methyl potassium dinitroacetate, 33717-84-9; potassium dinitroacetonitrile, 6928-22-9; ammonium dinitromethane, 12373-04-5; potassium dinitroethanol, 6928-29-6; fluorodinitroethanol, 17003-75-7; fluorodinitromethane, 7182-87-8; fluorodinitroacetonitrile, 15562-09-1; fluorodinitroacetamide, 15562-10-4; dimethyl dinitromalonate, 66901-53-9; dimethyl nitromalonate, 5437-67-2; fluorodinitroethyl methyl carbonate, 66901-54-0; methyl cyanodinitroacetate, 66901-55-1; diethyl nitromalonate, 603-67-8; dinitromethane, 625-76-3.

References and Notes

(1) This work was supported by the Air Force Rocket Propulsion Laboratory, Director of Science and Technology, Air Force Systems Command, U.S. Air Force, Edwards, Calif. 93523.
(2) R. Villiers, *Bull. Soc. Chim. Fr.*, **41**, 281 (1884).
(3) S. M. Loganitsch, *Ber.*, **15**, 471 (1882).
(4) P. Duden, *Ber.*, **26**, 3003 (1893).
(5) R. B. Burrows and L. Hunter, *J. Chem. Soc.*, 1357 (1932).
(6) H. Feuer, G. B. Backman, and J. P. Kispersky, *J. Am. Chem. Soc.*, **73**, 1360 (1951).
(7) For a review, see P. Noble, Jr.. F. G. Borgardt, and W. R. Reed, *Chem. Rev.*, **64**, 19 (1964).
(8) R. B. Kaplan and H. Schechter, *J. Am. Chem. Soc.*, **83**, 3535 (1961).
(9) L. Bouveault and W. Wahl, *C. R. Hebd. Seances Acad. Sci.*, **136**, 159 (1903).
(10) L. W. Kissinger and H. E. Ungnade, *J. Org. Chem.*, **23**, 1340 (1958).
(11) R. E. Strube, "Organic Syntheses", Collect. Vol. 4, Wiley, New York, N.Y., 1963, p 417.
(12) The formation of 3,4-bis(alkoxycarbonyl)furazan 2-oxides as the side reaction products in the nitration of ethyl acetoacetate has been reported by L. Bouveault and W. Wahl, *Bull. Soc. Chim. Fr.*, **31**, 847 (1904). For more recent work, see S. Sifniades, *J. Org. Chem.*, **40**, 3562 (1975), and references therein.
(13) L. I. Eremenko and F. Ya. Natsibullin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **4**, 912 (1968).
(14) M. J. Kamlet and H. G. Adolph, *J. Org. Chem.*, **33**, 3073 (1968).
(15) Houbein-Veil and Beilstein attributed the preparation of dinitromalonate to J. B. Manke, *Recl. Trav. Chim. Pays-Bas*, **49**, 381 (1930). This paper, dealing with the nitration of malonates, does not discuss the compound and does not even have an Experimental Section.
(16) D. I. Weisblat and D. A. Lyttle, *J. Am. Chem. Soc.*, **71**, 3079 (1949).
(17) C. O. Parker, *Tetrahedron*, **17**, 109 (1962).
(18) P. Duden and W. Pondorf, *Ber.*, **38**, 2031 (1905).
(19) V. Grakauskas and K. Baum, *J. Org. Chem.*, **33**, 3080 (1968).
(20) L. Herzog, M. H. Gold, and R. D. Geckler, *J. Am. Chem. Soc.*, **73**, 749 (1951).
(21) R. A. Wiesboeck and J. J. Ruff, *J. Org. Chem.*, **33**, 1257 (1968).
(22) Dimethyl nitromalonate, bp 80 °C (0.3 mm), was prepared in 95% yield following the procedure of D. I. Weisblat and D. A. Lyttle, ref 16, used for the synthesis of the diethyl derivative: NMR ($CDCl_3$) δ 3.83 (s, 6 H) and 6.63 (s, 1 H). Anal. Calcd for $C_5H_7NO_2$: C, 33.90; H, 3.98. Found: C, 33.61; H, 3.92.
(23) See V. Grakauskas, *J. Org. Chem.*, **35**, 3030 (1970), for the synthesis and NMR spectrum of fluorodinitroethyl methyl carbonate.

Competitive Processes in the Hydration of Dicarbonyl η^5-(Cyclopentadienyl)alleneiron Cations

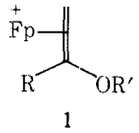
Philip Klemarczyk and Myron Rosenblum*

Department of Chemistry, Brandeis University, Waltham, Massachusetts 02154

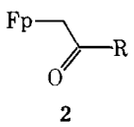
Received February 6, 1978

Hydration of the allene complex [**3**, Fp = $CpFe(CO)_2$], under acidic conditions, gives a mixture of ketone and aldehyde complexes (**4** and **5**). The aldehyde complex is shown to be derived by acid catalyzed rearrangement of the allyl alcohol complex (**6**) in a process involving the metal-stabilized cation (**7**). Rearrangement occurs at an appreciable rate even at pH 3.3, reflecting the unusually high stability of **7**. Hydration of *syn*-3-methylallene and *syn*-3-phenylallene complexes (**13a,b**) proceeds in a manner closely paralleling the parent complex, but the isomeric *anti*-3-methylallene and *anti*-3-phenylallene complexes (**14a,b**) behave differently. These undergo hydration principally through the less stable tautomeric 1-methylallene and 1-phenylallene complexes (**15a,b**) due to steric effects associated with the anti substituent.

Recently, our interest in the use of complexes such as **1** as organometallic synthons prompted us to examine the preparation of the precursor ketones (**2**) by routes other than those previously employed[1] [Fp ≡ η^5-$C_5H_5Fe(CO)_2$].



