gioselective hydration of acrylonitrile to acrylamide in 89% yield. Absence of byproducts such as ethylene cyanohydrin and β,β'-dicyanodiethyl ether testified to the remarkable regioselectivity of the reaction. Another sensitive substrate, 2-chloroacrylonitrile, was hydrated regioselectively to 2-chloroacrylamide in good yield.

The sparingly water soluble nitriles such as benzonitrile and phenylacetonitrile also underwent facile hydration to the respective amides. No cosolvents were needed to bring about hydration. With malonitrile, a mixture of mono- and diamides was obtained, the composition being dependent on the amount of catalyst and reaction time (Table I).

The reusability of the recovered catalyst was demonstrated by using phenylacetonitrile as the test case. No regression in the activity of the recovered catalyst was noticed.

Experimental Section

Melting points (uncorrected) were determined on a Mettler FP 5 instrument. Infrared spectra were recorded on a Perkin-Elmer 567 instrument, and ^{1}H and ^{13}C NMR spectra were taken on a JEOL FX-100 NMR spectrometer. X-ray diffractograms were obtained by using a Phillips Model PW (1140) X-ray generator with Cu Kα radiation. The BET surface area measurements were made on a Sorptomatic Model 1810 (Carlo Erba Strumentazione, Italy).

Preparation of the Copper Catalyst. In a 2-L three-necked flask equipped with a magnetic stirring bar, an addition funnel, and a nitrogen inlet were placed copper sulfate pentahydrate (31.2 g, 0.125 mol) and deaerated water (150 mL, 8.33 mol). An alkaline solution of sodium borohydride was prepared by dissolving sodium borohydride (5.28 g, 0.14 mol) in NaOH (5.2 g of NaOH in 250 mL of water). The sodium borohydride solution was transferred to the addition funnel and added dropwise to the cooled copper sulfate solution (5 °C) with stirring during a period of 2 h. A steady flow of N_2 was maintained throughout the addition. The stirring was continued for another 1 h. The flask was then transferred to a glovebox, the supernatant liquid was decanted off, and the catalyst was repeatedly washed with water until the washings were neutral. The wet catalyst, stored in an atmosphere of nitrogen, was used for the hydration reaction.

General Method for the Hydration of Nitriles. A 1-L Parr shaker bottle was charged with the copper catalyst (8 g, 0.125 mol), acrylonitrile (14 g, 0.263 mol), and water (220 mL, 12.2 mol). Hydroquinone (0.2 g) was added as the polymerization inhibitor. The flask was then flushed with N_2 and securely stoppered. All these operations were carried out inside the glovebox under an N_2 atmosphere. The reaction flask was then heated to 90 °C and maintained at that temperature for 2 h with vigorous shaking. The contents of the flask were cooled to room temperature, and the catalyst was filtered off. The filtrate was then evaporated to dryness under reduced pressure (15–20 mmHg) at 40–45 °C. The residue was collected and dried. The crude yield of acrylamide was 16.6 g (89%); mp 83.6 °C. A similar procedure was followed for the hydration of acetonitrile, 2-chloroacrylonitrile, and malononitrile (see Table I).

In the case of cold water insoluble amides (benzamide, phenylacetamide), the pressure was carefully released at the end of the reaction and the catalyst was filtered off while the solution was hot. The amide crystallized out from the solution on cooling. It was then filtered and dried.

Acknowledgment. We are grateful to Dr. I. S. Bhardwaj for his interest in this work. We also thank Dr. K. R. Krishnamurthy for X-ray and BET measurements and Mr. S. Kannan and J. G. Sheth for experimental assistance.

Registry No. Acetonitrile, 75-05-8; acrylonitrile, 107-13-1; 2-chloroacrylonitrile, 920-37-6; benzonitrile, 100-47-0; phenylacetonitrile, 140-29-4; malononitrile, 109-77-3; acetamide, 60-35-5; acrylamide, 79-06-1; 2-chloroacrylamide, 16490-68-9; benzamide, 55-21-0; phenylacetamide, 103-81-1; 2-cyanoacetamide, 107-91-5; copper, 7440-50-8; copper sulfate, 7758-98-7.

Communications

Donor-Atom Effects on Relative E2 Rate Constants for Reactions of Anions with Cyclohexyl Bromide

Summary: 2-Naphthoxide oxanions (2-NpO$^-$) and carbazole nitranions (Cb$^-$) react with cyclohexyl bromide in Me$_2$SO solution to give cyclohexene, whereas 9-methylfluorene carbanions (9-MeFl$^-$) give substitution and benzenethiolate thianions give both elimination and substitution. The relative order of E2 rate constants for anions of the same basicity is ArS$^-$ > 2-NpO$^-$ > Cb$^-$ > 9-MeFl$^-$.

