derivative. The third fraction, eluted with benzene/ethyl acetate (5:1 by volume), was the β-hydroxypropanal derivative.

In control experiments samples of acrolein were hydrated to mixtures of β-hydroxypropanal and the dimer **13**. The (2,4-dinitrophenyl)hydrazone derivative was prepared and chromatographed. Recovery of the β-hydroxypropanal derivative was 10–15% based on acrolein. The ^1H NMR spectra of the derivatives carbonyl of the products are given in Table II.

GLC Analysis. Several analyses for volatile products were carried out on neutralized reaction mixtures using a 6 ft. 20% Carbowax 20 M column on 60–80 mesh Chromosorb W. The column was programmed from 70–200 °C at 10 °C/min. Propanal and acrolein were not resolved by this procedure but by the use of standards it could be calculated this combined yield was 45–50%. Acetol could be identified and analyzed by the use of standard solutions. Its yield was 12–15%.

Chemical Analysis. As the dimer of β-hydroxypropanal is reported[8] to be depolymerized by oximation, total carbonyl products were determined by this method using a literature procedure.[39,40] The reaction was run on a 50-mL scale and, after removal of palladium, was diluted to 100 mL (A). A 10-mL portion of A was treated with 50 mL of freshly prepared 0.1 M hydroxylamine hydrochloride at 45 °C for 30 min, cooled, and potentiometrically titrated with 0.1 M NaOH (V_1). Another 10-mL portion of A was also titrated with the base (V_2). The difference $V_1 - V_2$ was a measure of the total carbonyl products.

A 50-mL portion of A was extracted several times with ether to remove acetone, acrolein, propanal, and unreacted alcohol. The residue ether was removed from A under vaccuum to give B which contained mono and dimeric β-hydroxypropanal and acetol. A 10-mL portion of B was oximated as described above and titrated potentiometrically with 0.1 M NaOH. The difference $V_1 - V_3$ was a measure of acetone, acrolein, and propanal while $V_3 - V_2$ was a measure of acetol and β-hydroxypropanal.

Acetol was determined by Fehling's solution which reacts rapidly with acetol even in the cold.[41,42] A 10-mL portion was reacted at 5 °C for 3–5 min, and the amount of Cu_2O was determined quantitatively in an inert atmosphere. From $V_3 - V_2$ and the acetal determination the amount of β-hydroxypropanal can be calculated.

In summary this analysis gave the following results: acetone plus acrolein plus propanal, 47%; acetol, 15%; β-hydroxypropanal, 38%.

Propene Analysis. As mentioned previously some runs were carried out in closed systems connected to gas burets to detect and measure any gaseous products such as propene. It was found that, in fact, a gas was given off which corresponded on a mole basis to about 7% of the Pd(0) formed. The gas was passed into a solution of Br_2 in CS_2. After the Br_2 color had disappeared, the solution was evaporated and the ^1H NMR of the solution taken in $CDCl_3$. The material was clearly 1,2-dibromopropane, indicating the gaseous product was propene: ^1H NMR CH_3, δ 1.85 (d, 3 H); CHBr, δ 4.18 (m, 1 H), CH_2Br, δ 3.80–3.49 (m, 2 H).

Deuterium-Labeling Experiments. The reactions were run in the same fashion as for the nondeuterated but on never more than a 25-mL scale. (2,4-Dinitrophenyl)hydrazone derivatives were prepared and chromatographed as previously described. The propene was also collected and converted to the dibromide derivatives. A combination of the ^1H and ^2H 400-MHz spectra readily permitted positive identification of all deuterated isomers as well as their relative amounts.

The propanal from the experiments in D_2O were converted to the (2,4-dinitrophenyl)hydrazone derivatives and the deuterium content analyzed by GC/MS.

Acknowledgment. We thank Mr. B. McDonald and Dr. R. Lenkinski for the Bruker 400-MHz ^1H and ^2H NMR measurements and Dr. D. Hung of Northwestern University for the mass spectral measurements. Acknowledgement is made the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Natural Sciences and Engineering Research Council of Canada for partial support of this research. K.Z. is grateful to Loyola University and the Searle Foundation for a Searle post-doctoral fellowship.

Registry No. D_2, 7782-39-0; $LiPdCl_4$, 15525-45-8; $CH_3CH_2CH{=}NNHC_6H_3(NO_2)_2$, 725-00-8; $CH_2{=}CHC{=}NNHC_6H_3(NO_2)_2$, 888-54-0; $HOCH_2CH_2CH{=}NNHC_6H_3(NO_2)_2$, 40365-04-6; $HOCH_2C({=}NNHC_6H_3(NO_2)_2)CH_3$, 96481-90-2; allyl alcohol, 107-18-6.