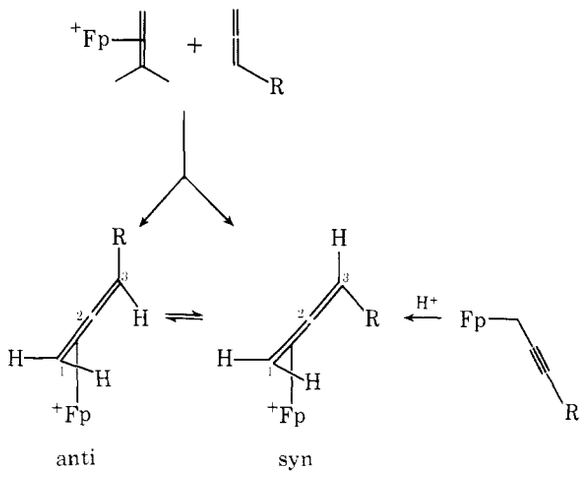
1



2

Since it is well known that coordinated olefins in Fp(olefin) cations readily add a number of carbon and heteronuclear nucleophiles,[2] we considered the prospect that Fp(allene) cations might serve as useful precursors of **2**. The allene complexes are readily available either through an exchange reaction involving the Fp(isobutylene) cation and an allene[3] or by protonation of a (σ-propargyl)Fp complex.[4] The latter are conveniently obtained by metalation with Fp anion of either 1-halo- or 1-tosyloxy-2-alkynes.[5] While the exchange reaction with monosubstituted allenes may be expected to afford mixtures of syn- and anti-3-substituted allene complexes,[3] protonation of (σ-progargyl)Fp complexes has been observed to proceed stereospecifically to give the syn stereoisomers exclusively.[6,7] Furthermore, syn and anti stereoisomers have been shown to be thermally interconvertible through a succession of 1,2 shifts by the Fp group[3] (Scheme I).

Scheme I



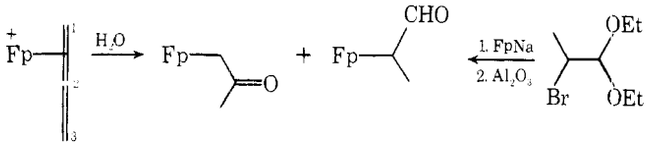
Results

Hydration of the Fp(allene) Cation. In general, the addition of nucleophiles, including hydroxide ion, to Fp(allene)

0022-3263/78/1943-3488$01.00/0

cations has been shown to occur preferentially at C(1).[7] However, hydration in acid media might be expected to yield the desired ketone, since under these conditions addition to C(1) would be expected to be reversible, while reaction at C(2) would not.

In the event, hydrolysis of the parent cation (**3**) in aqueous acetone at room temperature for 10 min gave a 1:2 mixture of the desired ketone (**4**) and a second component in 61% yield. This substance could not be separated chromatographically from the ketone, but an ^1H NMR spectrum of the mixture showed the presence of an aldehyde proton as a doublet signal at δ 9.2, as well as a methyl doublet at δ 1.20, a one proton double quartet at δ 2.3, and a singlet resonance at δ 4.67 for cyclopentadienyl protons. On the basis of these data, the complex was assigned the structure **5**, and this was readily



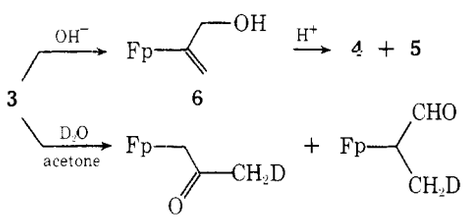
3 4 5

confirmed by its synthesis from α-bromopropionaldehyde diethyl acetal by metalation and hydrolysis.

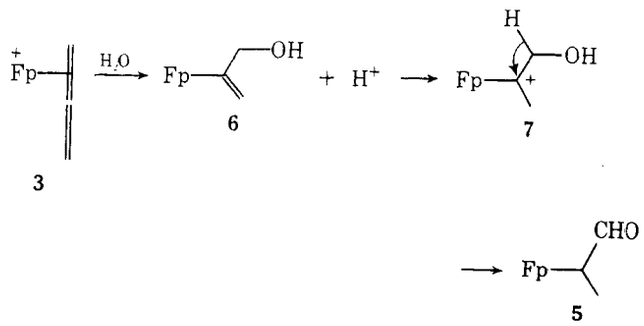
The formation of **4** in this reaction requires no special comment, but the aldehyde (**5**) represents a form of rearrangement product not hitherto observed in the reactions of Fp(allene) cations with nucleophiles.[7]

The allyl alcohol **6**, a likely intermediate in the rearrangement reaction, may be prepared by treatment of **3** with benzyltrimethylammonium acetate, followed by lithium aluminum hydride reduction of the acetate, or more directly by treatment of **3** with excess 0.1 N sodium hydroxide.

Brief exposure of the allyl alcohol (**6**) to 1 equiv of fluoroboric acid in aqueous acetone at room temperature converted it to a 1:2 mixture of **4** and **5** in 70% yield. Significantly, when hydration of **3** was carried out in D_2O–acetone, the propionaldehyde complex obtained was found to be monodeuterated exclusively at C(3).

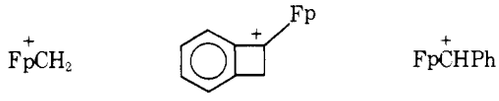


These results are in accord with a mechanism involving intermediacy of the cationic carbene complex (**7**), generated by protonation of the allyl alcohol (**6**). Subsequent hydride



shift within this cation yields the aldehyde (**5**). This latter step requires no special comment, since it is well precedented.[8] However, the formation of the carbene complex (**7**) under comparatively mild acid conditions is remarkable.

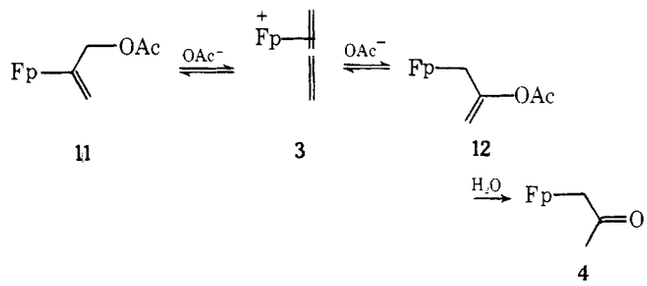
Evidence for the transient existence of the parent cationic carbene complex (**8**) was provided some years ago by Jolly and Pettit,[9] and by Green, Ishaq, and Whiteley.[10] More recently the phenyl-stabilized derivatives **9**[11] and **10**[12] have been isolated. The present results show that these ions may be generated even in relatively weak acid media. Thus, rearrange-



8 9 10

ment of the allyl alcohol (**6**) takes place rapidly in an aqueous–acetone solution 0.2 M in HBF_4, and formation of **4** and **5** from **3** occurs with equal ease in 0.06 M aqueous–acetone solutions of the salt, which therefore cannot be more than 0.06 M in HBF_4. Hydrolytic rearrangement of **3** takes place slowly even when the salt is suspended in an aqueous phosphate solution buffered to pH 3.3.

With these considerations in mind, we undertook an examination of the hydrolysis of **3** in aqueous acetic acid–sodium acetate solutions, under conditions which would preclude the



11 3 12

rapid formation of **7**, but would allow reversible formation of the acetate (**11**) and hydrolysis of the more reactive enol acetate intermediate (**12**). These reactions are summarized below.

