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THE EFFECT OF ALKYL SUBSTITUTION ON THE THERMODYNAMIC STABILITY AND KINETIC REACTIVITY OF α-ANIONS OF METAL—CARBENE COMPLEXES

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Summary

Alkyl substitution was found to have only small effects on the thermodynamic and kinetic acidity and on the reactivity of anions generated α to the carbene carbon atom in metal—carbene complexes. The thermodynamic acidities of (2-oxacyclopentylidene)pentacarbonylchromium(0), I, and of (5-methyl-2-oxacyclopentylidene)pentacarbonylchromium(0), II, were found to be nearly equal. The rate of the base catalyzed deuterium exchange of the less substituted complex I, is 1.57 times faster than that of II. The reactivity of the anions generated from the less substituted complex I is 2.6—5.2 times less than that of anions generated from II.

Introduction

The evolution of metal—carbene complexes into useful reagents for organic synthesis [1,2] requires the development of general synthetic methods for the preparation of a wide variety of metal—carbene complexes. Recently we demonstrated that anions generated α to the carbene carbon atom of metal—carbene complexes are useful synthetic intermediates for the elaboration of metal—carbene complexes [3—6]. These carbene anions are easy to generate from metal—carbene complexes using relatively mild bases such as $NaOCH_3$ [7,8] *; for example, in THF (methylmethoxycarbene)pentacarbonylchromium(0) is as acidic as *p*-cyanophenol which has a pK_a of 8 in water [8]. In spite of their great stability, carbene anions are moderately reactive toward reactive electrophiles such as epoxides [4], α-bromoesters [4], aldehydes [3] and chloromethyl methyl ether [5]. Carbene anions are, however, unreactive towards primary alkyl halides, and saturated ketones and esters.

In the course of studying the reactions of carbene anions with electrophiles

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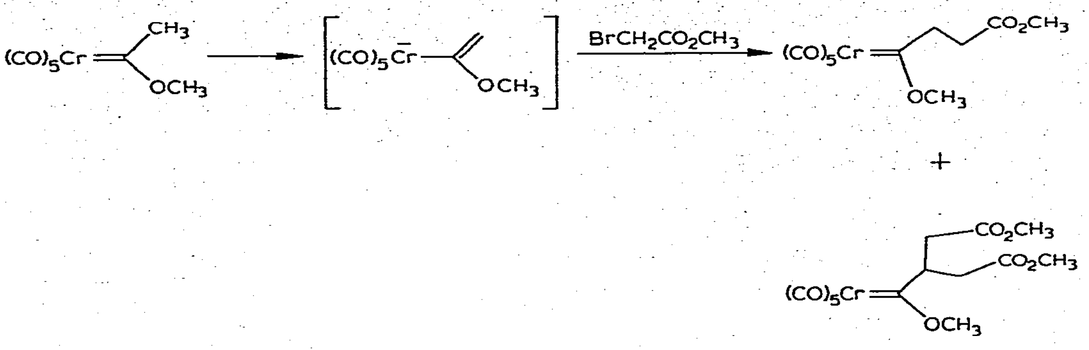
* Triethylamine has been shown to deprotonate the cationic nickel carbene complex, $[trans\text{-}C_6Cl_5(PPhMe_2)_2NiC(OCH_3)CH_3]^+ ClO_4^-$ [9].

we have found that dialkylation is a severe problem which detracts from the utility of this synthetic method [4,5]. For example, the reaction of the α-anion of (methylmethoxycarbene)pentacarbonylchromium(0) with methyl bromoacetate gives a 2 : 1 ratio of mono- and dialkylated material [4]. Presumably the

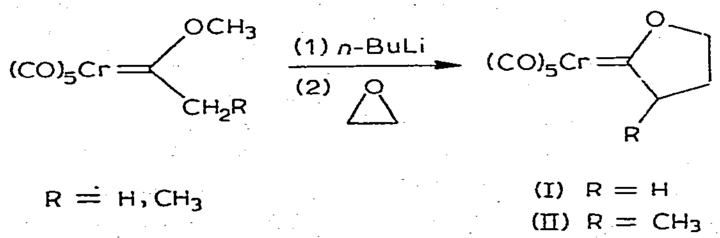


dialkylation proceeds via reaction of the initial alkylated product with a base to produce a more substituted carbene anion which is then further alkylated. Dialkylation would be favored; (1) if the more substituted carbene anion were greatly favored at equilibrium and/or (2) if the more substituted carbene anion were kinetically much more reactive. To understand the reasons underlying the dialkylation of carbene anions, we have studied the kinetic and thermodynamic stability and the kinetic reactivity towards alkylating agents of two metal—carbene complexes differing only in the degree of substitution at the carbon atom α to the carbene atom. The compounds chosen for the study were the cyclic carbene complexes I and II.

Results

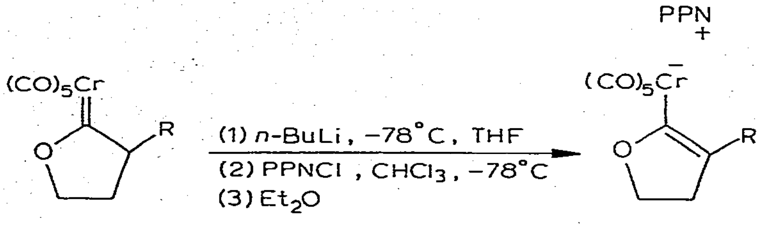
Synthesis

(2-Oxacyclopentylidene)pentacarbonylchromium(0), I, was obtained in 58% yield by reaction of $(CO)_5CrC(OCH_3)CH_3$ with ethylene oxide [4]. (5-Methyl-2-oxacyclopentylidene)pentacarbonylchromium(0), II, was prepared in 24% yield by reaction of $(CO)_5CrC(OCH_3)CH_2CH_3$ with ethylene oxide.

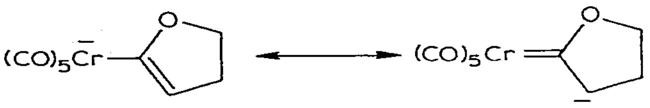


The bis(triphenylphosphine)iminium (PPN) salts, IA and IIA, were prepared in 76 and 40% yields, respectively, by treating the appropriate carbene complex with 1 equiv. of n-BuLi at −78°C followed by 1 equiv. of PPN chloride in $CHCl_3$.