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Relative Acidifying Effects of Tricarbonylchromium(0) and *p*-Nitro Groups upon Di- and Triphenylmethanes

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The kinetic and thermodynamic acidities of the tricarbonylchromium(0) or *p*-nitro-substituted di- and triphenylmethanes **1**–**6** have been measured in methanol–dimethyl sulfoxide solutions. The kinetic acidifying influence of a single tricarbonylchromium(0) group is found to be greater than that of a single *p*-nitro substituent in these molecules, but the acidifying effect of the tricarbonylchromium(0) group is not cumulative and steric effects become increasingly evident in these complexed molecules. The thermodynamic acidities of the nitro-substituted aromatics are greater than those of their tricarbonylchromium(0)-complexed analogues, in accord with the greater charge delocalization in their carbanions by the nitro group.

Introduction

There have been several studies reported on the generation[1-4] and structures[4-9] of aryl or arylmethyl carbanions stabilized by complexation with one or more tricarbonylchromium(0) groups. It has been demonstrated

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Table I. The Kinetics of Ionization of Compounds 1–3 in Methanol–Me_2SO Mixtures at 25 °C

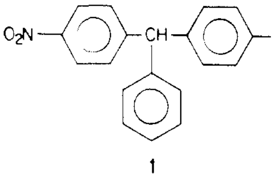
			% Me_2SO (v/v)							
compd	λ_{measd}, nm		20	40	60	70	80	90	95	98
1	575	$k_1{}^a$	0.5	1.24	18.83		221			(4000)[e]
		$k_{-1}{}^b$	0.375	0.29	0.13		0.04			
		K^c	1.33	4.27	145		5525			
2	755	k_1			8.55	33.1	136	843	3800	(2500)[e]
		k_{-1}			0.49	0.13	*d*	*d*	*d*	
		K			17.4	255				
3	520	k_1					1.5	6.5	39.1	250 (30)[e]
		k_{-1}					0.02		0.06	
		K					75		663	

[a] k_1 values in L mol^{-1} s^{-1}. [b] k_{-1} values in s^{-1}. [c] $K = k_1/k_{-1}$ (L mol^{-1}). [d] Too low for measurement. [e] Estimated—see text.

that the $Cr(CO)_3$ group can exercise an electron-withdrawing function, excess charge being delocalized into the metal carbonyls,[5] and hence enhance the kinetic and thermodynamic acidities of hydrogens on the α-carbon atoms of $Cr(CO)_3$-complexed arylmethanes.[10] In addition to carbanion formation $Cr(CO)_3$-complexed aromatics have been shown to undergo facile nucleophilic attack[3,11,12] in the presence of various bases, the $Cr(CO)_3$ activation of chlorobenzenes toward nucleophilic attack being comparable with that of a *p*-NO_2 group.[13] The exact nature of the electron-withdrawing effect of the $Cr(CO)_3$ group, noted in both enhanced kinetic benzylic hydrogen atom acidity and enhanced carbanion stabilization, is still unclear[5,14–17] although some authors have concluded that it is predominantly an inductive, rather than a resonance, effect.[18]

The degree to which the $Cr(CO)_3$ "substituent" affects the rates of abstraction of benzylic protons has, so far, only been measured qualitatively, and there are no reported acidity measurements comparing directly the $Cr(CO)_3$ with other electron-withdrawing groups. The relative rates of metalation of the mono-$Cr(CO)_3$ complexes of toluene, diphenylmethane, and triphenylmethane have been reported[8] to be 1:1:1.7 ((toluene)$Cr(CO)_3$ ≡ 1) in THF—a somewhat unexpected result when compared with the relative rates of tritium exchange for the uncomplexed hydrocarbons, with lithium cyclohexylamide in cyclohexylamine, of approximately 1:270:10^3 (toluene ≡ 1).[19] Rates of side-chain elimination reactions from $Cr(CO)_3$-complexed arenes have also been measured and the data compared with measurements on the corresponding uncomplexed and *p*-nitroarenes. These show a considerably greater activating (toward E2 reaction) influence of the *p*-NO_2 group.[18]

Recently, a number of interesting syntheses have appeared whereby the complexation by a $Cr(CO)_3$ group has enabled unusual or difficult reactions to be readily carried out on aromatic derivatives.[4,20–23] As most of these reactions proceed via carbanionic pathways, it is of interest to know the extent of activation toward base attack induced by the $Cr(CO)_3$ group, and the effects of multiple complexation etc. to facilitate the development of these novel synthetic methods. In connection with our interest in the elucidation of the factors affecting carbon acid strengths, particularly in nitro-substituted arylmethanes,[24–26] and to provide direct comparisons between the acidifying effects of the $Cr(CO)_3$ group and the strongly electron-withdrawing *p*-NO_2 group, we have measured the rates of proton abstraction from **1**–**6** by methoxide ion in CH_3OH–Me_2SO solutions. Where possible, measurements of the rates of carbanion protonation in these media have also been made to allow comparisons of both kinetic and thermodynamic acidities of the substrates.