We found that aqueous acetic acid–sodium acetate solutions (pH 3.3) were effective in converting the allene complex (**3**) to ketone (**4**). The crude product, obtained in 53% yield, contained <10% of the undesired aldehyde. Similarly, treatment of the allyl acetate (**11**) under these conditions converted it in 73% yield to the ketone (**4**), containing 10% of the isomeric aldehyde.

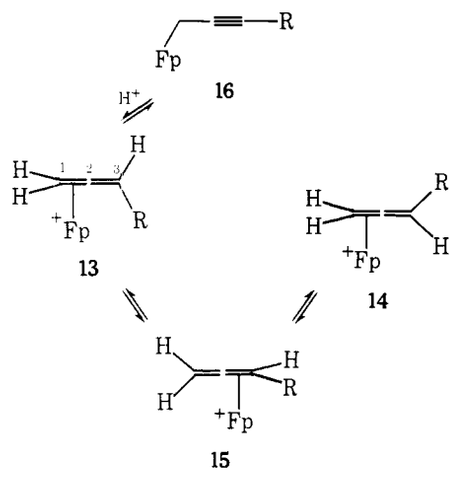
Preparation of Syn- and Anti-Substituted Allene Complexes. The results obtained with the parent allene complex (**3**) prompted us to examine the reactions of the related 3-methyl- and 3-phenylallene complexes. These substances may exist in geometrically isomeric syn and anti forms (**13** and **14**), which may equilibrate with one another through the intermediacy of the 1-substituted allene complex (**15**). The syn complexes (**13a,b**) were readily prepared by low-temperature protonation of the related σ-propargyl complexes (**16a,b**), a process shown earlier[3,6] to proceed with high stereospecificity (Scheme II).

Although the *anti*-3-methylallene complex (**14a**) is thermodynamically more stable than the syn isomer, it cannot be obtained in pure form by thermal isomerization of the latter complex, since equilibration results in a 2:1 mixture of anti and syn isomers. However, good advantage may be taken of the transperiplanar stereospecificity of the protonation reaction, which converts **16** to **13**. The reverse process should be equally stereospecific. In the event, deprotonation of an equilibrium mixture of **13a** and **14a** by treatment with dicyclohexylethylamine at 0 °C for 30 min smoothly deprotonated **13a**, leaving **14a** unchanged. The latter was then isolated by precipitation from methylene chloride solution with ether.

The preparation of the *anti*-3-phenylallene complex (**14b**) was more direct, since the syn complex (**13b**) is completely isomerized to **14b** on heating in methylene chloride solution at 40 °C for 30 min.

Before considering the hydration reactions of substituted Fp(allene) cations it is of interest to digress briefly to note the

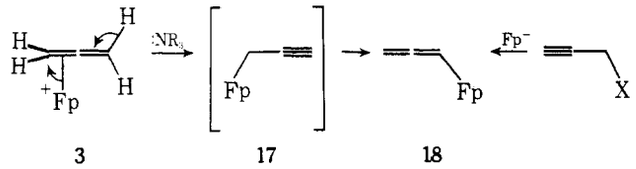
Scheme II



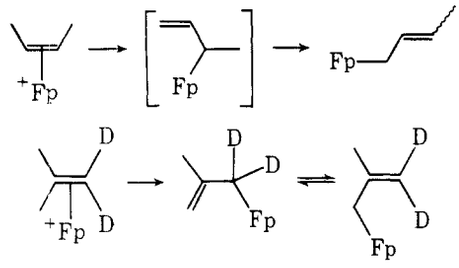
a, R = Me; b, R = Ph

behavior of the parent cation (3) on deprotonation with dicyclohexylethylamine. In contrast to the reaction of **13a**, which is smoothly converted to **16a** on treatment with this amine, similar treatment of **3** yields the σ-allenyl complex (**18**), rather than the anticipated σ-propargyl complex (**17**). We believe that **17** is the initial product of this reaction, but that it undergoes a rapid sigmatropic change to give the more stable allenyl complex (**18**).

The same process may intervene in the metalation of propargyl bromide[5,13] or benzenesulfonate[6] by Fp anion, which yields **18** rather than **17**, although a preference for S_N2' dis-



placement in this reaction cannot be excluded. A similar sigmatropic process appears to be involved in the formation of (*cis*- and *trans*-(2-butenyl)Fp on deprotonation of the



Fp(*cis*-2-butene) cation,[14] and in deuterium label scrambling on deprotonation of the Fp(1,1-dideuterioisobutylene) cation at 0 °C.[14]

Merour and Cadiot[15] have also reported that (1,1′-dideuterioallyl)Fp, prepared by metalation of 1,1′-dideuterioallyl tosylate, undergoes facile equilibration at ambient temperature.

The limited data would suggest that equilibrium between isomeric (η^1-allyl)Fp complexes favors the complex with a primary metal–carbon bond. Analogously, sigmatropic change, which interconverts (η^1-propargyl)Fp and (η^1-allenyl)Fp complexes, suggests the order of stability as:

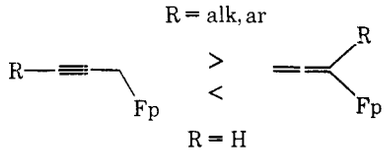
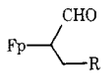
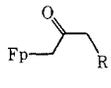
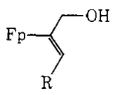
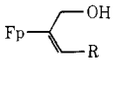
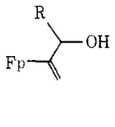


Table I. Hydration Products of Allene Complexes 13 and 14

allene complex	products and ratio			% yield
	 19	 20	 21	
syn (13)				
a, R = Me[a]	2^e	1^i	0	60
b, R = Ph[b]	10^f	1^j	0	70
	 22	 23	 24	
anti (14)				
a, R = Me[c]	2^g	0	1^l	30
b, R = Ph[d]	2^h	1^k	0	10

[a] Registry no.: 59752-01-1. [b] Registry no.: 66807-52-1. [c] Registry no.: 41357-51-1. [d] Registry no.: 66807-54-3. [e] Registry no.: 66769-04-8. [f] Registry no.: 66769-05-9. [g] Registry no.: 66769-15-1. [h] Registry no.: 66769-16-2. [i] Registry no.: 41611-23-8. [j] Registry no.: 41611-24-9. [k] Registry no.: 56810-66-3. [l] Registry no.: 66769-17-3.

The difference in energy between such isomers cannot, however, be great, since when R = CH_2OH[16] or CH_2OMe[3] equilibrium favors the allenyl form, possibly due to attractive interaction between the heteroatom and a carbonyl ligand.

