the H_- technique in Me_2SO–H_2O mixtures.[3] Relative acidities of a number of anilines have been determined in liquid ammonia,[4a] and these have been put on an absolute scale.[4b]

Table I. Equilibrium Acidities of Anilines and Toluenes in Dimethyl Sulfoxide at 25 °C

Substituent	Anilines, pK^a	Toluenes, pK^b
m-Me	31.0	
H	30.7	
m-MeO	30.5	
m-Cl	28.5[c]	
m-Br	28.4	
m-CF_3	28.2[d]	
m-CN	27.5	
p-$MeSO_2$	25.6	
p-CN	25.3[e]	30.8 ± 0.1[f]
p-$PhSO_2$	24.9	29.8 ± 0.02
p-PhCO	24.4	26.9 ± 0.1
p-F_3CSO_2	21.8	24.0 ± 0.2[f]
p-NO_2	20.9	20.4 ± 0.2[f]

[a] Three point titrations with two or more indicators (or standard acids);[11] agreement was generally better than ±0.05 p*K* units. [b] Titration with two or more indicators (or standard acids).[11] [c] Lit.[3] 25.63; lit.[2] 26.7. [d] Lit.[3] 25.40. [e] Lit.[3] 22.68. [f] Absorbance readings drifted.

Estimates of the "p*K*" of toluene[5] based on kinetic acidities range from 32 to 59.[6-9] The most reliable value of this type given to date appears to be the ion-pair p*K* of 41 in cyclohexylamine ($C_6H_{11}NH_2$) based on an extrapolation using a Brønsted plot.[9,10] Estimates from extrapolations based on measurements of absolute equilibrium acidities in Me_2SO solution place the p*K* of toluene in a dipolar aprotic solvent in the range 43–45.[12] Determinations of absolute acidities in Me_2SO for aniline[13] and some of its derivatives and for five para-substituted toluenes have now provided us with a new method of estimating the acidity of toluene in a dipolar aprotic solvent, and of determining the sensitivity of its acidity to substituent changes in the benzene ring.

The absolute acidities of aniline and five of its meta derivatives reported in Table I allowed us to derive a Hammett plot for this series ($\rho = 5.67 \pm 0.07$; $r = 0.9996$).[14] Toluene is much too weak an acid to be measured in Me_2SO, but measurements were obtained for five para-substituted toluenes (Table I). A plot of the p*K*s for these toluenes against the p*K*s of the corresponding anilines is linear (Figure 1; $r = 0.97$, slope $= 2.1 \pm 0.3$). Multiplication of the slope of this line by the ρ for meta-substituted anilines, gives an estimate of ρ for the equilibrium acidities of toluenes in Me_2SO ($\rho \simeq 12$). The p*K* of toluene in a dipolar aprotic solvent is estimated from the intercept of the line to be ~42 (Figure 1). The relative ρ values for toluenes and anilines show that the acidities of toluenes are over six orders of magnitude more sensitive to substituent effects than are the acidities of anilines. (As a consequence, it turns out that, although aniline is over 11 p*K* units more acidic than toluene, *p*-nitroaniline is slightly *weaker* than *p*-nitrotoluene in Me_2SO.) This huge difference is understandable since for anilines the parent acids, as well as their conjugate bases, are stabilized by resonance interactions with ring substituents, whereas for toluenes only the conjugate base can enter into such resonance interactions. It is indeed remarkable, for this reason, to find at least a rough correlation in substituent effects, even in situations where conjugative interactions are maximized (Figure 1). This suggests that not only are the resonance interactions between substituents in the corresponding $GC_6H_4CH_2^-$ and $GC_6H_4NH^-$ anions proportional, but that the resonance interactions in the corresponding $GC_6H_4NH_2$ molecules and $GC_6H_4NH^-$ anions are also proportional.