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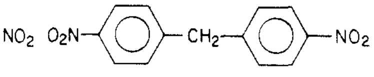

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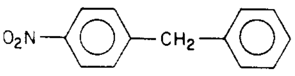

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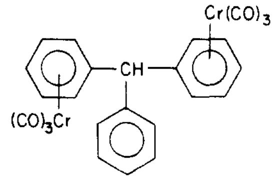

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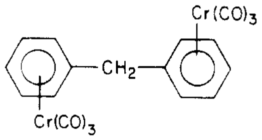

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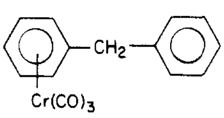

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Table II. The Kinetics of Ionization of Compounds 4–6 in Methanol–Me_2SO Mixtures at 25 °C.

			% Me_2SO (v/v)					
			95			98		
compd	λ_{measd}, nm		MeOH	MeOD	k_{MeOD}/k_{MeOH}	MeOH	MeOD	k_{MeOD}/k_{MeOH}
4	490	k_1[a]	66.8	89.2	1.33	497	500	1.0
		k_{-1}[b]	0.2	0.1	0.5	0.1	*d*	
		K[c]	334	892		4970		
5	472	k_1	104.8	156.4	1.49	870	937.5	1.08
		k_{-1}	9.85	5.93	0.6	0.5	0.5	1
		K	10.5	26.4		1740	1875	
6	466	k_1	*d*	*d*		810	870	1.07
		k_{-1}	*d*	*d*		1.2	0.3	0.25
		K				675	2900	

[a] k_1 values in L mol^{-1} s^{-1}. [b] k_{-1} values in s^{-1}. [c] $K = k_1/k_{-1}$ (L mol^{-1}). [d] Too low for measurement.

Results

In order to obtain directly comparable kinetic data for the relative activating influence of the $Cr(CO)_3$ and the p-NO_2 groups, measurements of the rates of proton abstraction, k_1, and of carbanion protonation, k_{-1}, in the same solvent are required (eq 1). As we have discussed else-

$$R_1R_2R_3CH + MeO^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_1R_2R_3C^- + MeOH \quad (1)$$

where, because it is not always practically possible to carry out measurements of k_1 for compounds of significantly different *thermodynamic*, as well as *kinetic*, acidities in the same medium, a series of values in different solvent mixtures is desirable to permit extrapolation of data to a common medium.[27] We have therefore studied the reactions of **1**–**3** in as many Me_2SO–MeOH mixtures as possible, taking account of experimental limitations and scientific relevance.

In Table I, values of k_1 and k_{-1}, where measurable, are reported, together with the derived equilibrium constants $K = k_1/k_{-1}$, for compounds **1**–**3** in a range of Me_2SO–MeOH mixtures at 25 °C. In each case, data correspond to measurements made on the first-formed species in solution, at the wavelengths indicated in Table I. Although there has been some discussion concerning the nature(s) of the species formed in the reactions of nitroaromatics with bases, especially with respect to mononitrotoluene derivatives,[28] the carbanion is normally the initial species formed in reactions with strong bases such as alkoxides. This may be followed by further reaction of the carbanion with unionized molecules, oxygen, solvent to form radicals, dimeric species, etc. For molecules such as **1** and **2** which yield reasonably stable carbanions, no evidence of any reaction of their carbanions, other than protonation, was observed on the time scale employed for measurement.

For compound **3**, evidence of subsequent reaction of the carbanion was observed by the decay of the absorption at 520 nm with time. However, carbanion loss is sufficiently slow in 95% and 98% Me_2SO solutions to allow measurements of k_1 to be obtained completely free of interference from this secondary reaction (see Table I). Evidence that the first-formed species in the reaction of **3** with methoxide ion is indeed the carbanion is provided by a consideration of the long wavelength band found for this species. The diphenylmethyl carbanion absorbs at 448 (Li^+ in THF),[29] 434 (Li^+ in ether),[30] and 440 nm (K^+ in NH_3),[31] and the effect of the introduction of a p-NO_2 group is reported to be a bathochromic shift of ca. 80 nm in benzyl and related carbanions.[32] Thus a value of 520–530 nm would be predicted for the absorbance of the carbanion derived from **3**, in excellent agreement with the measured value of 520 nm (K^+ in 60% Me_2SO–MeOH).