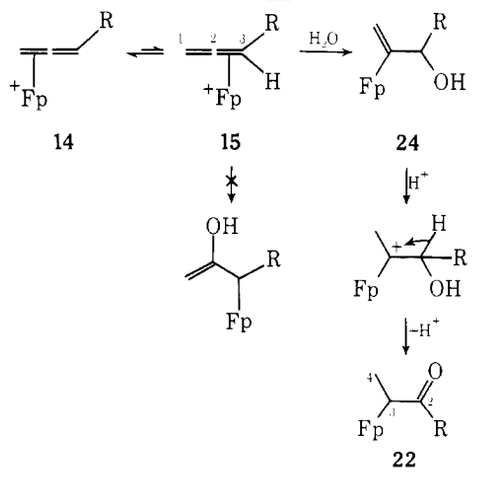
Hydration of Substituted Allene Complexes. With both syn and anti isomers (**13** and **14**) in hand, we proceeded to examine their behavior on hydration. The *syn*-3-methyl- and 3-phenylallene complexes (**13a,b**) behaved like the parent complex, yielding mixtures of ketone and aldehyde complexes (**19** and **20**). These results are summarized in Table I.

The allyl alcohol complexes (**21a,b**) were not isolated in these reactions, but could be prepared independently, as for the parent complex, by quenching the cations (**13a,b**) with hydroxide. As anticipated, treatment of these alcohols with a catalytic amount of HBF_4 in acetone solution converted them to the corresponding aldehydes (**19a,b**).

The corresponding *anti*-3-methyl- and 3-phenylallene complexes (**14a,b**) behaved very differently on hydration. Complex **14a** yielded only the rearranged ketone and allyl alcohol complexes (**22a** and **24a**) in low yield when treated under conditions used in the hydration of **13a** and **13b**. Similarly, **14b** gave only the rearranged ketone complex (**22b**) and a smaller amount of the unrearranged allyl alcohol (**23b**).

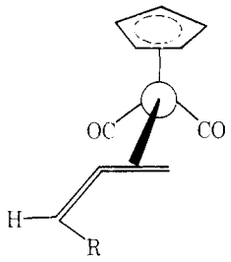
The formation of ketones **22a,b** may be depicted as proceeding through hydration of the less stable tautomeric form of the allene complexes (**15a,b**), as shown in Scheme III.

Scheme III



This sequence of steps closely resembles the course of reaction leading to the aldehyde (**5**) from the parent complex (**3**). The formation of the butanone complex (**22a**) does not involve hydration at C-2 of the allene complex (**15a**) rather than at C-3, since when the reaction of **14** is carried out in D_2O, monodeuteration occurs at C-4 in the product in accord with the steps: **14** → **15** → **24** → **22.** The failure of water to add to the internal carbon atom in the reactive intermediate allene complexes (**15a,b**), as it does with **3** and with the isomeric syn complexes (**13a,b**), is noteworthy and may possibly reflect increased charge accumulation at the terminal allene carbon center (C-3) due to substitution at this point. Evidence for the role of allyl alcohols (**24a,b**) as intermediates in the formation of ketone complexes (**22a,b**) is provided by the observation that mixtures of **22a** and **24a** are converted to **22a** on treatment with HBF_4.

The failure of the anti complexes (**14a,b**) to undergo hydration competitive with isomerization to their less stable tautomers (**15a,b**) must be attributed to steric effects associated with the substituent at C-3. Pronounced steric effects are to be expected, since, unlike the uncomplexed ligand, allenes bound to transition metals through π complexation are distorted from linearity.[17] In Fp(tetramethylallene) tetrafluoroborate the allene carbon framework forms an angle of 145.7°, with the uncoordinated carbon atom being bent away from the iron atom, but in the plane defined by this atom and the coordinated carbon atoms.[18] The consequence of this distortion is to greatly increase the steric hindrance of an anti substituent at C-3 for nucleophilic addition to both C-1 and C-2, since such reaction takes place trans to the iron–olefin bond[2a,19] (**25**).



25

Since hydration of the syn complex (**13a**) gives none of the products formed from its anti isomer (**14a**), the activation energy for hydration must be at least 2 kcal/mol less than the energy barrier (23 kcal/mol)[3] separating these isomers, assuming a symmetrical energy barrier between **15a** and both **13a** and **14a.** Furthermore, the activation energy for hydration of **14a** must then be at least 2 kcal/mol higher than the activation energy for conversion of **14a** to **15a.** Thus, steric effects associated with the methyl substituent in **14a** must contribute at least 4 kcal/mol to the activation energy for hydration of this complex compared with its syn isomer **13a.**

Finally, since hydration of **14** proceeds through the less stable isomer (**15**), and hydration of this species competes effectively with its further isomerization to **13,** it follows that the rate-limiting step in the hydration of **14** is its conversion to **15.** It is therefore not surprising that hydration of **14** under conditions similar to those applied to **13** is a much slower process, as is evidenced by the comparative yields of hydration products. This is particularly so for **15b,** where steric effects[18] due to the phenyl group would be expected to appreciably destabilize the complex relative to its isomer **14b** and raise the energy barrier for the exchange of **14b** with **15b.** The formation of a small amount of the unrearranged alcohol (**23b**) in the hydration of this substance no doubt reflects the balance between steric effects which retard rearrangement to **15b** as well as nucleophilic attack at C-1 in complex **14b.**

Experimental Section

Solvents were routinely dried by standard procedures, maintained under nitrogen over molecular sieves, and degassed prior to use.

All reactions, subsequent purification procedures, and spectroscopic examinations were performed under nitrogen. Reactions were conducted in flame-dried apparatus.

Infrared spectra were recorded on Perkin-Elmer Model 137 and 457 spectrophotometers. Nuclear magnetic resonance spectra were recorded on Varian Model A 60-A (NIH GM-13183), Perkin-Elmer R-32 (NSF GU-3852), and Bruker WH-90 (NSF GU-3852, GP-37156) spectrometers.

