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ALKYLATION OF SILVER(I) WITH TETRAETHYLLEAD

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SUMMARY

The alkylation of silver(I) trifluoromethanesulfonate by tetraethyllead is studied in a protic (acetic acid) and an aprotic (tetrahydrofuran) medium. Ethane is formed in acetic acid by protonolysis of the ethylsilver intermediate, but the reaction is not truly catalytic [as it is with copper(I)] due to the thermal instability of ethylsilver. The decomposition of ehylsilver in tetrahydrofuran can afford high yields of ethane or butane depending on the concentrations of the reactants. The formations of ethane and butane show different sensitivity toward molecular oxygen. The role of ethyl radicals generated by homolysis of the ethylsilver intermediate is discussed.

INTRODUCTION

Tetraalkyllead compounds are desirable agents for the alkylation of metal complexes, since they are reactive yet relatively stable as monomeric entities in protic media[1]. The previous study[2] showed that organocopper intermediates are involved in the facile copper(I)-catalyzed decomposition of tetraethyllead in acetic acid via the following mechanism:

$$(CH_3CH_2)_4Pb + Cu^IOAc \rightarrow (CH_3CH_2)_3PbOAc + CH_3CH_2Cu^I \tag{1}$$

$$CH_3CH_2Cu^I + HOAc \rightarrow CH_3CH_3 + Cu^IOAc \tag{2}$$

Silver(I) nitrate has also been found to react readily with a variety of tetraalkyllead compounds in alcoholic solutions[3–7]. The intermediate organosilver, however, decomposed with the formation of metallic silver together with a mixture of hydrocarbons.

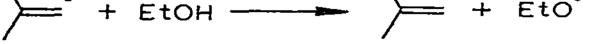
$$R_4Pb + AgNO_3 \rightarrow R_3PbONO_2 + RAg \tag{3}$$

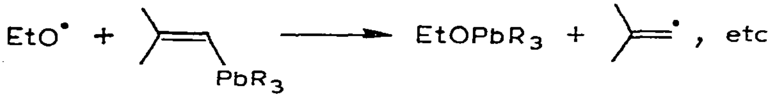
$$RAg \rightarrow [RH, R\text{–}H, R_2] + Ag \tag{4}$$

For example, tetraethyllead in ethanol afforded a mixture consisting of ethane (69 %), ethylene (10 %) and n-butane (21 %) in approximately 60 % yield[3]. On the other hand, a 1-isobutenyllead derivative reacted with silver(I) nitrate under equivalent conditions to produce more than the expected one equivalent of hydrocarbons [isobutylene, 2,5-dimethylhexa-2,4-diene] relative to the silver(I) charged[5a]. In the latter instance, the deposition of silver and the decreased hydrocarbon yields at lower silver(I) concentrations were indicative of an inefficient catalytic process. The polymerization of vinyl monomers[5a,8] as well as the production of glycols (butanediol-2,3)[3] and diethyl ether[4] suggested that radicals derived via homolysis of the organosilver species were involved, *e.g.*[5]:


(3)


(5)


(6)


(7)

Hydrogen atom transfer to isobutenyl radicals in eqn. (6) was postulated to account for the deuterium labeling (EtOD) studies, which showed that isobutylene [$(CH_3)_2C{=}CHD$] resulted from transfer of the hydroxyl proton[5b]. However, alcohols are known to be attacked preferentially at the α-CH bond by free radicals to produce 1-hydroxyalkyl radicals[9]. Our previous results indicate that these labeling

$$R^{\bullet}+CH_3CH_2OD \rightarrow RH+CH_3C^{\bullet}HOD \tag{8}$$

studies can be reconciled if a proton transfer to the organosilver intermediate is postulated, analogous to copper in eqn. (2)[2], *e.g.*,


(9)

It has also been suggested that ethane, ethylene and butane arose from tetraethyllead and silver nitrate by disproportionation and combination of ethyl radicals[3].

The efficiency of alcohols in hydrogen atom transfer to radicals (eqn. 8) as well in proton transfer (eqn. 9) to alkylmetals, thus, lends ambiguity to the foregoing studies. In this study we carried out a comparative study of the alkylation of silver(I) by tetraethyllead in a protic (acetic acid) and an aprotic (tetrahydrofuran) solvent in an attempt to distinguish between these processes. Furthermore, silver triflate (trifluoromethanesulfonate) was used instead of silver nitrate to obviate complications due to the redox reactions between the nitrate ion and silver[10].