Values of k_1 and k_{-1} for the reactions of compounds **4**–**6** with methoxide ion in 95% and 98% Me_2SO–MeOH solutions at 25 °C, together with the derived equilibrium constants K, are shown in Table I. Also shown in this table are the wavelengths of measurement (λ_{max}) and values of k_1 and k_{-1} obtained from measurements in the corresponding Me_2SO–MeOD mixtures. Compound **6** is insufficiently acidic to allow measurements to be made in 95% Me_2SO–MeOH solution.

To confirm that the data obtained refer to carbanion formation by benzylic proton abstraction, as opposed to other possible reaction paths noted above, the dideuterated derivative of **5** was prepared by base-catalyzed proton exchange to yield **5**-d_2 (>97% from a 250-MHz proton NMR spectrum). Measurements of k_1 for this compound in 95% Me_2SO–MeOH gave a value of 8.6 L mol^{-1} s^{-1} and hence a primary kinetic isotope effect of 10.6 (corrected for an assumed secondary isotope effect of 1.15).[33] This value, together with the solvent isotope effects shown in Table II, confirms that these data refer to benzylic proton abstraction (and carbanion protonation) for **5**, and by analogy for **4** and **6**.

Discussion

Nitroaromatics. As can be seen from the data of Table I, increasing the percentage of Me_2SO increases the value of k_1, while decreasing the value of k_{-1}, as is *normally* found for carbon acid ionization equilibria, results in a large increase in K with Me_2SO concentration. The addition of a p-NO_2 group to **3**, to yield **2**, increases the value of k_1 considerably (ca. 100-fold) whereas the addition of a phenyl group to **2**, to yield **1**, results in only a two-fold increase in k_1. This small effect of a phenyl group has been observed in other similar systems[27] and may well arise from the increase steric hindrance to approach of the solvated base to **1**.

The influence of the second p-NO_2 group in **2** is extremely strong and would suggest that the carbanion derived from **1** probably has the two p-nitrophenyl rings coplanar. Steric interactions in this latter carbanion could be relieved by greater than normal out-of-plane twisting of the phenyl group—cf. (9-phenylfluorenyl)lithium[34] —

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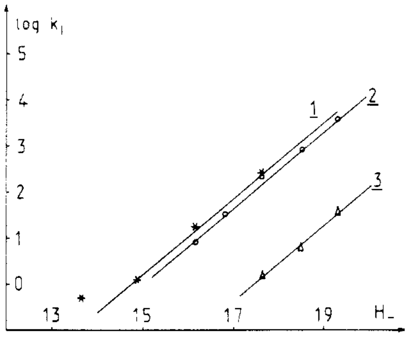


Figure 1. The deprotonation rates of the (nitrophenyl)methanes 1–3 as a function of the acidity function H_ for methanol–dimethyl sulfoxide mixtures (k_1 in l mol^{-1} s^{-1}; t = 25 °C).

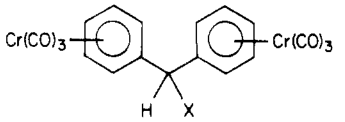
thus decreasing the resonance charge delocalization effect of the phenyl substituent.

As will be seen from the subsequent discussion and by reference to the tables, the comparison of data for **1**–**3** with those for **4**–**6** requires extrapolation of the k_1 values to solutions of very high Me_2SO content (95–98%). In this regard, it is of interest to note that k_1 values for compounds **1**–**3** exhibit identical behavior toward changing the percent of Me_2SO in the reaction, up to 90% DMSO. This is evidenced by parallel linear plots of log k_1 vs. H_ (and/or mole fraction of Me_2SO), as shown in Figure 1. Above 90% Me_2SO content, H_ values in methanol increase rapidly and nonlinearly with increasing percent Me_2SO,[35] and thus the *linear* extrapolation of log k_1 values into this region will yield estimated values which, perforce, lie *below* the experimental log k_1 vs. H_ curve. These estimates are thus *minimum* values, but this will not affect the conclusions drawn in the discussion which follows.

That the estimated k_1 values for **1** and **2** in 98% Me_2SO–MeOH are indeed minimum values can be seen in Table I by comparisons of either the measured and estimated k_1 values for **3** in this medium or of the measured k_1 for **2** in 95% Me_2SO with its estimated value in 98% Me_2SO—a value which must be, experimentally, greater than that in 95% Me_2SO–MeOH.