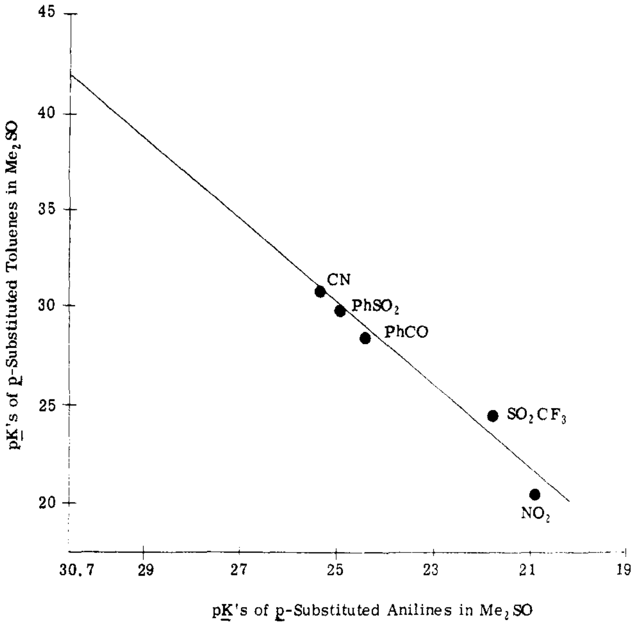

Figure 1. Plot of p*K*s for para-substituted toluenes vs. p*K*s for the corresponding para-substituted anilines.

The ρ of 12 for toluenes is remarkably large. Note, for example, that ρ_k for tritium exchange rates of toluenes with $C_6H_{11}NHLi$ in $C_6H_{11}NH_2$ is only 4.0.[15] Using the Brønsted α of 0.31 indicates, however, that the ion-pair ρ_K in $C_6H_{11}NH_2$ is ~13 ($\rho_K = \rho_k/\alpha$).[10] These data provide a new perspective with regard to the sensitivity of benzylic carbanions to substituent effects, and syntheses and mechanisms involving such anions. For example, in deducing the degree of carbanion formation in the transition state for "concerted" base-initiated eliminations with β-arylethyl halides, and the like, $ArCH_2CH_2Z$, in hydroxylic solvents a ρ of 4 to 5 is assumed for "carbanion formation".[16] These hydrogen-bonded and counterion-stabilized carbanions are evidently many orders of magnitude less sensitive to aryl substituent effects than are Me_2SO-solvated carbanions. With regard to synthesis possibilities we note, for example, that *p*-PhCO- and *p*-$PhSO_2$-substituted toluenes have acidities in Me_2SO (Table I) that do not differ greatly from those of analogues where the electron-withdrawing group is attached directly to the methyl group (e.g., $PhCOCH_3$, 24.7; CH_3COCH_3, 26.5; $PhSO_2CH_3$, 29.0; $CH_3SO_2CH_3$, 31.1).[11]

Acknowledgment. The authors wish to express their appreciation to the National Science Foundation for support of this work.

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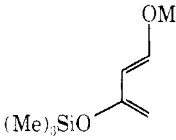
F. G. Bordwell,* Donald Algrim, Noel R. Vanier
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Received November 29, 1976

A Diels-Alder Route to Functionalized Cyclohexadienones

Summary: The diene 1-phenylseleno-2-trimethylsilyloxy-4-methoxy-1,3-butadiene provides a direct route to 4-acyl-4-substituted cyclohexadienones.

Sir: Recently our laboratory has been investigating the preparation and use of new dienes for Diels-Alder reactions. The dienes are so arranged as to impart to their cycloadducts ready-made handles for the elaboration of functionality which is otherwise difficultly accessible. Toward this end, we have prepared and demonstrated the utility of enophiles **1**[1-3] and **2**.[4] In the consequence of its overall cycloaddition with olefins, diene **1** is a functional equivalent of $^{+}CH{=}CHC(O)CH_2^{-}$. Similarly, diene **2** is a latent version of $^{+}C(O)CH_2C(O)CH_2^{-}$.



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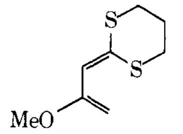
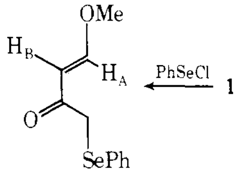


2

Some other very interesting dienes have been reported from a variety of sources.[5]

In the light of the value of α-phenylseleno ketones in the generation of enones, as demonstrated through the elegant research of Reich,[6] and Sharpless,[7] and Grieco,[8] we have studied the possibility of incorporating a phenylseleno grouping into a properly constructed enophile, with the objective of generating the requisite array for the synthesis of 4-acyl-4-substituted cyclohexadienones of the type **5**. Such compounds, which have intriguing possibilities for various synthetic objectives, were virtually unknown.[9] Toward this end, we have prepared 1-phenylseleno-2-trimethylsilyloxy-4-methoxy-1,3-butadiene (**4**) and studied its value in Diels-Alder reactions.