The NMR and IR spectra of anions IA and IIA support the formulation of

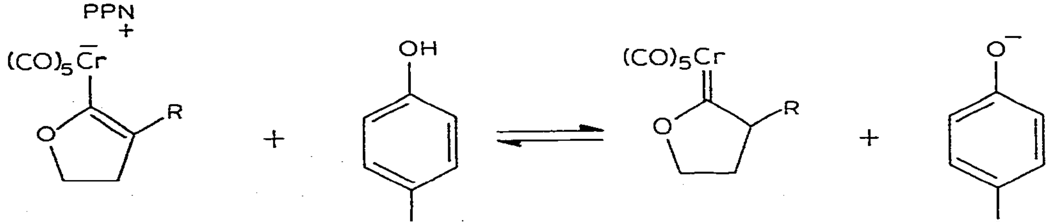

(IA) R = H
(IIA) R = CH_3

these species as vinylpentacarbonylchromium anions rather than as carbanions. The α-protons of I which appear as a triplet at δ 3.9 ppm are shifted downfield to δ 4.44 in anion IA; this is consistent with a change from protons on a saturated carbon to vinylic protons, (Fig. 1). Similarly, the methyl group of II at δ 1.50 shifts downfield to δ 1.78 upon formation of the vinyl chromium anion IIA. The CO bands in the IR spectrum of I occur at 2063 and 1943 cm^{-1}. Upon formation of anion IA, the stretching frequencies decrease to 2030, 1901, and 1850 cm^{-1} indicating a large increase in negative charge on chromium upon formation of the anion.



Thermodynamic acidity of I and II

The thermodynamic acidity of carbene complexes I and II in THF at 0° C was determined by adding various amounts of *p*-cyanophenol to a known concentration of their PPN salts, IA or IIA, to establish an equilibrium as shown below. In separate experiments, the ratios IA/I and IIA/II were determined by infrared spectroscopy at 0° C. The IR spectrum of I has an intense ($\epsilon = 3610$) band at 1943 cm^{-1} while the IR spectrum of anion IA has an intense ($\epsilon = 3770$) band at 1901 cm^{-1}, (Fig. 2). Since there is little overlap between these bands, an accurate IR analysis is possible. Similarly II has an intense band at 1943 cm^{-1} ($\epsilon = 2990$) while IIA has an intense band at 1901 cm^{-1} ($\epsilon = 2930$).


(IA) R = H
(IIA) R = CH_3
(A)
(I) R = H
(II) R = CH_3
(A^-)

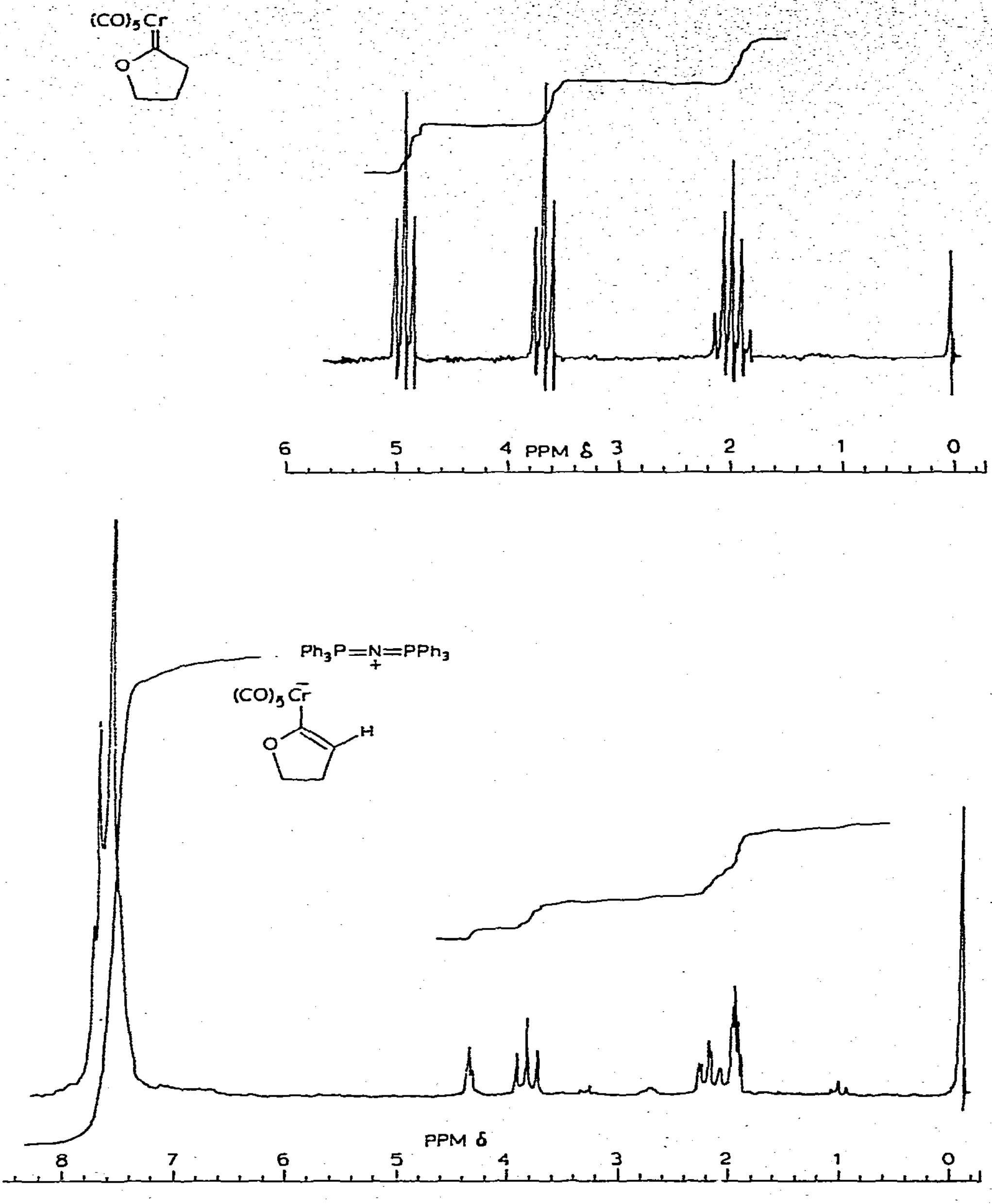


Fig. 1. 100 MHz NMR spectra of carbene complex I in CS_2 (top), and of carbene anion IA in acetone-d_6 (bottom).

The results in Table 1 indicate that carbene complex II has a slightly higher thermodynamic acidity compared to I and that both I and II have about the same pK_a as *p*-cyanophenol in THF. We have previously found that (methylmethoxycarbene)pentacarbonylchromium(0) also has a pK_a similar to that of *p*-cyanophenol in THF [8].