From the data obtained in 80% Me_2SO–MeOH solutions, the relative kinetic acidities of **1**–**3** are ca. 150:90:1, and the relative thermodynamic acidities of **1** and **3** are of a comparable magnitude, i.e., ca. 75:1. If one assumes a similar decrease in k_{-1} for **2** on changing from 70% Me_2SO to 80% Me_2SO as is found for the change from 60% Me_2SO to 70% Me_2SO, an estimate of the relative thermodynamic acidities of **1**–**3** of ca. 75:70:1 may be made for 80% Me_2SO–MeOH. It must be noted, however, that these values of K are *extremely* sensitive to solvent composition, as can be seen from the ca. 4000-fold increase in K for **1** on changing from 20% Me_2SO to 80% Me_2SO solution. Further, we have not, so far, observed a regularity in the variation of k_{-1} values for nitroaromatics **1**–**3** of the form noted above for their k_1 values with changing solvent composition, and thus the variation of K with solvent is different for each compound studied and possibly becomes increasingly divergent in mixtures containing >90% Me_2SO.

$Cr(CO)_3$-Complexed Aromatics. Comparison of the k_1 values of Table II for **5** and **6** in 98% Me_2SO–MeOH shows that there is virtually no increase in kinetic acidity as a result of the introduction of a second $Cr(CO)_3$ group onto diphenylmethane. This may be due to either a "saturation" effect, whereby the second $Cr(CO)_3$ group does not further increase the exocyclic C–H bond acidity, or to steric hindrance to approach of the base caused by the bulky $Cr(CO)_3$ groups. Other workers have suggested that the $Cr(CO)_3$ group causes significant steric interaction with attacking groups in the vicinity of the benzylic hydrogen atoms,[4] and the view that adverse steric interactions account for the k_1 data for **5** and **6** is supported by the data for **4** in 98% Me_2SO (and for **4** and **5** in 95% Me_2SO) solutions. Thus the introduction of a phenyl group into **5**, giving **4**, *decreases* k_1, as would be anticipated if some steric hindrance to base approach already exists in **5**. Proof of steric hindrance in **4** is provided from its ^{13}C NMR and from studies of analogous compounds. Thus the $SiMe_3$ silyl derivative **7** shows evidence of restricted rotation of the $Cr(CO)_3$-complexed aromatic rings at room temperature, two ^{13}C signals being observed for the ortho carbons and two for the meta carbons.[9] This steric hindrance to rotation is removed in the planar carbanion generated from **7**, no separation of ^{13}C signals from the ortho or meta carbons being observed even at −110 °C. The $SiMe_3$ group and a phenyl ring are not too dissimilar in size, and thus **4** would also be expected to exhibit steric crowding, which should be partially relieved upon carbanion formation—partially as opposed to completely—because of the well-known steric interactions present in triphenylmethyl systems.[36] The ^{13}C NMR spectrum of **4** at ambient temperature does possess separate signals for each ring carbon atom of the $Cr(CO)_3$-complexed phenyls, confirming their high rotational energy barrier resulting from the phenyl substitution of **5**. Similar observations have been recorded for the alcohol **8**, which also exhibits restricted rotation at room temperature.[37] The steric hindrance to rotation may be removed in this case by formation of the planar carbonium ion (cf. **7**).



7, X = $SiMe_3$
8, X = OH

While allowing for the possibilities of steric hindrance to approach of the base in **4** and **5**, their carbanions are stabilized, progressively, by the extra $Cr(CO)_3$ group and the phenyl substituent, as can be seen from the k_{-1} data in Table II. The more highly stabilized triphenylmethyl carbanion derived from **4** shows virtually no solvent dependence of k_{-1} (over this *very* narrow range where measurements were possible), whereas considerable solvent dependence of k_{-1} is shown by **5** and presumably by **6**. The K values, however, show solvent dependence for both **4** and **5**, reflecting the solvent variation of k_1 in the case of **4**. These systems may be compared with reactions involving $Cr(CO)_3$-complexed cations derived from diphenylmethane. Although not evident for mono-$Cr(CO)_3$-complexed secondary cations,[37] steric effects become important in the stabilization of mono$Cr(CO)_3$ complexed tertiary carbonium ions.[38] The greater spatial requirement of the filled orbital in the carbanion than the empty orbital of

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[34] S. E. Browne, S. E. Asher, E. H. Cornwall, J. K. Frisoli, L. J. Harris, E. A. Salot, E. A. Sauter, M. A. Trecoske, and P. S. Veale, *J. Am. Chem. Soc.*, **106**, 1432–1440 (1984).