Sir: In 1956 the observation was made independently in three laboratories that weakly basic, highly nucleophilic anions are surprisingly effective at promoting elimination reactions. In EtOH, PhS$^-$ ions were shown to rival EtO$^-$ ions in their ability to promote E2 reactions with t-BuCl[1] or cyclohexyl tosylate (c-C$_6$H$_{11}$OTs),[2] and in acetone Cl$^-$ ions were shown to be effective in promoting elimination from c-C$_6$H$_{11}$OTs.[3] These results were later confirmed and extended by additional investigations of E2 reactions of (a) ArS$^-$ ions with c-C$_6$H$_{11}$Br and c-C$_6$H$_{11}$OTs in EtOH,[4] (b) EtS$^-$ and MeO$^-$ with PhCH$_2$C(X)Me$_2$ in MeOH,[5a] (c) Cl$^-$, Br$^-$, I$^-$, with RC(Br)Me$_2$ in acetone,[5b] and (d) Cl$^-$, Br$^-$, I$^-$, AcO$^-$, CN$^-$, N$_3^-$, PhO$^-$, and PhS$^-$ with c-C$_6$H$_{11}$X in acetone and other dipolar nonhydroxylic ("aprotic") solvents such as dimethylformamide (DMF) and Me$_2$SO.[6] In the latter study, the observation that the relative E2 rate constants appeared to correlate well with anion nucleophilicities, as defined by S$_N$2 rate constants in hydroxylic solvents, and not at all with anion basicities, as defined by pK_a values in DMF solvent, led to the conclusion that the anion is bonded to carbon, as well as to hydrogen, in the E2 transition state.[6] Eck and Bunnett have argued, however, that the interaction of the anion with carbon cannot be significant because it fails to respond to S$_N$2-type steric effects.[5b] A counter argument has been presented,[7] and Saunders and Cockerill conclude that "there is no

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Table I. Rate Constants for Reactions of Cyclohexyl Bromide with 9-Methylfluorenyl Carbanions (9-MeFl$^-$), Carbazole Nitranions (Cb$^-$), 2-Naphthoxide Oxanions (2-NpO$^-$), and Benzenethiolate Thianions (ArS$^-$) in Dimethyl Sulfoxide Solution at 25 °C

anion (A$^-$)	pK_a (HA)[a]	10^3k[c]	k^E(rel)[d]	product[e]	β[j]
9-MeFl$^-$	22.34	280	<0.1	S_N2 (>90%)[f]	
2-Br-9-MeFl$^-$	20.05	29.0			
2,7-Br_2-9-MeFl$^-$	17.7	3.2			0.42
Cb$^-$	19.9	21.2	(1.0)	E2 (>95%)[g]	
3-Cl-Cb$^-$	18.5	5.80			
3,6-Br_2Cb$^-$	17.15	1.69			0.40
2-NpO$^-$	17.1	55.0	30		
6-Br-2-NpO$^-$	16.2	16.0		E2 (>90%)[h]	
4-$MeOC_6H_4S^-$	11.2[b]	18.6	~10^3	S_N2/E2 (1:1)[i]	
3-$CF_3C_6H_4S^-$	8.1	0.64			
2,4,5-$Cl_3C_6H_2S^-$	6.0[b]	0.055			0.49

[a] Reference 9. [b] Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1982**, *47*, 3224–3232. [c] Total second-order rate constant (M^{-1} s^{-1}) measured spectrophotometrically by the method described in ref 9; reproducible to ±10% or less. [d] Estimated at the same basicity from the product distribution and the Brønsted correlations (Figure 1). [e] Equimolar quantities of A$^-$ and c-$C_6H_{11}Br$ were allowed to react for several days. The percent of E2 product was estimated from the amount of HA isolated (NMR analysis). [f] No 9-MeFlH was detected; 80% of recrystallized S_N2 product was isolated. [g] NMR analysis of the solid product showed only CbH; 98% of cyclohexene was formed (GLC analysis). [h] NMR analysis of the solid product showed only 6-bromo-2-naphthol. [i] NMR analysis showed equimolar amounts of 4-methoxythiophenol and cyclohexyl 4-methoxyphenyl sulfide. [j] Brønsted coefficient.

really decisive evidence either for or against such interaction".[8]

Recent results in our laboratory have provided new insights into the correlation of S_N2 and E2 rate constants with (a) anion basicities and (b) the nature of the anion donor atoms. In an earlier paper we reported that S_N2 rate constants for carbanions, nitranions, oxanions, and thianions in Me_2SO solution can be correlated *solely* with anion basicities, as long as the donor atom in the anion and steric effects are kept constant. On the other hand, when the donor atom is changed, S_N2 rate constants for anions of the *same basicity* may vary by as much as 10^5.[9] In this paper we shown that anion E2 rate constants can also be correlated with anion basicities as long as the donor atom is kept constant and that donor-atom E2 rate constants for anions of the same basicity may vary by as much as 10^4. Anion donor-atom E2 rate constants do not correlate, however, with anion donor-atom S_N2 rate constants.