Melting points were determined in sealed capillaries and are uncorrected.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Hydration of $Fp(CH_2CCH_2)BF_4$ (3). Formation of 4 and 5. The salt (**3;** 0.2 g, 0.7 mmol) was dissolved in 10 mL of acetone at room temperature and to this was added 1 mL of water. An immediate color change from yellow to orange took place. Reaction was allowed to continue for 10 min and the solution was then poured into a mixture of 10 mL each of methylene chloride and water. The organic layer was separated and the aqueous layer was extracted once with 10 mL of methylene chloride. The combined organic extracts were dried, solvent was removed, and the residue was chromatographed on 10 g of activity III neutral alumina. Elution with ether–petroleum ether mixtures of increasing polarity removed the product as a single yellow band (with 70% ether–petroleum ether). The yield of product (**4** and **5**), obtained as a yellow oil, was 0.094 g (61%). **4:** IR (CH_2Cl_2) 1965, 2030, 1640 cm^{-1}; NMR (CS_2) δ 4.76 (s, 5, Cp), 1.92 (s, 3, CH_3CO), 1.60 (s, 2, CH_2CO). **5:** IR (CH_2Cl_2) 1965, 2030, 1640 cm^{-1}; NMR (CS_2) δ 9.2 (d, 1, J = 3 Hz, CHO), 4.67 (s, 5, Cp), 2.3 (dq, 1, J = 3, 6 Hz, FpCH), 1.20 (d, 3, J = 6 Hz, CH_3). Anal. Calcd for $C_{10}H_{10}FeO_3$: C, 51.32; H, 4.30. Found: C, 51.32; H, 4.15.

Preparation of $Fp(CH_3CHCHO)$ (5). A 0.5 M solution of NaFp in THF was prepared from dicarbonyl η^5-cyclopentadienyliron dimer,[20] and this was added (160 mL, 80 mmol) to 2-bromopropionaldehyde diethyl acetal (16.7 g, 80 mmol) at room temperature. After stirring the solution for 3.5 h, solvent was removed in vacuo and the residue was extracted with petroleum ether. The combined extracts were filtered under nitrogen, and the solution was concentrated and then chromatographed on 200 g of activity III neutral alumina. The acetal, which hydrolyzes on the column, was eluted with 60–80% ether–petroleum ether as a yellow band. Removal of the solvent left a yellow solid, which was recrystallized from ether–petroleum ether by blowing a stream of nitrogen through the mixture. The yield of **5,** mp 70–72 dec, was 2 g (11%). Its ^1H NMR spectral properties were identical with the product obtained in the hydration of **3.** Anal. Calcd for $C_{10}H_{10}FeO_3$: C, 51.32; H, 4.30. Found: C, 50.81; H, 4.10.

Deprotonation of $Fp(CH_2CCH_2)BF_4$ (3). Formation of 18. The allene complex (0.15 g, 0.40 mmol) was suspended in 5 mL of methylene chloride and cooled to 0 °C. Dicyclohexylethylamine (0.086 g, 0.4 mmol) was added to the solution. After 30 min reaction was complete. The solution was filtered under nitrogen through a short column of activity III alumina and the solvent was evaporated to give 0.060 (70%) of Fp(allenyl) (**18**).[6]

Synthesis of $Fp(AcOCH_2CCH_2)$ (11). The allene complex (**3**) was added to a methylene chloride solution (5 mL) of benzyltrimethylammonium acetate (0.15 g, 0.70 mmol), prepared from benzyltrimethylammonium tetrafluoroborate by exchange on Dowex 1. After stirring for 30 min, 30 mL of ether was added and the resulting mixture was filtered under nitrogen. Evaporation of solvent left the product (**11**), 0.114 g (83%), as an orange oil, which was used without purification: IR (CH_2Cl_2) 1960, 2030, 1725 cm^{-1}; NMR (CS_2) δ 5.65 (t, 1, J = 1.5 Hz, CH=), 5.0 (t, 1, J = 1.5 Hz, CH=), 4.82 (s, 5, Cp), 4.4 (t, 2, J = 1.5 Hz, CH_2OAc), 1.95 (s, 3, CH_3).

Synthesis of $Fp(HOCH_2CCH_2)$ (6). A. $LiAlH_4$ (0.06 g, 1.5 mmol) was suspended in 50 mL of ether and cooled to 0 °C. The allyl acetate complex (**11;** 0.57 g, 2.0 mmol) was dissolved in 5 mL of ether and added to this by stringe. After 30 min the reaction was quenched successively with 1 mL of H_2O, 1 mL of 15% NaOH, and 3 mL of water. The mixture was filtered under nitrogen and the ether solution was separated and dried. After removal of solvent, the residue was taken up in petroleum ether and chromatographed on 10 g of activity III alumina with 60–80% ether–petroleum ether to give 0.162 g (35%) of allyl alcohol complex (**6**), mp 58–59 °C. The product could be further purified by crystallization as yellow needles from ether–petroleum ether: IR (CH_2Cl_2) 3600, 2020, 1960 cm^{-1}; NMR (CS_2) δ 5.75 (t, 1, J = 1.5 Hz, CH=), 5.0 (br s, 1, CH=), 4.78 (s, 5, Cp), 4.0 (br s, 2, CH_2OH), 1.55 (br s, 1, OH). Anal. Calcd for $C_{10}H_{10}FeO_3$: C, 51.32; H, 4.30. Found: C, 51.20; H, 4.31.

B. The allene complex (**3**; 0.2 g, 0.7 mmol) was dissolved in 20 mL of carefully dried acetone and to this was added 7 mL of a 0.1 N NaOH solution. The reaction mixture turned brown immediately. After 10 min the reaction was worked up and chromatographed on alumina. Elution with ether–petroleum ether gave the alcohol, 0.53 g (35%), identical with the product obtained above.

Rearrangement of Fp(HOCH$_2$CCH$_2$) (6). The allyl alcohol complex (0.02 g, 0.1 mmol) was dissolved in 5 mL of acetone and 1.0 mL of 0.1 M HBF_4 was added. The solution was stirred at room temperature for 10 min and then worked up. Chromatography on 10 g of activity III neutral alumina gave 0.014 g (70%) of product as an amber oil. A ^{1}H NMR spectrum of the product showed it to be a mixture of **4** and **5** in a ratio of 1:2.

Preparation of Fp(CH$_2$COCH$_3$) (4) from 3. The allene complex (**3**; 0.20 g, 0.70 mmol) and potassium acetate (0.070 g, 0.7 mmol) were taken up in a solution of 1.0 mL of acetic acid and 0.1 mL of water. The solution was stirred at room temperature for 0.5 h. At the end of this period, 20 mL of methylene chloride was added, and the organic layer was separated and dried. After removal of solvent, the product was taken up in a small amount of ether and chromatographed on 10 g of activity III neutral alumina. Elution with 60–80% ether–petroleum ether gave 0.073 g (50%) of product shown by its ^{1}H NMR spectrum to be **4**. A small amount, estimated to be <10%, of the aldehyde (**5**) was also present.