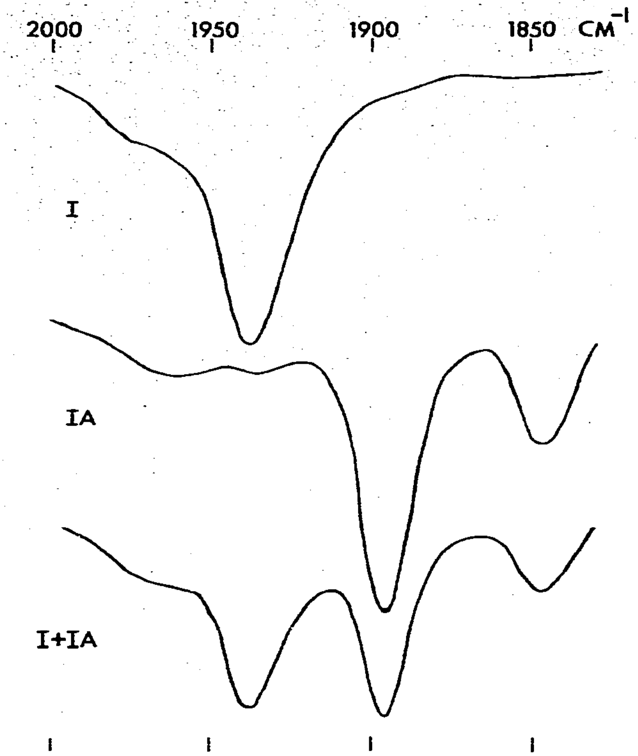


Fig. 2. Infrared spectra in THF at 0°C of carbene complex I (top), of carbene anion IA (middle), and of a mixture of I and IA obtained by addition of one equivalent of p-cyanophenol to IA (bottom).

Kinetic acidity of I and II

The kinetic acidity of carbene complexes I and II was determined by measuring the rate of base-catalyzed exchange of the α-hydrogens with D_2O. Acetone/ D_2O solutions (3.6 : 1.0 by volume) 0.42 M in I or II were monitored at 38°C by 100 MHz NMR. The data in Table 2 indicate an approximate first-order depen-

TABLE 1

RELATIVE THERMODYNAMIC ACIDITY OF I AND II

Equiv. p-cyanophenol	IA/I [a]	$K_I = \frac{[A^-][I]}{[A][IA]}$ [c]	IIA/II [a]	$K_{II} = \frac{[A^-][II]}{[A][IIA]}$ [c]	K_{II}/K_I
1.00 [b]	54 : 46	0.73 ± 0.04 [d]	53 : 47	0.79 ± 0.04	1.08 ± 0.05
1.10	51 : 49	0.77 ± 0.04	51 : 49	0.77 ± 0.04	1.00 ± 0.05
1.20	48 : 52	0.83 ± 0.04	47 : 53	0.89 ± 0.04	1.07 ± 0.05
					1.05 ± 0.05

[a] This ratio was determined from the IR spectra taken at 0°C in THF by observing the relative intensities of the bands at 1943 cm^{-1} for I or II and at 1901 cm^{-1} for IA or IIA. [b] The initial concentration of p-cyanophenol is 0.024 M. [c] A represents p-cyanophenol and A^- is the conjugate base of p-cyanophenol.
[d] Standard deviation assuming an error of ±5%.

TABLE 2

RATE OF BASE CATALYZED DEUTERIUM EXCHANGE OF I AND II [a]

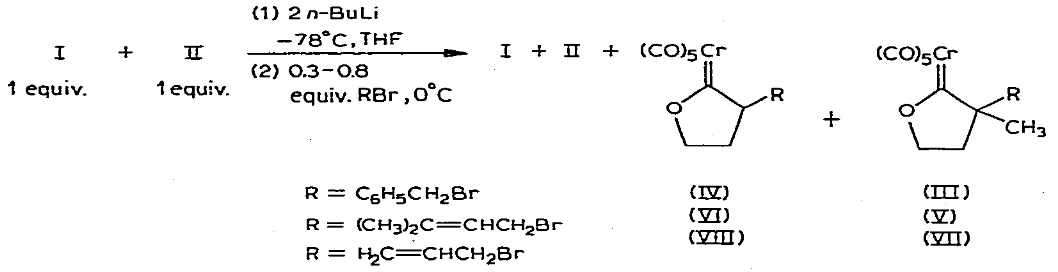
$[OD^-]$ (mol/l)	I $10^3k_{obs}(sec^{-1})$ [c]	II $10^3k_{obs}(sec^{-1})$ [c]	I $k_2(M^{-1}sec^{-1})$ [d]	II $k_2(M^{-1}sec^{-1})$ [d]	$\frac{k_{obs(I)}}{k_{obs(II)}}$
5.8×10^{-4} [b]	1.71 ± 0.13	1.22 ± 0.04	2.94 ± 0.22	2.10 ± 0.07	1.40 ± 0.11
8.7	2.58 ± 0.07	1.76 ± 0.11	2.96 ± 0.08	2.02 ± 0.13	1.46 ± 0.04
11.6	3.88 ± 0.26	2.08 ± 0.13	3.33 ± 0.22	1.80 ± 0.11	1.86 ± 0.12
			3.07 ± 0.24	1.97 ± 0.12	1.57 ± 0.12

[a] Reactions were performed in an NMR tube in 100 MHz NMR probe at 38°C using an acetone-d_6/D_2O solution (3.6 : 1 by volume). [b] 5 μl of a 0.04 *M* NaOD solution. [c] k_{obs} is a pseudo first order rate constant, $k_{obs} = k_2[OD^-]$ where rate $= k_2[OD^-][I]$. [d] [I] or [II] = 0.42 *M*. Each k_{obs} listed is an average of three separate experiments. k_2 is the calculated second order rate constant.

dence of the rate of exchange on the base concentration. The rate of exchange of the less substituted carbene complex I is 1.40—1.86 times faster than that of II. This difference in kinetic acidity is small but well outside of experimental error.

Relative reactivity of I and II towards alkylating agents

The relative reactivity of the α-anions of I and II with three alkylating agents was determined by allowing a mixture of the α-anions of I and II (1 equiv.each) to compete for a limited amount of alkylating agent (0.3—0.8 equiv.). Samples of the reaction mixture were analyzed at regular time intervals by high pressure liquid chromatography.