A summary of the rate constants for the reactions of c-$C_6H_{11}Br$ with carbanion,[10] nitranion, oxanion, and thianion families is given in Table I. Brønsted plots of these data are linear (Figure 1), showing that the rate constants are correlated with anion basicities.

The Brønsted plots allow an estimate to be made of relative donor-atom E2 rate constants for ArS$^-$ thianions, 2-NpO$^-$ (2-naphthoxide) oxanions, and Cb$^-$ (carbazole) nitranions of the same basicity. These estimates are rough because slopes (β's) for the ArS$^-$ and Cb$^-$ ion lines differ somewhat (Figure 1). Consequently, the relative rate constants vary somewhat depending on the basicity chosen for comparison. Comparisons with 2-NpO$^-$ are further hampered because sufficient data are not yet available to define a Brønsted line for 2-NpO$^-$ ions. Nevertheless, the order of donor-atom E2 rate constants for anions of the same basicity reacting with c-$C_6H_{11}Br$ is clearly ArS$^-$ > 2-NpO$^-$ > Cb$^-$ > 9-MeFl$^-$, and the relative rate constants vary by a factor greater than 10^4 (Table I). The larger E2 rate constants for thianions than oxanions is in accord with previous findings.[1,2,5a] Information concerning E2 rate constants of nitranions and carbanions has not been available previously. The Cb$^-$/9-MeFl$^-$ rate constant ratio can only be estimated as larger than 10 at present, since the reaction between 9-MeFl$^-$ carbanions and c-$C_6H_{11}Br$ in Me_2SO gives but little elimination product.[10]

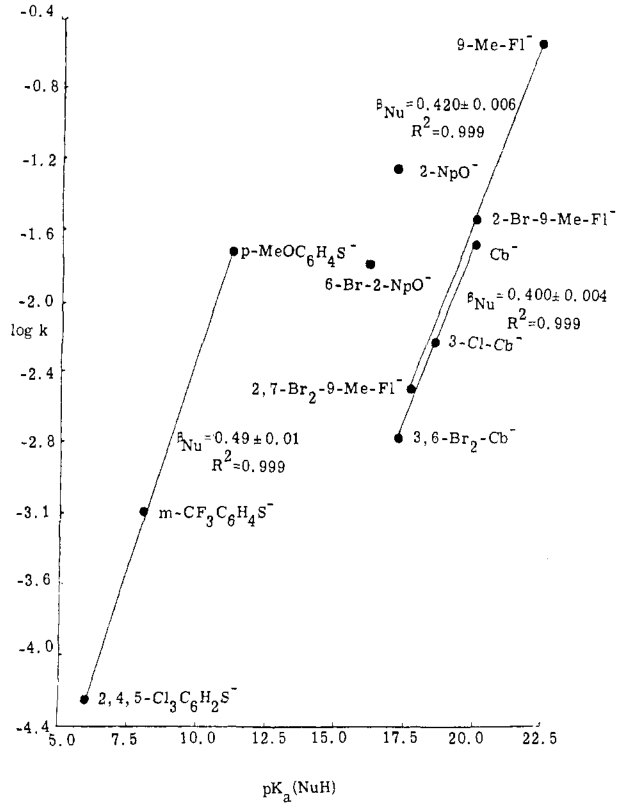

Figure 1. Plots of second-order rate constants (log k) vs. pK_a values for reactions of benzenethiolate ions, 2-naphthoxide ions (2-NpO$^-$), 9-methylfluorene carbanions (9-MeFl$^-$), and carbazole nitranions (Cb$^-$) reacting with cyclohexyl bromide in dimethyl sulfoxide solution at 25 °C; R^2, the square of the correlation coefficient, provides a measure of the relative precisions of these correlations.

The correlation of anion basicities with E2 rate constants for nitranions, oxanions, and thianions (Figure 1) is contrary to the earlier report that E2 rate constants do not correlate at all with anion basicities.[6] The correlation of anion basicities with E2 rate constants emerges only when a substrate is allowed to react with families of anions so as to keep donor-atom and steric effects constant. These Brønsted correlations then allow comparisons of anion E2

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rate constants at the same basicities. The order of anion E2 rate constants with c-C_6H_{11}Br thus revealed, ArS$^-$ > 2-NpO$^-$ > Cb$^-$ > 9-MeFl$^-$, contrasts sharply with the order of the anion S_N2 rate constants with PhCH$_2$Cl, ArS$^-$ > 9-MeFl$^-$ > 2-NpO$^-$ > Cb$^-$.[9,11] The E2 rate constants of oxanions and nitranions reacting with c-C_6H_{11}Br are much greater than their S_N2 rate constants, causing essentially complete elimination to occur. On the other hand, the S_N2 rate constants of carbanions reacting with c-C_6H_{11}Br are much greater than their E2 rate constants, causing essentially complete substitution.[10] We conclude that the apparent correlation between anion E2 and S_N2 rate constants observed earlier was fortuitous and that there is no reason to believe that in some E2 transition states the anion is bonded to carbon as well as to hydrogen.