Hydrolysis of Fp(CH$_2$CCH$_2$)BF$_4$ with D$_2$O. The allene complex (0.2 g, 0.7 mmol) was dissolved in 10 mL of carefully dried acetone and 1.0 mL of D_2O (99.8%) was added. The solution was stirred for 10 min, acetone was then evaporated, and the product was worked up as described in the hydrolysis of **3**. The yield of product was 0.080 g (52%). A NMR spectrum of the product showed the aldehyde component to have resonances at δ 9.2 (CHO), 4.67 (Cp), 2.3 (FpCH), and 1.2 (CH_3) in ratios of 0.9:4.6:1.0:2.2 (average of three integrations). The ketone component similarly showed resonances at δ 4.76 (Cp), 1.92 (CH_3CO), and 1.60 (CH_2CO) in a ratio of 5.0:1.9:1.9.

Conversion of Fp(AcOCH$_2$CCH$_2$) (11) to FpCH$_2$COCH$_3$ (4). The acetate (0.050 g, 0.2 mmol) was taken up in 1 mL of acetic acid containing 0.1 mL of water and 0.1 g of potassium acetate. After stirring at room temperature for 0.5 h, methylene chloride and water were added and the organic layer was separated and dried. Solvent was removed in vacuo and the residue was taken up in petroleum ether and chromatographed on activity III alumina. Elution with 60–80% ether–petroleum ether gave the product as a 10:1 mixture of **4** and **5** in 73% yield.

Hydration of Fp(CH$_2$CCH$_2$)BF$_4^-$ at pH 3.3. The allene salt (**3**; 0.30 g, 1.0 mmol) was suspended in 1.5 mL of a phosphate buffer solution (pH 3.3) and stirred at room temperature for 15 min. The resulting gummy material was added to 5 mL of methylene chloride, and the organic phase was separated. After extraction of the aqueous phase with methylene chloride, the combined organic solutions were dried, solvent was removed, and the residue was chromatographed on 10 g of activity III alumina. Elution gave 55 mg of product (25%), shown by NMR spectral analysis to be a 3:2 mixture of Fp(CH_2COCH_3) and Fp(CH_2CHCHO).

Preparation of Fp(*anti*-CH$_2$CCHCH$_3$)BF$_4$ (14a). The *syn*-3-methylallene complex (**13a**), prepared by protonation of **12**,[3] was allowed to equilibrate in refluxing methylene chloride solution. A solution of this mixture (0.50 g, 1.6 mmol) in 10 mL of methylene chloride was cooled to 0 °C and was then treated with 0.63 mmol of dicyclohexylethylamine for 30 min. At the end of this time 50 mL of ether was added and the precipitate was collected under nitrogen in a Schlenk tube and washed with 100 mL of 1:1 methylene chloride–ether mixtures. The residue was dissolved in 10 mL of methylene chloride and filtered. Addition of ether to this solution gave 0.14 g of **14a** (41% based on the presence of 0.33 g of this isomer in the initial mixture). An NMR spectrum taken in CD_3NO_2 did not indicate the presence of syn isomer in the product: NMR (CD_3NO_2) δ 6.4 (m, 1, =CH), 5.7 (s, 5, Cp), 3.2 (m, 2, =CH_2), 2.1 (m, 3, CH_3).

Preparation of Fp(*syn*-CH$_2$CCHPh)BF$_4$ (13b) and of Fp(*anti*-CH$_2$CCHPh)BF$_4$ (14b). The *syn*-3-phenylallene complex (**13b**; 0.5 g, 1.3 mmol) was prepared by protonation of **16**,[5] following the procedure employed in the preparation of **13a**: NMR (acetone-d_6, 0 °C) δ 8.2 (s, 1, =CH), 7.3–7.9 (m, 5, Ph), 6.1 (s, 5, Cp), 3.6 (d, 2, J = 4 Hz, =CH_2). This product was suspended in 10 mL of methylene chloride and the solvent was brought to reflux for 30 min. Ether (30 mL) was then added to ensure complete precipitation of product, which was collected in a Schlenk tube and washed with methylene chloride–ether (1:1). The product (**14b**) was dried in vacuo: yield 0.43 g (86%); NMR (acetone-d_6) δ 7.3–7.9 (m, 6, Ph, =CH), 6.05 (s, 5, Cp), 3.9 (d, 2, J = 4 Hz, =CH_2); NMR (CD_3NO_2) δ 7.3–7.7 (m, 6, Ph, =CH), 5.85 (s, 5, Cp), 3.7 (d, 2, J = 4 Hz, =CH_2).

Hydration of Fp(*syn*-CH$_2$CCHCH$_3$) (13a). Formation of 19a and 20a. The procedure employed for the hydration of **3** was followed. From 0.21 g of **13a**, 0.09 g (60%) of a 2:1 mixture of **19a** and **20a** was obtained after chromatographic purification on alumina. The mixture, which could not be separated, showed: IR (CH_2Cl_2) 2030, 1965, 1640 cm^{-1}; NMR (CS_2) δ 9.2 (d, 1, J = 3 Hz, CHO), 4.78 (s, 5, Cp), 4.68 (s, 5, Cp), 0.6–2.4 (m, CH, CH_2, CH_3). Anal. Calcd for $C_{11}H_{12}FeO_3$: C, 53.26; H, 4.84. Found: C, 53.58; H, 5.01.

Hydration of Fp(*syn*-CH$_2$CCHPh) (13b). Formation of 19b and 20b. Hydration of 1.0 g of **13b**, following standard conditions, except that reaction time was 1 h, gave 0.38 g (47%) of a 10:1 mixture of **19b** and **20b** after purification of the crude product on alumina. The mixture showed: IR (CH_2Cl_2) 2030, 1965, 1640 cm^{-1}; NMR (CS_2) of **19b** δ 9.15 (s, 1 CHO), 7.05 (s, 5, Ph), 4.72 (s, 5, Cp), 3.33 (m, 1, FpCH), 2.5 (m, 2, CH_2); NMR of **20b** δ 7.15 (s, 5, Ph), 4.46 (s, 5, Cp), 3.28 (s, 2, $PhCH_2$), 1.76 (s, 2, $FpCH_2$).

Preparation of Fp(*cis*-HOCH$_2$CCHCH$_3$) (21a). Fp(*syn*-3-methylallene) tetrafluoroborate (**13a**; 0.21 g, 0.7 mmol) was taken up in a small volume of carefully dried acetone and treated with 7 mL of 0.1 N NaOH. After stirring for 10 min, the solution was extracted with methylene chloride and finally chromatographed on 10 g of alumina. Recrystallization from ether–petroleum ether gave 0.05 g (30%) of **21a**; IR (CH_2Cl_2) 3590, 2020, 1955 cm^{-1}; NMR (CS_2) δ 6.22 (q, 1, J = 7 Hz, CH=) 4.8 (s, 5, Cp), 4.0 (br s, 2, CH_2), 1.74 (d, 3, J = 7 Hz, CH_3), 1.18 (br s, 1, OH). Anal. Calcd for $C_{11}H_{12}O_3Fe$: C, 53.26; H, 4.84. Found: C, 53.10; H, 5.02.