The relative rates were calculated using eq. (1) to take into account differences in initial and final concentrations of substrate. X is the fraction of IV, VI, or VIII formed from I; and Y is the fraction of III, V, or VII formed from II.

$$k_{II}/k_I = \frac{\ln(II/II_0)}{\ln(I/I_0)} = \frac{\ln(1-Y)}{\ln(1-X)} \qquad (1)$$

The α-anion of II was found to be more reactive than the α-anion of I by a factor of 3.26 for 1-bromo-3-methyl-2-butene, 2.60 for benzyl bromide, and 5.18 for allyl bromide.

In a separate experiment, one equivalent of the α-anion of II was reacted with a two-fold excess of benzyl bromide and 1-bromo-3-methyl-2-butene to give a 61% yield of V and a 19% yield of III. Therefore, in the reaction with II, 1-bromo-

TABLE 3

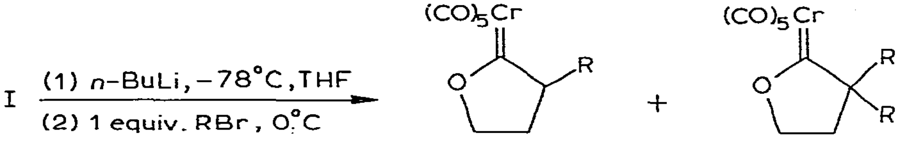
RELATIVE REACTIVITY OF I AND II TOWARD ALKYLATING AGENTS[a]

RBr	k_{II}/k_I [b]	Relative reactivity with anion of II [c]	Relative reactivity with NaOEt [d]	Relative reactivity with thiourea [e]
$(CH_3)_2C{=}CHCH_2Br$	3.26 ± 0.20	3.2	—	—
$C_6H_5CH_2Br$	2.60 ± 0.10	1	1	1
$H_2C{=}CHCH_2Br$	5.18 ± 0.65	—	0.59	0.25

[a] Reactions performed at 0°C in THF with 1 equiv. each of the α-anions of I and II and with 0.3—0.8 equiv. of RBr. Products analyzed by high pressure liquid chromatography. [b] k_{II}/k_I is the ratio of the rate of reaction of the α-anion of II compared to the α-anion of I with RBr. [c] Determined by addition of 2 equiv. each of the alkyl bromides to 1 equiv. of the anion of II. [d] Value obtained from ref. 10. [e] Value obtained from ref. 11.

3-methyl-2-butene has a reactivity about 3.2 times as large as that for benzyl bromide. It is known that benzyl bromide is 1.7 to 4 times as reactive as allyl bromide in various S_N2 displacement reactions [10,11]. The reactivity of I and II with the three alkylating agents should be in the order: 1-bromo-3-methyl-2-butene > benzyl bromide > allyl bromide. As Table 3 shows, there is no relation between the magnitude of k_{II}/k_I and the relative reactivity of RBr. The relative reactivity drops in moving down Table 3 from 1-bromo-3-methyl-2-butene to allyl bromide but k_{II}/k_I decreases for benzyl bromide and then increases for allyl bromide.

Samples of III, V, and VII were synthesized from II and the appropriate alkyl bromide as shown below while IV, VI, and VIII were obtained by the reaction of I and the appropriate alkyl bromide.

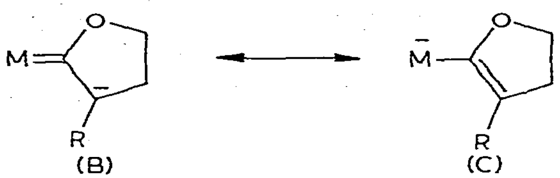


R = $C_6H_5CH_2Br$	(IV) 60%	(XI) 9%
R = $(CH_3)_2C{=}CHCH_2Br$	(VI) 47%	(X) 32%
R = $H_2C{=}CHCH_2Br$	(VIII) 40%	(IX) 27%

Discussion

Dialkylation is a severe synthetic problem in the alkylation of carbene anions. A priori, dialkylation might have been due to one or both of the following effects: the more substituted carbene anion might be (1) the principal species at equilibrium or (2) the kinetically most reactive species. The present studies were undertaken to delineate the factors responsible for dialkylation.

The factors which might influence the relative thermodynamic acidity of carbene complexes as a function of alkyl substitution can be considered in the context of resonance forms B and C.



If resonance form B were the best description of the carbene anion, electron donating alkyl groups would be expected to destabilize the anion. A methyl substituent in the 2-position of 1,3-dithiane lowers thermodynamic acidity by about 6 pK_a units [12]. Isopropyllithium has been estimated to be a stronger base than ethyllithium by 2 pK units [13]. On the other hand, if resonance form C were the best description of the carbene anions, alkyl substitution would be expected to stabilize the anion. Alkyl groups attached to double bonds lead to a stabilization of about 2.6 kcal per alkyl group *. Apparently, these two competing effects cancel one another in the case of carbene complexes I and II since the thermodynamic acidity was found to vary by only about 5%. It should be pointed out that both carbene complexes I and II are remarkably acidic in that their acidity is approximately the same as *p*-cyanophenol. The effect of alkyl substituents on the stability of carbanions has been found to depend markedly on the nature of the functional group stabilizing the anions. For nitro compounds, α-alkyl substitution increases the acidity; but for ketones, α-alkyl substitution can either decrease or increase the thermodynamic acidity **.

The kinetic acidity of metal—carbene complexes is remarkably high. The half time for exchange of I in acetone /D_2O at 38°C in the presence of 5.8×10^{-4} *M* NaOD was found to be 6.7 min. Under the reaction conditions used for alkylation reactions, the base concentration is ~0.1 *M* and the rate of equilibration of carbene complexes with carbene anions is fast (seconds) relative to the rate of alkylation of carbene anions (minutes). Methyl substitution at the α carbon of a metal—carbene complex was found to decrease the kinetic acidity by a factor of 1.5. Alkyl substitution also decreases the kinetic acidity of ketones [16—21]; the relative rate of hydrogen—deuterium exchange of $CH_3CH_2COCH_2CH_3/(CH_3)_2CHCOCH(CH_3)_2$ is 18 : 1 [16]. Alkyl substitution also decreases the kinetic acidity of nitro compounds; the relative rate of hydrogen—deuterium exchange of $CH_3NO_2/CH_3CH_2NO_2$ is 5.3 : 1 [22].

The alkylation of the more substituted carbene complex II was found to be 2.6—5.2 times faster than I with allylic and benzylic halides. This seems surprising in view of the fact that anions IA and IIA are of comparable thermodynamic stability and that anion IIA is more sterically hindered than IA. We have no good explanation for this greater reactivity of the more substituted anions. However, similar effects have been found for ketone enolates; the enolate of $C_6H_5COCH(CH_3)_2$ is 1.4 times more reactive than $C_6H_5COCH_2CH_2CH_3$ towards n-propyl chloride [23] and the more substituted enolate of 2-methylcyclohexanone is 1.5 times more reactive than the less substituted enolate of the same compound [24].