[35] See, e.g., J. R. Jones, "The Ionization of Carbon Acids", Academic Press, London, 1973.

[36] T. J. Brooks and G. D. Stucky, *J. Am. Chem. Soc.*, **94**, 7333–7338 (1972); P. Anderson and B. Klewe, *Acta Chem. Scand.*, **21**, 2599–2607 (1967); A. H. Gomes de Mesquita, C. H. McGillavry, and K. Eriks, *Acta Crystallogr.*, **18**, 437–443 (1965).

[37] D. Seyferth, J. S. Merola, and C. S. Eschbach, *J. Am. Chem. Soc.*, **100**, 4124–4131 (1978).

[38] S. P. Gubin, V. S. Klandkarova, and A. Z. Kreindlin, *J. Organomet. Chem.*, **64**, 229–238 (1974).

the cation will accentuate any unfavorable steric interactions in the anion derived from **4**. The small decrease in k_{-1} with solvent variation (Table II) is in accord with this interpretation.

In contrast to the relative kinetic acidities for **6**, **5**, and **4** in 98% Me_2SO of 1:1:0.6, their corresponding thermodynamic acidities increase in the ratios 1:2.6:7.4. This relative ordering of thermodynamic acidity is anticipated from general considerations of the progressive introduction of electron-withdrawing groups into **6**, thus stabilizing the resulting carbanions to a greater extent than the reactant molecules. The differing kinetic and thermodynamic acidity ratios provide further evidence that the former are governed by ground-state (i.e., steric) as opposed to transition-state effects, as proposed above.

The solvent isotope effects obtained from the data of Table II show the expected behavior in that proton abstraction proceeds faster in the deuterated solvent, but carbanion protonation is slower in this medium. Notwithstanding the fact that even solutions containing 98% Me_2SO by volume contain a sufficiently large excess of methanol (ca. 0.35 M) to solvate the methoxide ions ($<10^{-2}$ M), the observed effects upon k_1 in this medium approximate the value of unity predicted for 100% Me_2SO. Somewhat higher values are found for k_1^{MeOD}/k_1^{MeOH} in 95% Me_2SO–MeOH, but these are also, as expected,[39] less than reported values for proton abstractions.

Relative Acidifying Effects of $Cr(CO)_3$ and p-NO_2 Groups. Comparison of the k_1 data in 98% Me_2SO for compounds **1**–**6** shows clearly the very great acidifying influence of two p-NO_2 groups, relative to one p-NO_2 group or to one or two $Cr(CO)_3$ groups, but also reveals that the kinetic acidifying effect of one $Cr(CO)_3$ group is greater than that of one p-NO_2 group in diphenylmethane by a factor of 3–4. Even allowing for the fact that the extrapolated data for **1** and **2** are minimum values the relative k_1 data for **1** and **4** are ca. 8:1, indicating that steric hindrance to base approach is not a major factor in the ionization of **1**. The ca. 3:1 ratio for the k_1 values for compounds **2** and **5** is also in accord with a lack of appreciable steric hindrance in **2**.

The >10-fold increase in k_1 between **3** and **2** presumably reflects the extremely efficient resonance electron delocalization in the ground-state molecules by the second p-NO_2 group, increasing the acidity of the C_α hydrogen atoms. This contrasts with the essentially identical k_1 values for **6** and **5** to also yield planar (with respect to the carbon skeleton) anions. For **5** and **6**, some charge in the ground-state molecules must be delocalized by interactions with the $Cr(CO)_3$ group(s), but this delocalization is noncumulative.

Examination of the thermodynamic acidity data shows a completely different picture however. Estimates of K values in 98% Me_2SO for **1**–**3** may be made for comparison purposes as follows. For **1**, assuming the estimated k_1 value of 4×10^3 L mol^{-1}s^{-1} and using the k_{-1} value obtained in 80% Me_2SO, a minimum K value of 10^6 L mol^{-1} may be obtained. For **2**, taking the measured k_1 value in 95% Me_2SO and the measured k_{-1} value in 70% Me_2SO, an estimated minimum K value of 3×10^5 L mol^{-1} is calculated. Similarly for **3**, with use of the experimental k_1 value in 98% Me_2SO and an estimate of $k_{-1} \simeq 0.01$ s^{-1} (cf. value in 80% Me_2SO), a minimum value of $K = 2.5 \times 10^4$ L mol^{-1} is determined. Comparison of the estimated thermodynamic acidity for the weakest nitroaromatic **3**, with the experimental values for both the strongest, **4** and weakest, **6**, $Cr(CO)_3$-substituted carbon acids yields K ratios of **3**:**4** of 5:1 and **3**:**6** of ca. 40:1, indicating that the p-NO_2 group has a far greater thermodynamic acidifying effect than one or two $Cr(CO)_3$ groups in diphenylmethane. **1** and **2** are, thermodynamically, some orders of magnitude stronger carbon acids than the corresponding $Cr(CO)_3$ derivatives **4** and **5**.