Acknowledgment. This work was supported by the National Science Foundation. We are grateful to a reviewer for helpful comments.

Registry No. 9-MeFl$^-$, 31468-21-0; 2-Br-9-MeFl$^-$, 81255-42-7; 2,7-Br$_2$-9-MeFl$^-$, 73872-46-5; Cb$^-$, 23560-25-0; 3-ClCb$^-$, 80010-03-3; 3,6-Br$_2$Cb$^-$, 79990-92-4; 2-NpO$^-$, 15147-55-4; 6-Br-2-NpO$^-$, 78232-03-8; 4-MeOC$_6$H$_4$S$^-$, 26971-83-5; 3-CF$_3$C$_6$H$_4$S$^-$, 78232-02-7; 2,4,5-Cl$_3$C$_6$H$_2$S$^-$, 78232-01-6; cyclohexyl bromide, 108-85-0.

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(11) S_N2 rate constant orders for these anions have been found to be somewhat substrate dependent,[9] but there is no evidence for a correlation with anion E2 rate constants.

Frederick G. Bordwell,* Susan Romberg Mrozack
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

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A Novel Entry into the Bicyclo[5.4.0]undecane Ring System

Summary: A four-step cycloaddition–oxyanion Cope rearrangement sequence starting from 2,4,6-cycloheptatrien-1-one leads to a cis-fused 11-substituted bicyclo[5.4.0]undec-8-en-4-one species.

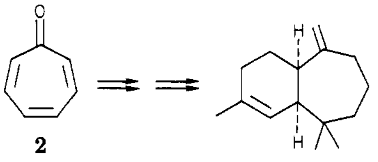
Sir: In recent years considerable effort has been expended in developing stereoselective syntheses of natural products that possess seven-membered carbocycles.[1] The bulk of these studies have been directed toward compounds possessing the hydroazulene moiety. Comparatively little work has been reported on the construction of other related ring systems. A particularly intriguing structural array from a synthetic point of view is the bicyclo[5.4.0]undecane series which is characteristic of several classes of sesquiterpenes, including the himachalenes (e.g., α-himachalene (1)).[2] Several approaches to this general ring system have been disclosed in recent years,[3,4] but at present the ability to control the critical ring fusion stereochemistry in a general fashion remains a synthetic challenge. We herein report a potentially general strategy for the construction of cis-fused bicyclo[5.4.0]undecanes with complete control of the ring fusion stereochemistry.

Table I. C-9 Substituted Cycloadducts of Tropone[a]

cycloadduct[12]	rctn condtns	% yield	ratio of epimers[b] at C-9
3a, X = *n*-BuO	95 °C, 24 h	63[c]	1:1[d]
3b, X = *n*-BuS	130 °C, 4 h	68	5:1[d]
3c, X = SPh	130 °C, 4 h	64	1.5:1[d]
3d, X = OAc	140 °C, 24 h	50[e,f]	1:1[g]

[a] The identity of the regioisomer was determined by 300-MHz ^{1}H NMR decoupling experiments on the corresponding saturated ketones **5**. [b] No effort was made to assign epimer structures. [c] Based on recovered starting material. [d] Ratio of epimers based on weight of each component after careful chromatography. [e] Accompanied by considerable decomposition products. [f] Prepared in a sealed tube experiment. [g] Determined by ^{1}H NMR integration on **3d**.

Tropone (2,4,6-cycloheptatrien-1-one (**2**))[5] is a very attractive starting material for the synthesis of complex natural products because it possesses considerable functionality in a relatively small molecule and exhibits rather unique reactivity that is particularly amenable for exploitation in carbon–carbon bond-forming reactions.[6,7]



2 **1**

In the present work, an alkoxide accelerated Cope rearrangement[8] is employed as the key step for formation of the requisite cis ring fusion. The overall brevity of our process results from the ease with which the bicyclo[3.2.2]non-6-en-2-one precursor is prepared from tropone (**2**).

Several examples of [4 + 2] cycloaddition reactions of troponoids with a variety of dienophiles have been reported.[9] However, most of these examples have involved electron-poor olefin partners such as acrylonitrile and usually resulted in the formation of mixtures of the regioisomers **3** and **4** (X = CN) in which **3** was the major adduct.[9a] In view of the well-established electrophilicity of tropone and through consideration of the reactant frontier orbital coefficients,[10] it was anticipated that reversing the electronic sense of the dienophile would result

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