Our results indicate the detailed nature of the problem of dialkylation of car-

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* The heat of hydrogenation of 1-butene is 2.64 kcal mol^{-1} greater than that of *trans*-2-butene [14].

** In DMSO, the pK_a values of CH_3NO_2 and $CH_3CH_2NO_2$ are 17.2 and 16.7 respectively. The pK_a's of $C_6H_5COCH_3$, $C_6H_5COCH_2CH_3$, and $C_6H_5COCH(CH_3)_2$ are 24.7, 24.4, and 26.3 in DMSO; the pK_a's of CH_3COCH_3 and $CH_3CH_2COCH_2CH_3$ are 26.5 and 27.1 in DMSO [15].

bene complexes. We have found that the rate of base catalyzed exchange of the protons α to the carbene carbon atom is much faster than the rate of alkylation. Thus equilibrium between a more substituted and a less substituted carbene anion is fully established during the course of alkylation. The effect of substitution at the α carbon atom upon the equilibrium acidity of the carbene complexes was found to be negligible. Thus, there are comparable quantities of both the more and less substituted anions in solution. Somewhat surprisingly, the more substituted anion is 2—4 times more reactive towards alkylating agents even though it is more sterically hindered and thermodynamically no less stable than the less substituted anion. Thus, the problem of dialkylation of carbene anions is primarily due to the greater reactivity of the more substituted anion.

Experimental

All reactions were performed under a nitrogen atmosphere. Ether and tetrahydrofuran (THF) were distilled from sodium and benzophenone under a nitrogen atmosphere. NMR spectra were taken on a JEOLCO MH-100 spectrometer. Mass spectra were taken using an AEI-902 mass spectrometer. Infrared spectra were recorded on a Perkin—Elmer 267 Infrared spectrophotometer at 5X expansion. A variable temperature cell VLT-2 purchased from Research and Industrial Instruments Co. was used for IR measurements at 0° C. Preparative thin-layer chromatography (prep TLC) was performed on Merck PF 254 silica gel. A Chromatec Model 3100-2 liquid chromatograph was employed for the liquid chromatography studies. Carbene complexes I and II were prepared according to the method of Casey and Anderson [4]. Triphenylphosphine iminium chloride (PPNCl) was prepared according to the procedure of Ruff [25].

We did not obtain combustion analyses on the carbene complexes reported. We have fully characterized the elemental composition of these compounds by high resolution mass spectrometry. The structures of the compounds follow straight-forwardly from the methods of synthesis and IR and ^{1}H NMR. The purity of the compounds is attested to by (1) clean ^{1}H NMR spectra, (2) homogeneity on silica gel TLC, and (3) homogeneity on high pressure liquid chromatography using a reverse phase column. The HPLC is particularly useful in assessing the purity of these compounds since the retention times of the likely impurities (unalkylated or dialkylated material) are quite different.

PPN salt IA

n-BuLi (0.215 ml, 1.77 *M*, 0.38 mmol) was added to I (100 mg., 0.38 mmol) in 5 ml of THF at —78° C. After 2 min, PPNCl (220 mg, 0.38 mmol) in 1 ml of $CHCl_3$ was transferred by cannula into the solution. After an additional 2 min, 70 ml of Et_2O was added at —78° C over a ten min period to give a pale yellow precipitate which was filtered and washed with 15 ml of H_2O and 20 ml of Et_2O to give 231 mg(76%) of IA as a pale yellow solid, mp 138—139° C (decomp). NMR (acetone-d_6) δ 2.26 (dd, $J = 2, 9$ Hz, 2 H), 3.90 (t, $J = 9$ Hz, 2H, CH_2O), 4.44 (t, $J = 2$ Hz, 1H, C=CH), 7.4—7.9 ppm (mult., 30H, C_6H_5). IR (THF, 0° C) ν(CO) 2030(w), 1901(s), 1851(m) cm^{-1}.

The PPN salt IA (200 mg, 0.25 mmol) was dissolved in 2 ml of THF at 25° C. Addition of HCl in Et_2O (0.08 ml, 3.67 *M*, 0.29 mmol) gave a yellow solution and PPNCl as a white precipitate which was filtered. Evaporation of solvent gave I (64 mg, 98%) identified by comparison of its NMR spectrum with that of an authentic sample.

Extinction coefficients were determined in THF at 0°C for 0.012—0.020 *M* solutions using a 0.01 cm cell path and a 5X expansion: IA, 1901 cm^{-1} (ϵ = 3770); I, 1943 cm^{-1} (ϵ = 3610).

PPN Salt IIA

n-BuLi (0.29 ml, 1.54 *M*, 0.45 mmol) was added to II (126 mg, 0.45 mmol) in 5 ml of THF at —78°C and two min later PPNCl (263 mg, 0.45 mmol) in 1 ml $CHCl_3$ was added. After the addition of 25 ml of hexane to give an oil at —78°C, the solution was warmed to 0°C, and the solvent removed by cannula. When the oil was dissolved in 5 ml of THF and 30 ml of Et_2O was added, a yellow precipitate was obtained which was filtered and washed with 20 ml H_2O and 20 ml of Et_2O to give 148 mg (40%) of IIA as a yellow solid, mp 147—150°C (decomp.). NMR (acetone-d_6) δ 1.78(s, 3H, CH_3), 2.24(t, J = 9Hz, 2H), 3.90(t, J = 9Hz, 2H, CH_2O), 7.4—7.9 ppm (mult, 30H, C_6H_5). IR (THF, 0°C) ν(CO) 2033(w), 1901(s), 1850(m) cm^{-1}.

Extinction coefficients were determined as above: IIA, 1901 cm^{-1} (ϵ = 2930); II, 1943 cm^{-1} (ϵ = 2990).

Reaction of IA and IIA with p-cyanophenol

The thermodynamic acidity of II was determined by adding various amounts of a 0.4 *M* solution of *p*-cyanophenol in THF to a 0.024 *M* solution of IIA in THF at 0°C for a total volume of 1 ml of THF. Using the low temperature IR cell at 0°C, an IR was taken using 5X expansion of the THF solution of the anion. By measuring the absorbances of II and IIA from the peaks at 1943 and 1901 cm^{-1}, respectively, the relative amounts of II and IIA could be found. The maximum absorbance for each peak does not involve any contribution from the other peak so the absorbances at 1943 cm^{-1} and 1901 cm^{-1} can be read directly from the spectra.

