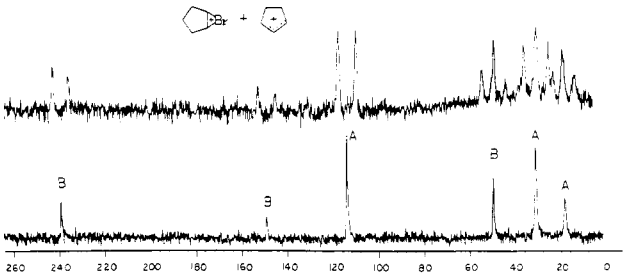
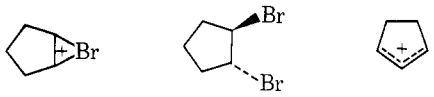


Figure 1. (a) Proton noise-decoupled carbon-13 nmr spectrum of **1** (peaks marked A) and **3** (peaks marked B). (b) Proton coupled carbon-13 nmr spectrum.

observed. We wish to report now the direct observation of the cyclopentenebromonium ion, the first such bicyclic halonium ions.

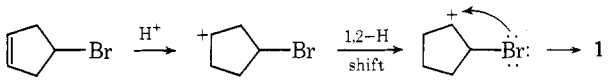
The cyclopentenebromonium ion (**1**) was prepared by ionization of *trans*-1,2-dibromocyclopentane in SbF_5-SO_2ClF solution at −120°. The pmr (60 MHz) spectrum of



1 2 3

the ion solution shows a broadened peak at δ 7.32 (two protons) and two broad peaks centered at δ 3.14 (four protons) and 2.50 (two protons). The solution of **1** in SbF_5-SO_2ClF also shows the presence of the related cyclopentenyl cation **3**.[4] When the solution was slowly warmed to −80°, **1** gradually and cleanly transformed into the allylic ion **3**.[4] Ion **3** present initially in solution of **1** might be formed due to local overheating during preparation. This reaction sequence is in accordance with our previously reported ionization of **2** in SbF_5-SO_2ClF solution at −78° where only the allylic ion **3** was observed.[4] Apparently the bromonium ion **1** is not stable at this higher temperature and was completely converted into allylic ion **3**.

The bromonium ion **1** was also obtained *via* protonation of 4-bromocyclopentene (**4**) in FSO_3H-SbF_5-SO_2ClF solution at −120°.



4 5 6

4 underwent protonation in FSO_3H-SbF_5 to first give 3-bromocyclopentyl cation **5**, which then underwent a 1,2-hydride shift to give 2-bromocyclopentyl cation **6**. Subsequently, **6** gave **1** *via* neighboring bromine participation as in the case of direct ionization of 1,2-dibromocyclopentane (**2**).

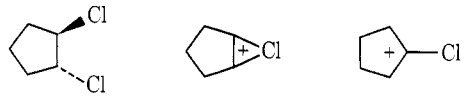
In order to further ascertain the structure of cyclopentenebromonium ion (**1**), we also have obtained its carbon-13 nmr spectrum.[5] The proton noise-decoupled ^{13}C spectrum (Figure 1a) shows three carbon resonances at $\delta(^{13}C)$ 114.6 (doublet, J_{C-H} = 190.6 Hz), 31.8 (triplet, J_{C-H} = 137.6 Hz), and 18.7 (triplet, J_{C-H} = 134.0 Hz). In addition the cmr spectrum of **1** shows three additional minor peaks which exactly correspond to those reported for the cyclopentenyl cation **3**.[6] The cmr assignments for ion **1** were made with the aid of the proton coupled cmr spectrum (Figure 1b). The bicyclic structure of the bromonium ion **1** is, therefore, firmly established.