RESULTS AND DISCUSSION

Silver(I) triflate and tetraethyllead in acetic acid

The reaction of silver(I) triflate and tetraethyllead in acetic acid afforded ethane principally, with minor amounts of ethylene and n-butane (Table 1). The rate of formation of ethane under these conditions was much faster than that derived by acetolysis[2,11] of tetraethyllead as shown in Fig. 1.

TABLE 1

SILVER TRIFLATE AND TETRAETHYLLEAD IN ACETIC ACID[a]

AgOTf (*mmole*)	$(CH_3CH_2)_4Pb$ (*mmole*)	*Products* (*mmole*)				$\Sigma Et/Ag(I)$
		CH_3CH_3	$CH_2{=}CH_2$	$n\text{-}C_4H_{10}$	ΣEt^b	
0.086	0.51	0.087	0.007	0.032	0.156	1.8

[a] In 3 ml acetic acid at 20°. [b] Including all ethyl fragments.

Silver(I) was reduced quantitatively to a mirror of silver metal during the course of reaction. The amounts of ethylene and n-butane formed, however, were insufficient to account for all of the silver deposited, and the formation of ethane also must have been associated with the reduction of silver(I). The latter is supported by the observation that the reaction in acetic acid-d_1 produced a mixture of ethane-d_1 and ethane.

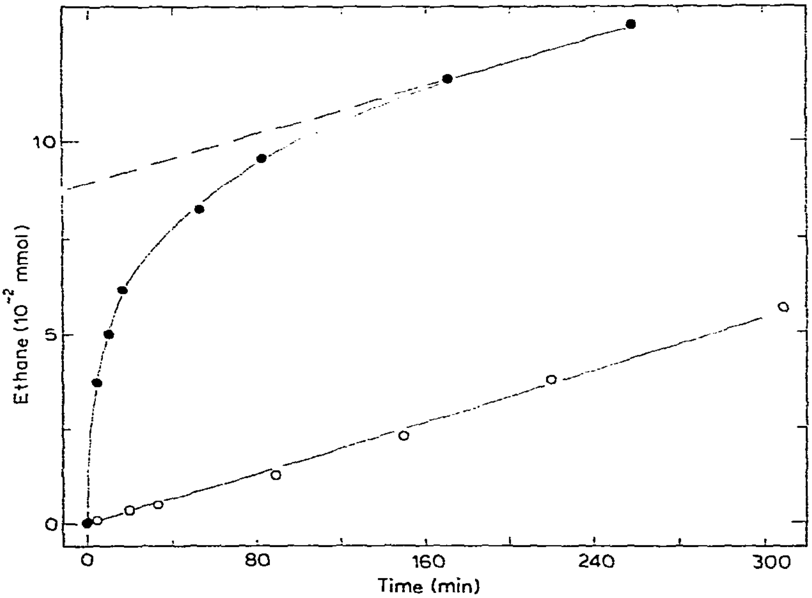


Fig. 1. Reaction of 0.17 *M* tetraethyllead with 0.029 *M* silver(I) triflate in acetic acid at 20° ● ethane liberated; ○ ethane in absence of silver(I) due to acetolysis. Dotted line is extrapolation of acetolysis.

The formation of ethane during the reaction of silver(I) with tetraethyllead in analogy with that established for copper(I)[2], can be written as:

$$(CH_3CH_2)_4Pb+AgOTf \rightarrow (CH_3CH_2)_3PbOTf+CH_3CH_2Ag \tag{10}$$

$$CH_3CH_2Ag+HOAc \rightarrow CH_3CH_3+AgOAc, \text{ etc.} \tag{11}$$

However, silver(I) differs from copper(I) in that its facile reduction to the metal (eqn. 12) under these conditions precludes an efficient catalytic decomposition of tetraethyllead (see last column, Table 1). The reduction of silver(I) can be ascribed to a metastable ethylsilver intermediate[3-7], the reductive decomposition (eqn. 12) of which can compete effectively with protonolysis (eqn. 11) even in glacial acetic acid.

$$CH_3CH_2Ag \begin{array}{ll} \rightarrow [CH_3CH_3+CH_2{=}CH_2]+Ag & \qquad (12a) \\ \rightarrow CH_3CH_2CH_2CH_3+Ag & \qquad (12b) \end{array}$$

The decomposition of the ethylsilver species was investigated further in an aprotic medium to minimize competition from protonolysis.