The data presented here are in accord with those of Ceccon for base-catalyzed eliminations, from p-NO_2-substituted, or $Cr(CO)_3$-complexed, 2-phenylethyl derivatives, where he found the influence of a p-NO_2 group to be much greater (i.e., accelerating) than that of the $Cr(CO)_3$ group toward E2 eliminations.[18] These workers found that the activation toward elimination by the p-NO_2 group was 28 times greater for tosylate and 55 times greater for bromide, than the activation by the $Cr(CO)_3$ group. They interpreted their data in terms of the far greater resonance interaction between the partial negative charge developed on the α-carbon atom and the p-NO_2 group in the transition state, than is possible in the σ-framework effect of the $Cr(CO)_3$ group, but found no evidence of steric hindrance to approach of the base for these monocyclics.[18] These values are comparable in magnitude with the estimated ratio of K values for **3** and **6**, in which a full negative charge is developed as opposed to the partial charges in the variable transition states for E2 elimination. The results obtained in the present study thus strongly support an interpretation that the charge-stabilizing effect of the $Cr(CO)_3$ group is via inductive or σ-framework interactions rather than via a resonance pathway.

Carbanion Structure. Although there has been some discussion of the detailed structure of carbanions derived from di- and triphenylmethanes, because of the steric hindrance between the benzene rings, it is generally agreed that these species are sp^2 hybridized at the ionizing center,[34] and similar conclusions have been reached for $Cr(CO)_3$ complexed derivatives.[9] The presence of p-NO_2 groups in **1**–**3** enhances the probability of coplanarity of the substituted rings in their carbanions, although all three phenyl rings in the carbanion from **1** cannot be coplanar. Similar considerations of **4**–**6** would also suggest that whereas coplanar benzene rings are found in the carbanion derived from **5**, and hence probably in that from **6**, such a situation cannot exist in the carbanion from **4**. However, a ~30° angle of twist of *all* rings in **4** or its carbanion would seem to us improbable, as this would bring the $Cr(CO)_3$ -complexed rings into conflict with the uncomplexed ring. A structure for the carbanions from **1** and **4**, comparable to that of the carbanion derived from 9-phenylfluorene, in which the phenyl group is orthogonal to the coplanar substituted rings,[34] would seem most likely.

Experimental Section

Materials. Compounds **1**–**3** were synthesized by standard literature procedures and recrystallized to constant melting points in accord with reported values. Compounds **4**–**6** were obtained according to reported methods and purified by chromatography.[40]

(Diphenylmethane-α,α-d_2)bis(tricarbonylchromium(0)) (5-d_2) was obtained according to the procedure of Trahanovsky.[41] Compound **5** (1.32 g, 3×10^{-2} mol) was stirred with a solution of potassium *tert*-butoxide (0.16 g, 1.5×10^{-3} mol) in Me_2SO-d_6 (10 mL) for 2 h. After addition of D_2O (10 mL), the reaction mixture was poured onto ice and extracted with CH_2Cl_2 and the solvent removed to yield 1.3 g (93%) of a mixture of **5** (22%) and **5**-d_2 (78%) (calculated from the ^1H NMR spectrum). Repeating the procedure on this mixture finally gave a sample of **5**-d_2 with