Preparation of Fp(*cis*-HOCH$_2$CCHPh) (21b). Treatment of Fp(*syn*-3-phenylallene) tetrafluoroborate (**13b**; 0.25 g, 0.7 mmol) with 8 mL of 0.1 N NaOH as with **13a** above gave 0.05 g (25%) of the alcohol (**21b**): mp 109–110 °C; IR (CH_2Cl_2) 3590, 2030, 1960 cm^{-1}; NMR (acetone-d_6) δ 7.66 (br s, 1, =CH), 7.29 (m, 5, Ph), 4.88 (s, 5, Cp), 4.28 (d, 2, J = 6 Hz, CH_2), 3.8 (t, 1, J = 6 Hz, OH). Anal. Calcd for $C_{16}H_{14}FeO_3$: C, 61.97; H, 4.55. Found: C, 61.21; H, 4.31.

Rearrangement of 21b to 19b. The allylic alcohol (**21b**; 0.06 g, 0.2 mmol) was dissolved in 5 mL of acetone and 0.2 mL of 0.1 M HBF_4 (48%) was added at room temperature. After 90 min of reaction, 30 mL of CH_2Cl_2 was added, the solution was dried, and solvent was removed. An NMR spectrum of the product revealed it to be 3:1 mixture of **21b** and **19b**.

Hydration of Fp(*anti*-CH$_2$CCHCH$_3$)BF$_4$ (14a). Preparation of 22a. The salt (**14a**; 0.064 g, 0.2 mmol) was taken up in 5 mL of acetone and 0.2 mL of water was added. After stirring at room temperature for 10 min, 20 mL of CH_2Cl_2 was added and the solution was dried and filtered. Chromatography of the product on 10 g of activity III neutral alumina with ether–petroleum ether gave **22a** as a yellow solid (0.015 g, 30%); IR (CH_2Cl_2) 2030, 1960, 1635; NMR (CS_2) δ 4.66 (s, 5, Cp), 2.40 (q, 1, J = 7 Hz, FpCH), 1.98 (s, 3, CH_3CO), 1.18 (d, 3, J = 7 Hz, CH_3). Anal. Calcd for $C_{11}H_{12}O_3Fe$: C, 53.26; H, 4.84. Found: C, 53.10; H, 4.86.

Treatment of 14a with D$_2$O. Formation of 22a and 24a. When the reaction was carried out on a larger scale (0.2 g of **14a**) in D_2O, the product, obtained as a yellow oil (0.050 g, 30%) after chromatography on alumina, exhibited NMR absorption (CS_2) at δ 5.76 (br s, =CH), 4.94 (br s, =CH), 4.8 (s, Cp), 4.15 (m, CHOH), and 1.14 (d, CH_3), in addition to resonances assigned to the major product (**22a**). The ratio of major to minor products (**22a**/**24a**) estimated from the relative intensities of cyclopentadienyl resonances was 2:1.

The product obtained above was taken up in 10 mL of THF and 0.5 mL of CF_3COOD was added at room temperature. Reaction was allowed to continue at room temperature for 30 min. Solvent was then removed in vacuo and the crude product was chromatographed on 10 g of alumina. Elution with ether–petroleum ether gave 0.036 g of product identified as the monodeuterated complex (**22a**).

Hydration of Fp(*anti*-CH$_2$CCHPh)BF$_4$ (14b). Formation of 22b and 23b. The hydration of 0.31 g (0.8 mmol) of **14b** following reaction and workup conditions for **3** gave 0.025 g (10%) of a mixture of **22b** [IR (CH_2Cl_2) 2030, 1965, 1640 cm^{-1}; NMR (CS_2) 6.9–7.8 (m, Ph), 4.58 (s, 5, Cp), 3.3 (q, 1, J = 7 Hz, FpCH), 1.4 (d, 3, J = 7 Hz, CH_3)] and **23b** [IR (CH_2Cl_2) 2030, 1965 cm^{-1}; NMR (CS_2) δ 6.9–7.1 (m, Ph), 5.93 (s, 1, =CH), 5.1 (s, 2, CH_2OH), 4.4 (s, 5, Cp), 2.05 (br s, 1, OH)]. A third singlet resonance at δ 4.87 about half the intensity of the resonance assigned to cyclopentadienyl protons may indicate the presence of the isomeric allyl alcohol **24b**.

Preparation of the Allyl Alcohol (24a). Treatment of Fp(*anti*-3-methylallene) tetrafluoroborate (0.2 g, 0.6 mmol) in acetone solution with 7 mL of 0.1 N NaOH solution at room temperature for 10 min gave 0.013 g (10%) of the allyl alcohol (**24a**), after chromatography on alumina; IR (CH_2Cl_2) 3590, 2020, 1950 cm^{-1}; NMR (CS_2) δ 5.47 (q, 1, J = 7 Hz, =CH), 4.8 (s, 5, Cp), 4.15 (br s, 2, CH_2), 4.1 (br s, 1, OH) 1.75 (d, 3, J = 7 Hz, CH_3).

Preparation of the Allyl Alcohol (24b). Treatment of Fp(*anti*-3-phenylallene) tetrafluoroborate (0.76 g, 2 mmol) as above with 21 mL of 0.1 N NaOH in acetone gave 0.10 g (16%) of the allyl alcohol (**24b**): IR (CH_2Cl_2) 3590, 2030, 1960 cm^{-1}; NMR (CS_2) δ 7.1–7.4 (m, 5, Ph), 5.94 (s, 1, =CH), 5.1 (s, 2, CH_2), 4.4 (s, 5, Cp). 1.65 (d, 1, J = 4 Hz, OH).

Acknowledgment. This research was supported by grants from the National Institutes of Health (GM-16395) and the National Science Foundation (GP-27991), which are gratefully acknowledged.

Registry No.—**3,** 62685-81-8; **4,** 42065-40-7; 4 deuterium derivative, 66769-18-4; **5,** 66769-19-5; 5 deuterium derivative, 66769-20-8; **6,** 65097-84-9; **11,** 66769-21-9; **18,** 42043-77-6; **21a,** 66791-89-7; **21b,** 66791-90-0; **22a** deuterium derivative, 66769-22-0; **24b,** 66769-23-1; NaFp, 12152-20-4; 2-bromopropionaldehyde diethyl acetal, 3400-55-3; benzyltrimethylammonium acetate, 16969-11-2.