Silver triflate and tetraethyllead in tetrahydrofuran

Silver(I) triflate unlike the nitrate salt is soluble in tetrahydrofuran (THF), and the homogeneous reaction with tetraethyllead was complete within a few minutes at 20°. The relative yields of ethane, ethylene and n-butane were highly dependent on the concentration of reactants. Thus, the yield of ethane increased relative to butane as the concentration of tetraethyllead was raised (Table 2). On the other hand, when the concentration of silver(I) was increased, n-butane became the dominant product. These results suggest that the formation of ethane and butane arise by separate processes involving reactions of different kinetic order in silver. In all cases, high yields of silver metal separated from the reaction mixtures.

The addition of small amounts of water (up to 0.5 %v) to the solution caused an increase in the amount of butane mainly at the expense of ethylene (Table 2). However, in the presence of large amounts of water, the results were similar to those obtained in acetic acid.

TABLE 2

SILVER TRIFLATE WITH TETRAETHYLLEAD IN TETRAHYDROFURAN[a]

AgOTf (mmole)	*$(CH_3CH_2)_4Pb$ (mmole)*	*Additive (%v)*	*Products (mole %)*			*Overall Yield (mole %)*
			CH_3CH_3	*$CH_2{=}CH_2$*	*n-C_4H_{10}*[b]	
0.073	0.757	0	48	8	44	69
0.074	0.104	0	71	6	24	69
0.359	0.757	0	28	11	61	79
0.085	0.757	0	52	8	40	75
0.085	0.757	H_2O(0.2)	54	4	42	87
0.085	0.757	H_2O(0.4)	51	3	46	94
0.085	0.757	H_2O(15)	90	tr	10	—

[a] In 4.9 ml THF at 20°. [b] Two equiv. of C_2H_5.

No reaction with tetraethyllead was observed when silver(I) triflate was converted to the bipyridine or 1,10-phenanthroline complex. Moreover, the reaction was retarded in the presence of crown ethers [cyclohexyl-15-crown-5 and dibenzo-18-crown-6[12]] and the reaction afforded mainly ethane and only small amounts of butane and ethylene.

This pattern of reactivity of tetraethyllead with various silver(I) complexes is similar to that observed with copper(I) complexes, in which the reaction rate is limited by the alkylation step (eqn. 10) and is in accord with earlier studies[2,13].

Previous investigators[3-7] have suggested the alkylsilver intermediate is subject to subsequent homolysis, and the hydrocarbon products formed by disproportionation and recombination of alkyl radicals[3], *e.g.*,

$$CH_3CH_2Ag \rightarrow CH_3CH_2^{\bullet} + Ag \tag{13}$$

$$2CH_3CH_2^{\bullet} \begin{cases} \xrightarrow{k_d} CH_3CH_3 + CH_2{=}CH_2 & (14) \\ \xrightarrow{k_c} CH_3CH_2CH_2CH_3 & (15) \end{cases}$$

However, the formulation presented in eqns. (13)-(15) *alone* is insufficient to account for the results given in Table 2, since the relative rates of disproportionation and combination of ethyl radicals are constant and lie in the range $k_d/k_c = 0.15$–0.18, depending on the solvent[14]. The latter are also not in accord with the observed dependence of the yields of ethylene and butane on the concentration of silver(I) and tetraethyllead as well as other reaction conditions.

Ethane can arise in a protic medium (such as alcohol or acetic acid) by protonolysis of the alkylsilver intermediate as shown in Table 1. However, the formation of ethane in the aprotic THF suggests alternative routes, such as the attack of ethyl radicals on the solvent. Indeed, the formation of ethane is strongly inhibited by the addition of small amounts of molecular oxygen under conditions in which the yields