One equivalent (0.060 ml, 0.40 *M* in THF, 0.024 mmol) of *p*-cyanophenol was injected into 0.94 ml of THF at 0°C containing IIA (19.5 mg, 0.024 mmol). The resulting IR at 0°C shows a 53 : 47 ratio of IIA/II after correcting for the different ϵ values. All the data in Table 1 were obtained similarly.

Deuterium exchange of the α-hydrogens of I using NaOD, D_2O, and acetone-d_6

The acetone-d_6 used in the exchange experiments was dried by stirring over K_2CO_3 followed by bulb to bulb distillation. The NaOD (0.04 *M* in D_2O) solution was prepared by the addition of a small piece of sodium to D_2O. Compound I (38 mg, 0.145 mmol), 270 μl of acetone-d_6, D_2O (70 μl, 3.5 mmol), and NaOD (5 μl, 0.04 *M*, 1.9 × 10^{-4} mmol) were added to a carefully cleaned NMR tube and the tube inserted into the NMR probe (38°). The deuterium exchange was followed by integration using the triplet at δ 5.0 (corresponding to the CH_2O protons) as an internal reference. The triplet at δ 3.8 corresponding to the Cr=C—CH_2 protons decreased with time as a singlet at δ 4.1 ppm for the HOD proton gradually increased. Integrations were taken every 15 seconds up to about one half life. The observed first order rate constant k_{obs} was found by using a least squares plot to find the slope of the line of ln A_0/A vs. time where A_0 = area of peak at δ 3.8/ area of peak at δ 5.0 at time = 0 and A = area of peak at δ 3.8/ area of peak at δ 5.0 at time = t. Typical r^2 values were 0.99. The average of three runs was used to determine k_{obs} for each base concentration. The experiment was repeated with 7.5 μl NaOD and 67.5 μl D_2O and again with 10 μl NaOD and 65 μl D_2O. In each case 270 μl of acetone-d_6 and 0.145 mmol of I were used. With 5 μl of NaOD and 70 μl D_2O, the three values for k_{obs} were 1.72, 1.59, and 1.85 × 10^{-3} sec^{-1} for an average of 1.71 ± 0.13 × 10^{-3} sec^{-1}. The three values obtained for k_{obs} when using 7.5 μl NaOD and 67.5 μl of D_2O were 2.54, 2.66, and 2.53 × 10^{-3} sec^{-1} for an average of 2.58 ± 0.07 × 10^{-3} sec^{-1}. When 10 μl of NaOD and 65 μl of D_2O were added, values of 4.08, 3.58, and 3.97 × 10^{-3} sec^{-1} were obtained for k_{obs} for an average of 3.88 ± 0.26 × 10^{-3} sec^{-1}.

Deuterium exchange of the α-hydrogen of II using NaOD, D_2O, and acetone-d_6

The exchange experiments involving II were carried out with the same procedure as for I. The amount of II used in each experiment was 40 mg (0.145 mmol). Otherwise, the amounts of acetone-d_6, NaOD, and D_2O remained the same. When 5 μl of NaOD and 70 μl of D_2O were added, the values of k_{obs} obtained were 1.28, 1.19, 1.19, and 1.24 × 10^{-3} sec^{-1} for an average of 1.22 ± 0.04 × 10^{-3} sec^{-1}. The addition of 7.5 μl of 0.04 *M* NaOD and 67.5 μl of D_2O resulted in values of 1.79, 1.86, and 1.64 × 10^{-3} sec^{-1} for an average k_{obs} of 1.76 ± 0.11 × 10^{-3} sec^{-1}. With the addition of 10 μl of 0.04 *M* NaOD and 65 μl D_2O, the values found for k_{obs} were 1.95, 2.04, and 2.21 × 10^{-3} sec^{-1} for an average of 2.08 ± 0.13 × 10^{-1} sec^{-1}.

(5-Benzyl-2-oxacyclopentylidene)pentacarbonylchromium(0), IV, and (5,5-dibenzyl-2-oxacyclopentylidene)pentacarbonylchromium(0), XI

The α-anion of I was generated by the addition of n-BuLi (0.25 ml, 1.61 *M*, 0.40 mmol) to I (100 mg, 0.382 mmol) in 10 ml of THF at −78°C. Benzyl bromide (47 μl, 0.40 mmol) was injected and the solution warmed to 0°C for 15 min and then stirred at 25°C for another 35 min. Prep TLC (hexane) after three elutions gave three yellow bands. The bottom band (R_f = 0.29) afforded 35 mg (35%) of I. The middle band yielded IV (R_f = 0.37, 52 mg, 60% based on recovered I) as a yellow solid, mp 76—78°C. NMR ($CDCl_3$) δ 1.80 (mult., 2H, $\underline{CH_2}CH_2O$), 2.38 (dd, J = 11, 13 Hz, 1H, benzylic H), 3.6—4.0 (mult., 2H, one methine and one benzylic H), 4.84 (mult., 2H, CH_2O), 7.26 ppm (mult, 5H, phenyl). IR (hexane) ν(CO) 2064(w), 1989(w), 1963(s), 1954(s), 1935(s) cm^{-1}. Exact mass: found: 352.0046 $C_{16}H_{12}O_6Cr$ calcd.: 352.0038.

The upper band gave XI ($R_f \sim$ 0.43, 9 mg, 9% based on recovered I) as a yellow solid, mp 101—104°C. NMR ($CDCl_3$) δ 1.82(t, J = 7 Hz, 2H), 3.16 (d, J = 14 Hz, 2 H, benzylic H's), 3.36 (d, J = 14 Hz, 2H, benzylic), 3.97 (t, J = 7 Hz, 2H, CH_2O), 7.0—7.3 (mult., 10H). IR (hexane) ν(CO) 2063(w), 1986(w), 1957(s), 1948(s), 1934(s) cm^{-1}. Exact mass: found: 442.0445 $C_{23}H_{18}O_6Cr$ calcd.: 442.0407.