It is instructive to compare both proton and carbon shifts of **1** with those of suitable model ions. The most closely related known acyclic bromonium ion containing a three-membered ring is the *cis*-1,2-dimethylethylenebromonium ion (**7**).[3] The chemical shift for the two carbon atoms where bridging takes place in **7**[2a] is found at $\delta(^{13}C)$ 110.9 which is

1 7

in good accordance with that in **1** (114.6). The proton shifts for the two equivalent olefinic-type protons in both ions **1** and **7** are also similar.[3]

Acyclic three-membered ring chloronium ions are known.[2,3] Consequently, we have attempted to prepare the cyclopentenechloronium ion *via* ionization of *trans*-1,2-dichlorocyclopentane in SbF_5-SO_2ClF at −120°. We have obtained, however, instead of the chloronium ion **8**, only the 1-chloro-1-cyclopentyl cation (**9**).[7] Apparently, the partici-



8 9

pation of the smaller chlorine atom could not effectively compete with the fast 1,2-hydride shift forming the tertiary ion, **9**. The larger bromine atom, however, preferentially participates with the neighboring electron-deficient center forming the bicyclic bridged ion **1**.

The rearrangement of cyclopentenebromonium ion (**1**) to allylic cyclopentenyl cation **3** can take place *via* thermal ring-opening to give 2-bromocyclopentyl cation (**6**), which can deprotonate to give 3-bromocyclopentene. Subsequent ionization of the latter would give the allylic ion **3**.[4,7]

A comprehensive report on our continued study concerning bicyclic halonium ions and their significance to addition and rearrangement reactions will be published.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

References and Notes

(1) Part X. G. A. Olah, P. W. Westerman, E. G. Melby, and Y. K. Mo. *J. Amer. Chem. Soc.*, **96**, 3565 (1974).
(2) For a review, see G. A. Olah, "Halonium Ions in Organic Chemistry," Wiley-Interscience, New York, N.Y., in press.
(3) G. A. Olah, J. M. Bollinger, and J. Brinich, *J. Amer. Chem. Soc.*, **90**, 2587 (1968).
(4) G. A. Olah, G. Liang, and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 3544 (1972).
(5) Carbon-13 nmr spectra were obtained by Fourier-transform method using a Varian XL-100 nmr spectrometer equipped with a variable temperature probe. External tetramethylsilane (TMS, capillary) was used as reference for carbon shifts.
(6) G. A. Olah and G. Liang, *J. Amer. Chem. Soc.*, **94**, 6434 (1972).
(7) G. A. Olah, G. Liang, and Y. K. Mo, *J. Org. Chem.*, **39**, 2394 (1974).

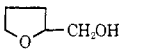
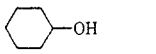
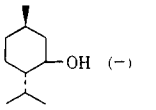
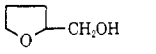
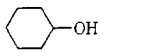
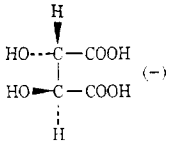
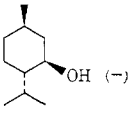
George A. Olah,* Gao Liang, John Staral
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106
Received August 19, 1974

Graphite Electrolytic Lamellar Reagents in Organic Chemistry. Esterifications in the Presence of Graphite Bisulfate

Sir:

The chemical behavior of molecules intercalated in graphite[1,2] may differ in various ways from that of the free or bulk reagents, as was observed in the case of bromine[3]

Table I

Acid	Alcohol	% ester[a]	Time (hr)
HCOOH	$CH_3CH_2CH_2CH_2OH$	98	1
		98	1
		98	17
		98[b]	17
CH_3COOH	$C_6H_5CH_2CH_2OH$	97	22
	$CH_3CH_2CH(CH_3)CH_2OH$	98	17
		94	17
		87	17
	$C_6H_5CH(OH)CH_3$	96	0.5
$C_6H_5CH_2COOH$	$CH_3CH_2CH(CH_3)CH_2OH$	95	26
	$CH_3CH_2\overset{*}{C}H(OH)CH_3$ (+)	74[b]	50
	$CH_3CH_2CH(CH_3)CH_2OH$	53	17
$HOCOCH_2COOH$	$C_6H_5CH_2OH$ (2 equiv)	94	17
$HOCO(CH_2)_3COOH$	$C_6H_5CH_2OH$ (2 equiv)	96	17
	CH_3OH (2 equiv)	99[b]	60
$C_6H_5COCOOH$		50[b]	17