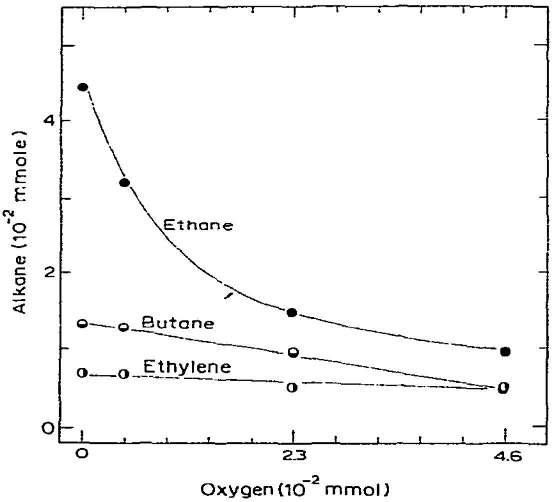


Fig. 2. Effect of added oxygen on alkane yields during the reaction of silver(I) triflate with tetraethyllead in THF at 20°.

of butane and ethylene are essentially unaffected. For example, the presence of 0.018 mmole oxygen reduced the yield of ethane by 0.013 mmoles as shown in Fig. 2. The influence of oxygen at high concentrations may be due to the slower autoxidation of the alkylsilver intermediate analogous to that of other organometals[15].

The insensitivity to oxygen suggests that butane does not arise primarily from ethyl radicals, and its strong dependence on the concentration of silver (Table 2) is consistent with a molecular process such as,

$$2CH_3CH_2Ag \rightarrow CH_3CH_2CH_2CH_3 + 2Ag$$

The alkylation of silver(I) by tetraalkyllead cannot be used to probe these processes further, since the rates of decomposition of alkylsilver intermediates are competitive with the rates of formation due to the instability of the latter. Non-homolytic routes to alkyl coupling have also been presented for alkyl– and alkenyl–silver species generated by other routes[16–18]. Since the role of free radicals in these processes will depend on a number of factors, including the ligands associated with silver as well as the solvent[13], further discussion of this point must await more detailed studies.

EXPERIMENTAL SECTION

Materials

Tetraethyllead was prepared from ethylmagnesium bromide, lead(II) chloride and ethyl iodide according to the procedure described by Gilman and Jones[19].

Silver(I) triflate was prepared from silver(I) carbonate and trifluoromethanesulfonic acid as a colorless crystalline solid[20]. It was purified further by recrystallization from a mixture of diethyl ether and petroleum ether.

Acetic acid was redistilled after refluxing with acetic anhydride. The results were the same as that obtained from Mallinckrodt reagent grade material used as such. Acetic acid-d_1 was prepared from deuterium oxide and 20% excess of freshly distilled acetic anhydride. The deuterioacetic acid was redistilled twice. The purity of deuterioacetic acid was determined by mass spectral analysis to be 93.5% deuterated by using the prominent ($\approx$70%) parent ion peak. The mass spectra of both HOAc and DOAc contained the same m/e fragments at 43 and 15 for the acetyl and methyl moieties, and there was no evidence for deuteration of the methyl group. Similarly, integration of the proton magnetic resonance spectrum for the methyl and hydroxyl resonance indicated 91–92% deuterium incorporation on oxygen.

Tetrahydrofuran, obtained in a sealed container from E. I. DuPont Co., was refluxed over lithium aluminum hydride and redistilled under nitrogen.

Reaction of silver(I) triflate and tetraethyllead

A flask containing a weighed amount of silver salt and a known volume of acetic acid or tetrahydrofuran was sealed with a gas-tight rubber serum. The solution was then swept with argon and equilibrated in a constant temperature bath. Measured volumes of methane and isobutane as marker gases were added with hypodermic syringes. The reaction was initiated by adding a known amount of deaerated tetraethyllead with a 50 μl syringe to the magnetically stirred solution.

Analysis

Ethane and ethylene were analyzed by gas chromatography on a 6ft. Porapak Q column at 80° using methane as the internal standard. Butane was analyzed on the same column at 135° with isobutane as the marker. Quantitative analysis was effected by carefully calibrating the system with known amounts of these gases under reaction conditions. Kinetics were determined by periodically extracting a small volume ($< 0.01\,\%$) of the equilibrated gas phase.

The ethane produced in the reactions carried out in mixtures of HOAc and DOAc was introduced into the mass spectrometer either through a gas chromatographic inlet (6 ft Porapak Q at 80°) or from a gas bulb. In the latter method, samples were first prufified by passing the gas through a small column of alumina. The parent ion peak was used in the analysis.

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