Preparation of (5-benzyl-5-methyl-2-oxacyclopentylidene)pentacarbonylchromium(0)III

n-BuLi (0.20 ml, 1.4 *M*, 0.28 mmol) was injected into 10 ml of THF at −78°C containing II (70.5 mg, 0.255 mmol) and the solution was warmed to 0°C. Benzyl bromide (36 μl, 0.306 mmol) was injected and after 80 min at 0°C a yellow-orange color resulted. Prep TLC (4 : 1 hexane/Et_2O) gave II (R_f = 0.18, 7 mg, 10%), and III (R_f = 0.30, 63 mg, 75% based on recovered II) as a yellow solid, mp 90—92°C. NMR ($CDCl_3$) δ 1.35(s, 3H, CH_3), 1.4—1.6 (d of t, J = 7, 12 Hz, 1H of $C\underline{H}_2CH_2O$), 1.9—1.2 (d of t, J = 7, 12 Hz, 1H of $C\underline{H}_2CH_2O$), 2.66 (d, J = 13 Hz, one benzylic H), 3.36 (d, J = 13 Hz, one benzylic H), 4.72 (mult., 2H, CH_2O), 7.21 ppm (mult., 5H, phenyl). IR(hexane) ν(CO) 2064(w), 1989(w), 1962(s), 1955(s), 1933(s) cm^{-1}. Exact mass: found: 366.0190 $C_{17}H_{14}O_6Cr$ calcd.: 366.0194.

[5-(3,3-Dimethylallyl)-2-oxacyclopentylidene]pentacarbonylchromium(0), VI and [5,5-(3,3-dimethylallyl)-2-oxacyclopentylidene]pentacarbonylchromium(0), X

n-BuLi (0.285 ml, 1.4 *M*, 0.40 mmol) was injected into 10 ml of THF at —78°C containing I (100 mg, 0.38 mmol). The pale yellow solution was warmed to 0°C and 1-bromo-3-methyl-2-butene (61 mg, 0.41 mmol) was added. After 30 min at 0°C the solution became orange. Prep TLC (hexane) provided three bands after three elutions. The lower band (R_f = 0.16) gave 35 mg (35%) of I. The middle band afforded VI (R_f = 0.25, 38 mg, 47% based on recovered I) as an orange oil. NMR ($CDCl_3$) δ 1.67(s, 3H, CH_3), 1.73(s, 3H, CH_3), 1.8—2.4 (mult., 3H, 1 allylic H and $C\underline{H}_2CH_2O$), 2.88 (mult., 1H, allylic H), 3.67 (mult., 1H, methine H), 4.80 (mult., 2H, CH_2O), 5.00 ppm (br t, J = 8 Hz, 1H, vinyl H). IR (hexane) ν(CO) 2064(w), 1989(w), 1961(s, sh), 1954(s), 1938(s) cm^{-1}. Exact mass: found: 330.0182 $C_{14}H_{14}O_6Cr$ calcd.: 330.0194.

The top yellow band afforded X (R_f = 0.30, 32 mg, 32% based on recovered I) as a yellow solid, mp 55—57°C. NMR ($CDCl_3$) δ 1.68(s, 6H, CH_3), 1.73(s, 6H, CH_3), superimposed on a triplet at 1.76 (2H, $C\underline{H}_2CH_2O$), 2.50 (dd, J = 6, 15 Hz, 2H, allyl H), 2.78 (dd, J = 8, 15 Hz, 2H, allylic H's), 4.82 ppm (t, J = 7 Hz, 2H, CH_2O), superimposed on a multiplet (2H, vinyl H's). IR (hexane) ν(CO) 2063(m), 1987(w), 1956(s, (sh)), 1951(s), 1930(s) cm^{-1}. Exact mass: found: 398.0823 $C_{19}H_{22}O_6Cr$ calcd.: 398.0820.

[5-(3,3-Dimethylallyl)-5-methyl-2-oxacyclopentylidene]pentacarbonylchromium-(0), V

n-BuLi (0.22 ml, 1.61 *M*, 0.35 mmol) was injected into 10 ml of THF at —78°C containing II (92 mg, 0.334 mmol). After warming to 0°C, 1-bromo-3-methyl-2-butene (60 mg, 0.40 mmol) was added and the solution stirred for 80 min. Prep TLC (hexane) after two elutions gave II (17.5 mg, 19%, R_f = 0.23) and V (R_f = 0.35, 77 mg, 83% based on recovered II) as an orange oil. NMR ($CDCl_3$) δ 1.41 (s, 3H, CH_3), 1.5—2.1 (mult., 8H, two CH_3's and $CH_2C\underline{H}_2O$), 2.24 (dd, J = 7.5, 14.5 Hz, 1H, allyl H), 2.76 (dd, J = 7.5, 14.5 Hz, 1H, allyl H), 4.86 (t, J = 7.5 Hz, 2H, CH_2O), 5.07 ppm (broad t, J = 7 Hz, 1H, vinyl). IR (hexane) ν(CO) 2065(w), 1991(w), 1963(s), 1957(s), 1936(s) cm^{-1}. Exact mass: found: 344.0343 $C_{15}H_{16}O_6Cr$ calcd.: 344.0351.

(5-Allyl-2-oxacyclopentylidene)pentacarbonylchromium(0), VIII, and 5,5-diallyl-2-oxacyclopentylidene)pentacarbonylchromium(0), IX

n-BuLi (0.27 ml, 1.40 *M*, 0.38 mmol) was injected into 10 ml of THF at

—78°C containing I (100 mg, 0.38 mmol). The solution was warmed to 0°C and allyl bromide (34 μl, 0.40 mmol) was injected followed by stirring for 2 h at 0°C. Solvent was removed and prep TLC (2 : 1 hexane/Et_2O) gave I (R_f = 0.21, 34 mg, 34%) and a 3 : 2 mixture of VIII and IX (R_f = 0.29, 55 mg,); the mixture was rechromatographed on TLC and after 5 elutions in hexane the top one-third of the orange band gave IX as an orange oil. NMR ($CDCl_3$) δ 1.85 (t, J = 8 Hz, 2H, $C\underline{H}_2CH_2O$), 2.69 (d, J = 7 Hz, 4H, allyl H), 4.85 (t, J = 8 Hz, 2H, CH_2O), 5.10 (mult., 4H, $C{=}CH_2$), 5.64 ppm (mult., 2H, $HC{=}CH_2$). IR (hexane) ν(CO) 2064(w), 1986(w), 1958(s), 1931(s) cm^{-1}. Exact mass: found: 342.0186 $C_{15}H_{14}O_6Cr$ calcd.: 342.0194.

The lower two-thirds of the band was rechromatographed in hexane. After four elutions the bottom half of the band gave pure VIII as a yellow solid, mp 37—39°C. NMR ($CDCl_3$) δ 1.6—2.3 (mult., 3H, 1 allyl H and $C\underline{H}_2CH_2O$), 3.00 (mult. 1H, allyl H), 3.78 (mult., 1H, methine H), 4.84 (mult., 2H, CH_2O), 5.0—5.3 (mult., 2H, $C{=}CH_2$), 5.5—5.9 ppm (mult., 1H, $\underline{H}C{=}CH_2$). IR (hexane) ν(CO) 2064(w), 1987(w), 1962(s), 1953(s), 1937(s) cm^{-1}. Exact mass: found: 301.9867 $C_{10}H_{12}O_6Cr$ calcd.: 301.9881.