[a] Identifications were made by ir, nmr, and comparison with authentic samples. Vpc analyses were run on a Perkin-Elmer F11 chromatograph (2 m column, Carbowax 20M 15%). Yields are calculated from the isolated ester. [b] Esterification occurs with retention of configuration.

and antimony pentachloride in our laboratory[4] and in the case of chromic anhydride and aluminum chloride by Lalancette, *et al.*[5,6] Strong inorganic acids such as H_2SO_4, $HClO_4$, and H_3PO_4, may be intercalated under oxidizing conditions and give rise to electrolytic lamellar compounds. We have investigated the catalytic properties of such compounds, especially that of graphite bisulfate. This compound is easily prepared by electrolysis of 98% H_2SO_4 with a graphite anode.[2] The deep blue crystals have the formula $C_{24}{}^{+}HSO_4{}^{-} \cdot 2H_2SO_4$. It is hygroscopic and must be stored in a desiccator. We studied its properties in some acid-catalyzed, water eliminating reactions.

In this paper, we report our results on the esterification of carboxylic acids with alcohols. The reactions were performed under the following standard conditions: 8.5 mmol of RCO_2H, 8.5 mmol of R′OH, and 0.3 g (0.06 formula weight) of graphite bisulfate are stirred in 15 ml dry cyclohexane at room temperature. In the case of a cyclohexane-insoluble starting material (*e.g.*, tartaric acid) the solid progressively dissolves as the reaction proceeds. At the end point (determined by vpc or tlc) of the reaction, the ester is isolated by filtration, evaporation of the solvent, and, in some cases, filtration on a short silica gel column.

As shown in Table I, our procedure is very efficient for the formation of formates and acetates. Kinetic studies show that the yield of ester reaches 80–90% in less than 1 hr for primary alcohols. Esterification of other acids is slower than formylation or acetylation, but, in most cases, the yields are very high. Some tertiary alcohols have been investigated but the mixtures are complex and elimination is the main reaction. Phenol could not be acetylated and no esterification was obtained at room temperature with benzoic or cinnamic acid.[7] It should be noted that no excess alcohol is needed to obtain a maximum yield. Solubility does not seem to be an important factor in the process, since some acids (tartaric, malonic, etc.), though sparingly soluble in cyclohexane, can be esterified in high yield. The great ease of esterification under the influence of relatively small amounts of $C_{24}{}^{+}HSO_4{}^{-} \cdot 2H_2SO_4$ clearly gives to this process a preparative value. Since every reaction has been performed at room temperature, the method could be particularly useful for labile reactants.

Comparative experiments on acetylation of cyclohexanol showed that: (i) by using graphite and sulfuric acid, esterification could not rise above 55% after 20 hr, (ii) by using a calculated amount of sulfonic resin in its acid form (Dowex 50 × 8), no esterification was observed after 20 hr.

The mechanism of the reaction of graphite bisulfate is presently under investigation. It can be assumed that the graphite compound plays two combined roles: that of an acid catalyst, by activating the carboxylic acid, and that of a dehydrating agent which shifts the equilibrium to completion.[8] The reaction seems to occur on the solid phase, as evidenced by the following facts. If the graphite is stirred with acetic or formic acid in cyclohexane, the acid disappears from the solution and the graphite gathers as a brown solid which can be isolated; treatment of this solid with a fresh solution of 1 equiv (based on initial acetic acid) of an alcohol yields the expected ester in an almost quantitative yield. It seems therefore most probable that a very reactive species is formed from the acid with the graphite bisulfate, as is the case when acetic acid or its anhydride is mixed with sulfuric acid.[9] This species appears to be rather tightly bound to the solid support since: (i) the change in color indicates strong perturbations in the electronic distribution in the bulk of the solid reagent; (ii) the epr spectrum[10] of graphite bisulfate shows significant modifications after treatment by acetic acid; whereas the signal from the blue bisulfate[11] is Dysonian and very narrow (A/B = 1.7–2.2, depending on the type of pyrocarbon used, ΔH = 0.250–0.350 G peak to peak), that from the sample after contact with pure acetic acid is practically symmetrical and much wider (A/B = 1.1–1.3, ΔH = 0.70–1.2 G), indicating a significant localization of the paramagnetic electrons.