References and Notes

(1) A limited number of such complexes have been prepared either by metalation with the Fp anion of an α-halo ketone [J. K. P Ariyaratne and M. L. H. Green, *J. Chem. Soc.*, 1 (1964)] or of an α-halo acetal [A. Cutler, S. Raghu, and M. Rosenblum, *J. Organomet. Chem.*, **77,** 381 (1974)].
(2) (a) P. Lennon, A. M. Rosan, and M. Rosenblum, *J. Am. Chem. Soc.*, **99,** 8426 (1977); (b) P. Lennon, M. Madhavarao, A. Rosan, and M. Rosenblum, *J. Organomet. Chem.*, **108,** 93 (1976); N. Genco, D. Marten, S. Raghu, and M. Rosenblum, *J. Am. Chem. Soc.*, **98,** 848 (1976); (c) A. M. Rosan and M. Rosenblum, *J. Org. Chem.*, **40,** 3621 (1975).
(3) B. Foxman, D. Marten, A. Rosan, S. Raghu, and M. Rosenblum, *J. Am. Chem. Soc.*, **99,** 2160 (1977).
(4) J. Benaim, J.-Y. Merour, and J.-L. Roustan, *C. R. Hebd. Seances Acad. Sci., Ser. C,* **272,** 789 (1971).
(5) J.-L. Roustan and P. Cadiot, *C. R. Hebd. Seances Acad. Sci., Ser. C,* **268,** 734 (1969).
(6) S. Raghu and M. Rosenblum, *J. Am. Chem. Soc.*, **95,** 3060 (1973).
(7) D. W. Lichtenberg and A. Wojcicki, *J. Organomet. Chem.*, **94,** 311 (1975).
(8) C. J. Collins, *Carbonium Ions,* **1,** Chapter 9 (1968).
(9) P. W. Jolly and R. Pettit, *J. Am. Chem. Soc.*, **88,** 5044 (1966).
(10) M. L. H. Green, M. Ishaq, and R. N. Whiteley, *J. Chem. Soc. A,* 1508 (1967).
(11) A. Sanders, L. Cohen, W. P. Giering, D. Kenedy, and C. V. Magatti, *J. Am. Chem. Soc.*, **95,** 5430 (1973).
(12) M. Brookhart and G. O. Nelson, *J. Am. Chem. Soc.*, **99,** 6099 (1977).
(13) M. D. Johnson and C. Mayle, *Chem. Commun.*, 192 (1969).
(14) A. Cutler, D. Ehntholt, W. P. Giering, P. Lennon, S. Raghu, A. Rosan, M. Rosenblum, J. Tancrede, and D. Wells, *J. Am. Chem. Soc.*, **98,** 3495 (1976).
(15) J.-Y. Merour and P. Cadiot, *C. R. Hebd. Seances Acad. Sci., Ser. C,* **271,** 83 (1970).
(16) D. Marten, private communication.
(17) B. L. Shaw and A. J. Stringer, *Inorg. Chim. Acta Rev.*, **7,** 1 (1973).
(18) B. M. Foxman, *J. Chem. Soc., Chem. Commun.*, 221 (1975).
(19) K. M. Nicholas and A.-M. Rosan, *J. Organomet. Chem.*, **84,** 351 (1975); A. Sanders, C. V. Magatti, and W. P. Giering, *J. Am. Chem. Soc.*, **96,** 1610 (1974).
(20) J. J. Eisch and R. B. King Ed., "Organometallic Synthesis", Vol. 1, Academic Press, New York, N.Y., p 114.

Specific Ortho Bromination of Substituted Benzenes. 3.[1a] Gas-Phase Dealkylation of the *tert*-Butyl Group from 4-*t*-Bu-2-BrC_6H_3X

David Meidar*[1b] and Yuval Halpern

The Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

Tuvia Sheradsky

Department of Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

Received March 8, 1978

The use of solid acid catalyst for the gas-phase dealkylation of a *tert*-butyl group from 4-*t*-Bu-2-BrC_6H_3X was studied. Reactions were carried out in a flow system in the temperature range of 250–400 °C at atmospheric pressure. The tendency of the bromine atom to cleave under the experimental conditions was followed. The lifetime of the catalyst was limited, but it could be reactivated easily. The advantages and limitations of the process are discussed.

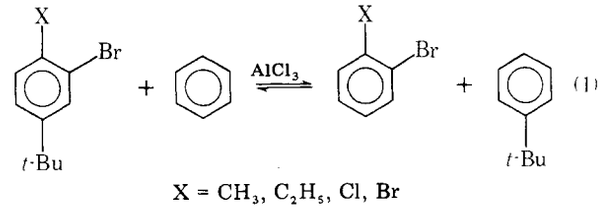
Introduction

Electrophilic aromatic substitution has been and still is being investigated, offering a large body of data including information on isomer distribution in the electrophilic substitution of substituted benzenes.[2] However, only a limited number of procedures for the selective introduction of a functional group into a substituted benzene using bulky positional protecting groups have been described earlier.[1,3-12] One of the bulk groups more frequently used as a positional protecting group is the *tert*-butyl group. In order to recover the final product, i.e., the 1,2-disubstituted aromatic compound, the *tert*-butyl group is usually removed by transfering it to another aromatic nucleus via a Friedel–Crafts type transalkylation reaction.[1,3-5,12] Catalysts for this reaction are generally based on aluminum chloride and related Lewis acid halides. However, this procedure requires an extensive separation technique due to the formation of a complex between the reactants and products with the catalyst as well as the formation of by-products.[12]

We now wish to report the easy and fast dealkylation of the *tert*-butyl group from 4-*t*-Bu-2-BrC_6H_3X over an acidic solid catalyst in a continuous process.

Results and Discussion

In the course of our studies on the specific ortho bromination of substituted benzenes,[1,3,4] we found that the removal of the *tert*-butyl group from 4-*t*-Bu-2-BrC_6H_3X to yield 2-BrC_6H_3X is achieved in the liquid phase by transalkylation reaction (eq 1), using $AlCl_3$ as catalyst, and excess benzene as



(1)

X = CH_3, C_2H_5, Cl, Br

solvent to shift the equilibrium composition to the right-hand side of eq 1.

Although resulting in high yields and high isomer purity, the batch reaction is not convenient for preparation on a large scale. Since it is known that the *tert*-butyl group attached to an aromatic ring has a great tendency to cleave over solid acidic catalysts at elevated temperatures,[13] we investigated

0022-3263/78/1943-3493$01.00/0