(5-Allyl-5-methyl-2-oxacyclopentylidene)pentacarbonylchromium(0), VII

n-BuLi (0.16 ml, 1.61 *M*, 0.26 mmol) was added to II (70.7 mg, 0.256 mmol) in 10 ml of THF at —78°C. The solution was warmed to 25°C and allyl bromide (23 μl, 0.30 mmol) was added. After 30 min the solvent was removed. Prep TLC (hexane) gave only one yellow band (R_f = 0.22) after two elutions. The top two-thirds of the band gave 45 mg of VII while the lower one-third of the band afforded 19 mg of a 2 : 1 mixture of VII/II according to NMR. The total yield of VII was 58.5 mg (80% based on recovered II) and 6 mg (8%) of II was recovered. Pure VII was obtained as a yellow solid, mp 47—49°C. NMR ($CDCl_3$) δ 1.42 (s, 3H, CH_3), 1.64 (d of t, J = 7, 12.5 Hz, 1H, 1H of $C\underline{H}_2CH_2O$), 1.94 (d of t, J = 7, 12.5 Hz, 1H, 1H of $C\underline{H}_2CH_2O$), 2.33 (dd, J = 7, 13.5 Hz, 1H, allylic H), 2.68 (dd, J = 7, 13.5 Hz, 1H, allylic H), 4.81 (t, J = 7 Hz, 2H, CH_2O), 5—5.3 (mult., 2H, $C{=}CH_2$), 5.45—5.9 ppm (mult., 1H, $C\underline{H}{=}CH_2$). IR (hexane) ν(CO) 2065(w), 1991(w), 1964(s, (sh)), 1957(s), 1937(s) cm^{-1}. Exact mass: found 344.0343 $C_{15}H_{16}O_6Cr$ calcd.: 344.0351.

Liquid chromatographic analysis of competition reactions

Liquid chromatographic analyses were performed on a Chromatec Model 3100-2 liquid chromatograph equipped with a UV detector (254 mμ) and a Chromasep RVP column (4′ × 2.1 mm). Response factors were obtained in all cases using an internal standard and carbene complexes that were homogeneous on TLC and liquid chromatography.

For the reaction of I and II with benzyl bromide, a 50 : 50 MeOH/H_2O mixture (by wt.) was employed as the mobile phase (2 ml/min flow rate) and 1,1-diphenyl-1-propene as internal standard. The retention times were the following: III (14.4 min); IV (9.5 min); 1,1-diphenyl-1-propene (4.6 min).

In the reaction of I and II with 1-bromo-3-methyl-2-butene, using the same mobile phase, flow rate, and internal standard as above, the retention time of V was 16.5 min and for VI was 11 min.

For the reaction of I and II with allyl bromide, the flow rate remained the same as above but the mobile phase was changed to a 46 : 54 $MeOH/H_2O$ mixture and the internal standard was 1,1-diphenyl-2-methyl-1-butene. The retention times were the following: VII (12.8 min.); VIII (8.1 min.); 1,1-diphenyl-2-methyl-1-butene (24 min).

Reaction of the α-anions of I and II with benzyl bromide

n-BuLi (0.10 ml, 1.60 *M*, 0.165 mmol) was injected into 12 ml of THF at —78°C containing I (23 mg, 0.088 mmol) and II (24.2 mg, 0.088 mmol). The solution was warmed to 0°C and benzyl bromide (6.2 mg, 0.036 mmol, 0.41 equiv.) and 1,1-diphenyl-1-propene (18 mg, int.std.) were added. Samples were taken at 20 min intervals between 1.5 and 3 h. and analyzed by liquid chromatography. Using eq. I, the anion of II was found in three separate experiments to be more reactive than the anion of I towards benzyl bromide by factors of 2.58 ± 0.14, 2.69 ± 0.15, and 2.54 ± 0.16, giving an average value of 2.60 ± 0.25.

Reaction of the α-anions of I and II with 1-bromo-3-methyl-2-butene

n-BuLi (0.15 ml, 1.61 *M*, 0.238 mmol) was added to I (31.2 mg, 0.119 mmol) and II (32.8 mg, 0.119 mmol) in 10 ml of THF at —78°C. The solution was warmed to 0°C and 1-bromo-3-methyl-2-butene (14.2 mg, 0.095 mmol, 0.80 equiv.) and 18.7 mg of standard were added. Six samples were taken at about 20 min intervals between 10 min and 2 h. Using eq. 1, the anion of II was found in three separate experiments to be more reactive than the anion of I towards 1-bromo-3-methyl-2-butene by factors of 3.31 ± 0.25, 3.39 ± 0.10, and 3.09 ± 0.31 for an average of 3.26 ± 0.30.

Reaction of the α-anions of I and II with allyl bromide

n-BuLi (0.093 ml, 0.149 mmol) was added to I (19.6 mg, 0.075 mmol) and II (20.6 mg, 0.075 mmol) in 16 ml of THF at —78°C. After the solution was warmed to 0°C, allyl bromide (4 mg, 0.033 mmol, 0.44 equiv.) and standard (7.5 mg) were added. Four samples were taken at 30 min intervals between 85 and 176 min. Using eq. 1, the anion of II was found in three separate experiments to be more reactive than the anion of I towards allyl bromide by factors of 5.82 ± 0.23, 4.58 ± 0.17, and 5.15 ± 0.26 for an average of 5.18 ± 0.65.

Reaction of the α-anion of II with benzyl bromide and 1-bromo-3-methyl-2-butene

n-BuLi (0.26 ml, 0.364 mmol) was added to II (100 mg, 0.364 mmol) in 10 ml of THF at —78°C. The solution was warmed to 0°C and benzyl bromide (89 μl, 0.728 mmol) and 1-bromo-3-methyl-2-butene (102 mg, 0.728 mmol) were simultaneously injected. After 35 min at 0°C the solvent was removed and prep TLC (hexane) gave V (R_f = 0.38, 76.6 mg, 61%) and III (R_f = 0.32, 25.4 mg, 19%). Compounds III and V were identified by comparison of their NMR's with those of authentic samples. The anion of II therefore reacts about 3.2 times faster with 1-bromo-3-methyl-2-butene than with benzyl bromide.

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