Hydrolysis of graphite bisulfate gives graphite oxides which are known to be hydrophilic. The second role of the reagent in the esterification process may find its origin in this property and the graphite bisulfate is not merely a catalyst since it is modified by the water formed as the reaction proceeds.

The esterifying capacity of graphite bisulfate can be estimated to be 5.5×10^{-2} mol of acid and alcohol per gram.

We are presently studying the regeneration and recycling, as well as various synthetic applications of graphite bisulfate and other electrolytic lamellar compounds.

Acknowledgment. We thank CNRS for financial support.

References and Notes

(1) P. Pascal, "Nouveau traité de Chimie Minérale," Vol. VIII, Masson, Paris, 1968, pp 374–411.
(2) G. Henning, *Prog. Inorg. Chem.*, **1**, 125 (1959).
(3) A. Page-Lécuyer, J. L. Luche, H. B. Kagan, G. Colin, and C. Mazières, *Bull. Soc. Chim. Fr.*, 1690 (1973).
(4) J. Bertin, J. L. Luche, H. B. Kagan, and R. Setton, *Tetrahedron Lett.*, 763 (1974).
(5) J. M. Lalancette, G. Rollin, and P. Dumas, *Can. J. Chem.*, **50**, 3058

(1972). See also L. B. Ebert, R. A. Huggins, and J. I. Brauman, *Carbon (Oxford)*, **12**, 199 (1974).
(6) J. M. Lalancette, M. J. Fournier-Breault, and R. Thiffault, *Can. J. Chem.*, **52**, 589 (1974). See also G. Henning, *J. Chem. Phys.*, **19**, 922 (1951).
(7) Under different conditions (heating to 70°) esterification proceeds at a fair rate. Temperature dependence of the reaction is under investigation.
(8) Polymer protected aluminum chloride serves a similar dual function in etherification: D. C. Neckers, D. A. Kooistra, and G. W. Green, *J. Amer. Chem. Soc.*, **94**, 9284 (1972).
(9) A. Casadevall, A. Commeyras, P. Paillous, and H. Collet, *Bull. Soc. Chim. Fr.*, 719 (1970).
(10) Epr spectra were recorded at 345.15 MHz on a slightly modified Alpha Scientific Laboratories AI 340 type spectrometer. For the sake of convenience, pyrocarbon was used instead of natural graphite for the spectral measurements. The known chemical properties of graphite bisulfate prepared from natural or artificial graphites (pyrocarbons) are identical.
(11) G. Henning, B. Smaller, and L. Yasaitis, *Phys. Rev.*, **54**, 1088 (1954).
(12) Associated to CNRS (ERA No. 070395).

Jean Bertin, Henri B. Kagan,* Jean-Louis Luche
Laboratoire de Synthèse Asymétrique,[1,2] *Bt 420*
Universite Paris-Sud
Centre d'Orsay, 91405, Orsay, France

Ralph Setton
Laboratoire de Chimie IV, Université d'Orléans
45045, Orléans, France

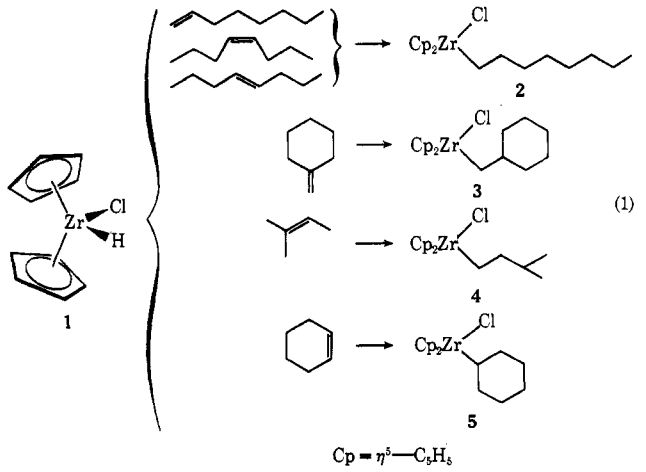
Received June 29, 1974

Hydrozirconation. Organic Synthesis *via* Organozirconium Intermediates. Synthesis and Rearrangement of Alkylzirconium(IV) Complexes and Their Reaction with Electrophiles

Sir:

We wish to report our observations concerning the synthesis and reactivity of alkylzirconium(IV) complexes of the type $(\eta^5\text{-}C_5H_5)_2Zr(Cl)R$ which we have shown to be useful as intermediates in rational organic syntheses. These compounds are of significance in that they are inexpensive and easy to prepare, require only moderate care in their handling, and undergo a wide range of transformations to organic products under mild conditions and in high yield.