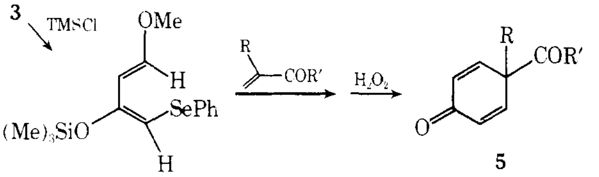
Compound **3**[10a] was obtained in 82% yield by the virtually instantaneous reaction of diene **1** with phenylselenenyl chloride in benzene at room temperature.[11] Resilylation of **3** under the conditions of Kitahara[1] afforded an 80% yield of a diene[12a] [$\lambda_{max}(CHCl_3)$ 3.31, 3.37, 3.45, 3.52, 6.10, 6.31 μm; $\delta(CDCl_3)$ 0.30 (s, 9), 3.62 (s, 3), 5.52 (d, $J = 13$ Hz, 1), 5.60 (s, 1), 6.84 (d, $J = 13$ Hz, 1), 7.2–7.6 (m, 5) ppm]. This compound could not be purified by distillation or chromatography but was used successfully in crude form.



3

$J_{AB} = 13$ Hz

Within the limits of NMR analysis, only one geometric isomer could be detected from the silylation reaction.[12b] We believe this to be the trans,cis compound **4**, on the basis of



4

5

analysis of the high-field (250 MHz) NMR spectrum of its maleic anhydride adduct (vide infra).

Compound **4** reacts with methacryloyl chloride in benzene under reflux for 2 h. Treatment of the adduct with methanol–pyridine followed by aqueous hydrogen peroxide afforded, after silica gel chromatography, a 29% yield of 4-methyl-4-carbomethoxycyclohexadienone (**6**).[10a] The less reactive methyl methacrylate in benzene (sealed tube) at 120 °C for 24 h gave an adduct which upon treatment with dilute HCl–THF afforded a 16% overall yield of α'-phenylselenoenone **7**.[10a,13] Treatment of **7** according to Reich[6] gave a 91% yield of dienone **6**.

Reaction of **4** with methacrolein (C_6H_6, reflux; 40 h) followed by workup as above afforded enone **8**[10a,13] in 38% yield (from **3**). Several attempts at oxidative deselenation using aqueous hydrogen peroxide afforded a virtually quantitative yield of *p*-cresol, presumably via the labile 4-methyl-4-formylcyclohexadienone (**9**). Similarly, treatment of dienone **6** with methanolic KOH gave *p*-cresol virtually instantaneously. The chemistry of the 4-acylated 4-substituted cyclohexadienones will be more fully described in a future publication.

Thus, while the cycloaddition reactions of **4** with easily polymerizable methacrylyl dienophiles lead to interesting new systems, the yields thus far are disappointing. The enophilic efficacy of **4** is far less than that of **1**. However, the power of the method is foreshadowed in its use with the less fragile dienophile, ethyl 2-phenylacrylate (**10**). The reaction of **4** with **10** was conducted in benzene (sealed tube) at 115 °C for 24 h. Workup with dilute acid followed by oxidative deselenation afforded a 50% overall yield of 4-phenyl-4-carbethoxycyclohexadienone (**11**).[10a,b]

Compound **4** reacts with maleic anhydride and with 4-phenyltriazoline-3,5-dione at room temperature. After workup with dilute acid, methoxy ketones **12**[10] (mp 136–137 °C) and **13**[10a] (mp 213–214 °C) were obtained in 67 and 77% yields, respectively.

Hydrolysis of the maleic anhydride adduct with DCl–$MeCO_2D-D_2O$ led to the introduction of one deuterium atom at the methylene center adjacent to the ketone of **12**. Therefore, it may safely be assumed that under the conditions of the experiment there is no epimerization of the methine center bearing the phenylseleno function. Accordingly, the relative configurations of the adduct itself may be derivable from the ketone. The pertinent coupling constants of the ketone are shown with the structure.

If it is assumed that cycloaddition has occurred in the usual suprafacial, endo sense, these coupling patterns of the maleic