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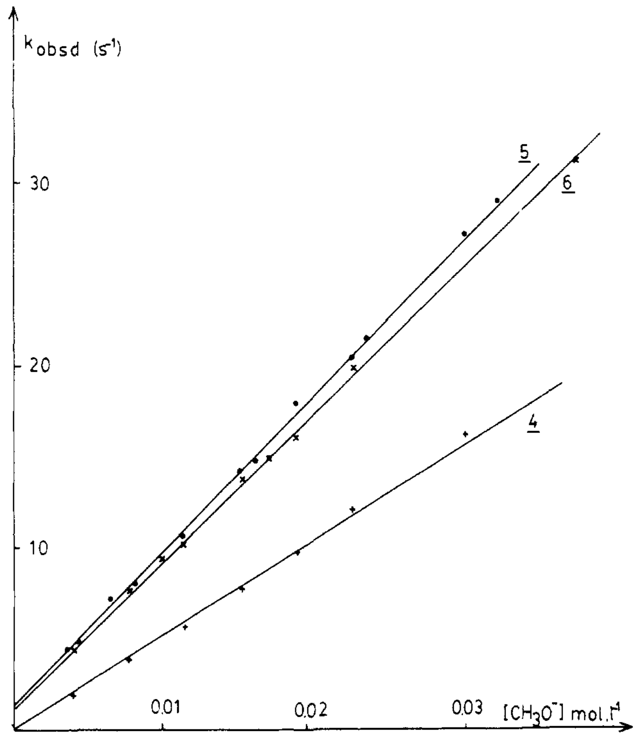

Figure 2. The methoxide ion concentration dependence of k_{obsd} (s^{-1}) for the ionization of the Cr(CO)$_3$ carbon acids **4**, **5**, and **6** in 98:2 Me_2SO–MeOH (t = 25 °C).

a deuterium content greater than 97% d_2 (which was evaluated from a 250-MHz proton NMR spectrum). The product was recrystallized from CH_2Cl_2–hexane to yield yellow crystals, mp 159 °C. All the kinetic experiments carried out with **5**-d_2 in the stopped-flow apparatus did not reveal any relaxation effect ascribable to the deprotonation of a hydrogen compound, further confirming the isotopic purity of **5**–d_2.

Solvents were purified and solutions made up as previously described.[42]

Measurements. Kinetic studies were carried out by using a Durrum stopped-flow spectrophotometer, with a thermostated cell compartment (±0.2 °C). All experiments were performed under first-order conditions, with a large excess of the base (10^{-3}–0.2 M) over the substrate concentration (($\sim$3–5) × 10^{-5} M). Under these experimental conditions, the observed first-order rate constant, k_{obsd}, for the approach to equilibrium

$$R_1R_2R_3CH + MeO^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_1R_2R_3C^- + MeOH$$

is simply given by

$$k_{obsd} = k_{-1} + k_1[MeO^-]$$

Plots of k_{obsd} vs. [MeO$^-$] were linear, as shown in Figure 2. This allowed determination of the rate constants k_1 and k_{-1} from slopes and intercepts, respectively. In some instances, the intercepts were too small to be accurately determined so that only the k_1 values could be obtained. The values of the equilibrium constants $K_1 = k_1/k_{-1}$ were calculated from the rate data obtained. The rate constants given in Tables I and II are considered accurate to ±5%.

The methoxide ion concentration dependence of k_{obsd} (s^{-1}) for the ionization of the Cr(CO)$_3$ carbon acids **4**–**6** in 98:2 Me_2SO–MeOH (t = 25 °C) is shown in Figure 2.

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Registry No. **1**, 21112-02-7; **2**, 1817-74-9; **3**, 1817-77-2; **4**, 73016-87-2; **5**, 32823-67-9; **6**, 32825-32-4.

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Stereochemistry and Mechanism of Palladium(II)-Induced Ring Opening of the Cyclopropane in a Vinylcyclopropane. Chloro- and Oxypalladation of (+)-2-Carene

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Reaction of (+)-2-carene (**1**) with $PdCl_2(MeCN)_2$ in a nonnucleophilic solvent such as chloroform or benzene resulted in a chloropalladation across the cyclopropane ring. The corresponding reaction performed in methanol or acetic acid gave a methoxy- and acetoxypalladation, respectively, across the cyclopropane ring. The chloropalladation showed a remarkable solvent dependence. Reaction in chloroform containing 2% of ethanol afforded mainly the six-membered ring (π-allyl)palladium complex **2** (**2**/**3** = 6.4:1), whereas reaction in benzene predominantly gave the seven-membered ring complex **3** (**2**/**3** = 1:6.1). Stereochemical studies showed that the ring opening by palladium has occurred with inversion for **1** → **2** but with retention for **1** → **3**, resulting in an overall trans chloropalladation in the latter case. The transformation of **1** to the methoxy and acetoxy complexes **5** and **7** occurred with the same stereochemistry as **1** → **2** (inversion). The (π-allyl)palladium complexes **2** and **7** were transformed to neomenthol (**12**) and α-terpineol (**14**), respectively.

Introduction

The activation of cyclopropanes by transition metals is an important type of reaction that has attracted considerable interest.[1-8] Two principal mechanisms for the activation, that result in opening of the ring, are possible. For example, the reaction may involve oxidative addition

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