The organometallic complexes of interest herein were prepared by reaction of $(\eta^5\text{-}C_5H_5)_2Zr(Cl)H$[1-3] (**1**) with olefins (hydrozirconation). In each case, the position of attachment of the zirconium in the alkyl product obtained is that one in which the transition metal moiety is attached to the sterically least hindered, accessible[4] position of the olefin *as a whole.* Formation of this product involves either the regiospecific addition of Zr–H to a terminal olefin or addition to an internal olefin followed by rapid rearrangement *via* Zr–H elimination and readdition[5] to place the metal in the less hindered position of the alkyl chain. Whereas organoboron[6] or -aluminum[7] compounds positionally rearrange slowly at elevated temperatures, internally metalated zirconium analogs undergo this process rapidly at room temperature. Functionalization at this least hindered position[4] can then be effected by replacement of the zirconium moiety with various other structural groups.



(1)

Hydrozirconation proceeds as follows. Shaking a suspension of 892 mg of **1** (3.47 mmol) in 15 ml of benzene[8] with 351 mg of 1-octene (3.13 mmol) produces **2** after a few hours at room temperature (reaction 1).[9] In similar fashion, reaction of either *cis*- or *trans*-4-octene also produces **2.** Zirconium migration in this system is fast and when the course of hydrozirconation is monitored by nmr, only the starting olefin and the ultimate 1-substituted alkyl are detected. This observation suggests that rearrangement of the postulated 4-substituted octane to **2** proceeds with an intrinsic rate at least as fast as olefin insertion into the Zr–H bond occurs. Other representative olefins react with **1** to yield the products shown in reaction 1.[10]

In contrast to their air-sensitive or pyrophoric boron or aluminum analogs, the alkylzirconium compounds described herein are not readily decomposed by dry air. They are susceptible to hydrolysis (to yield alkane) and are protonolyzed rapidly by dilute aqueous acid. It is by virtue of their ready reaction with a range of other electrophiles that these organometallic reagents play their role as valuable synthetic intermediates. For example, mixing a benzene solution of the alkylzirconium with Br_2, I_2, or $PhICl_2$ gives the alkyl halide as shown in Table I. In addition, the alkyl can be acylated in high yield by reaction with acetyl chloride. In each case, a $(\eta^5\text{-}C_5H_5)_2Zr(Cl)X$ species is recoverable which can be recycled to **1.**

Applications are apparent of the reactions described herein in which **1** adds to an olefin and then rapidly migrates along the alkyl chain thereby produced to generate a versatile synthetic handle at an unhindered part of the alkyl

Table I

Olefin	Electrophile	Product	Yield,[a] %
1-Octene or 4-octene	H^+ [b]	Octane	100
	Br_2[c]	1-Bromooctane	96
	I_2[d]	1-Iodooctane	91
	$PhICl_2$[e]	1-Chlorooctane	65
	$CH_3C(O)Cl$[f]	2-Decanone	80
2-Methyl-2-butene	Br_2	1-Bromo-3-methylbutane	100
	$CH_3C(O)Cl$	5-Methyl-2-hexanone	72
Cyclohexene	Br_2	Bromocyclohexane	95

[a] Yields were determined by vpc and are based on $(\eta^5\text{-}C_5H_5)_2Zr(R)Cl$ species. [b] Dilute HCl at 0° (instantaneous). [c] Br_2 added slowly at 0° (instantaneous). [d] Alkyl added to I_2–CCl_4 at room temperature (fast). [e] Solid $PhICl_2$ added at room temperature (fast). [f] As 1.5 equiv of $CH_3C(O)Cl$ in C_6H_6 added at room temperature (slow).