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Mild Oxidative Bromination of Alkenes and Alkynes with Zinc Bromide and Lead Tetraacetate

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Mild Oxidative Bromination of Alkenes and Alkynes with Zinc Bromide and Lead Tetraacetate

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ABSTRACT

Zinc bromide and lead tetraacetate is a practical and safe source of bromine. The combined reagents are used to brominate a variety of alkenes to vicinal dibromoalkanes. Similarly, alkynes can be converted into dibromoalkenes in high yields. The reagents are also capable of tetrabromination of alkynes.

Key Words: Bromination; Alkenes; Alkynes; Zinc bromide; Lead tetraacetate.

The electrophilic bromination of alkenes is one of the more thoroughly investigated reactions.^[1-3] It has been discussed from synthetic and

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mechanistic points of view.^[4–8] Using elemental bromine in this type of reaction presents a potential hazard. Accordingly, several alternative approaches have been developed to avoid direct contact with bromine, including the use of bromine-pyridine complexes, such as $PyBr_2$ and $PyHBr_3$.^[9]

The other approach involves oxidation of metal bromides or hydrobromic acid to elemental bromine with several oxidizing agents, e.g., hydrogen peroxide,^[10] sodium bismuthate,^[11] sodium perborate,^[12] and ceric ammonium nitrate.^[13] The chief drawbacks of this approach are insolubility of the metal bromides and the oxidizing agents in nonaqueous solvents, long reaction time, polymerization of the alkene with the reagents, and limited application to alkenes that are not affected by acids and aqueous media.

We have previously reported that chlorine can be generated from anhydrous tin(IV) chloride upon treatment with lead tetraacetate $Pb(OAc)_4$.^[14] Both reagents, which were soluble in dichloromethane, were used to chlorinate a wide variety of aromatic compounds. We would like to report the same technique for bromination of olefins, conjugated dienes, and acetylenes with zinc bromide and lead tetraacetate as a source of bromine.

Zinc bromide is insoluble in most chlorinated solvents, which are inactive towards bromonium ion intermediates as a result of olefins attacking the polarized bromine molecule.^[9] Since chloroform is known to form hydrogen bonds to bromide ions,^[15,16] we expected that the electrophilic solvation by hydrogen bonding to the bromide ion would make ZnBr₂ more soluble in CHCl₃ than any other solvents.

When a solution of dry $ZnBr_2$ in $CHCl_3$ was treated at room temperature with Pb(OAc)₄, a rapid formation of bromine was observed. Upon addition of the olefin, the red color of bromine faded instantaneously. The vicinal dibromide was isolated by filtration of the inorganic materials and evaporation of the washed and dried filtrate (Table 1). Changing the order of addition, i.e., treating a solution of the olefin and $ZnBr_2$ with Pb(OAc)₄, gave almost the same results (Sch. 1).

Bromination of conjugated dienes, e.g., isoprene (**I**), afforded the 1,4-addition product: 1,4-dibromo-2-methyl-*trans*-2-butene (**II**) and the 1,2-addition product: 3,4-dibromo-3-methyl-1-butene (**III**) (Sch. 2).



Scheme 1.

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| | | | | | Mp, $^{\circ}$ C, or | bp, °C/torr |
|-------|-------------------------|--------------------------------|--------------|-------------------|----------------------|--------------------------|
| Entry | Substrate | Product | Time min. | Yield % | Found | Lit. |
| 1. | 1-Hexene | 1,2-Dibromohexane | 5 | 91 ^a | 89-90/18 | 89/18 ^[17] |
| 2. | 1-Octene | 1,2-Dibromooctane | S | 90^{a} | 118 - 120/15 | $119/15^{[17]}$ |
| 3. | Cyclohexene | trans-1,2-Dibromoocyclohexane | S | $88^{\rm a}$ | 100 - 102/14 | $101/14^{[17]}$ |
| 4. | Cyclooctene | trans-1,2-Dibromoocyclooctane | 5 | 86^{a} | 95 - 97/1 | $94-97/^{[18]}$ |
| 5. | Isoprene | 1,4-Dibromo-2-methyl-trans- | 10 | 88^{b} | 51 - 53/0.2 | $48-50/0.1^{[19]}$ |
| | | 2-butene | | | | |
| | | 3,4- Dibromo-3-methyl-1-butene | | 12^{b} | 51 - 53/0.2 | $51 - 53/0.2^{[19]}$ |
| 6. | Styrene | 1,2-Dibromophenylethane | 5 | 92° | 72-74 | $74 - 75^{[20]}$ |
| 7. | trans- β -Methyl- | Eryth1,2-dibromo-1- | 5 | 81^{d} | 65-67 | $66.5 - 67^{[21]}$ |
| | Styrene | phenylpropane | | | | |
| 8. | trans-Stilbene | 1,2-Dibromo-1,2-diphenylethane | 5 | 75° | 240 - 242 | $241 \text{ dec}^{[20]}$ |
| 9. | Indene | trans-1,2-Dibromoindane | 5 | 76^{a} | 143 - 145/10 | $144/10^{[20]}$ |

Oxidative Bromination of Alkenes and Alkynes

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^cProduct was recrystallized from aqueous methanol. ^dProduct was recrystallized from pet. ether (40–60).

^bYield was determined by GC and NMR.

^eProduct was recrystallized from acetic acid.

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The same methodology was applied to bromination of alkynes. When an equivalent amount of alkyne was added to the brominating mixture, the isomeric mixture of the dibromoalkene (IV) and (V) was isolated in high yield. The reagents were also capable of further bromination. When the alkyne was treated with a stoichiometric amount of the reagents, the tetrabromo derivative (VI) was isolated in good yield (Sch. 3, Table 2).

EXPERIMENTAL

ZnBr₂ and Pb(OAc)₄ were purchased from Aldrich. ZnBr₂ (98%) was dried in the oven at 250°C for 3 hours. Pb(OAc)₄ (95%) was used without any purification. The H NMR spectra were determined in CDCl₃ on a JEOL 200 MHz spectrometer using tetramethylsilane as an internal standard. Gas chromatography was carried out on a 10-ft \times 0.25-inch column packed with an SE-30 on Chromosorb W. The product mixtures were analyzed by GLC.



Scheme 3.

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| | Mp, $^{\circ}$ C, or bp, |
|--|--------------------------|
| Bromination of alkynes with $ZnBr_2$ and $Pb(OAc)_4$. | |
| Table 2. | |

Oxidative Bromination of Alkenes and Alkynes

| | | | Ē | | Mp, °C, o | r bp, °C/torr |
|---|---|--|------|-------------------------------|--------------------------------|---|
| Entry | Substrate | Product | nin. | Y 1610 % | Found | Lit. |
| | 1-Hexyne | <i>trans</i> -1,2-dibromo-1-hexene <i>cis</i> -1.2-dibromo-1-hexane | 15 | $86^{a,b}$ $14^{a,b}$ | 62 - 64/10 | $64/10^{[13]}$ |
| 2. | Phenylacetylene | <i>trans</i> -1,2-dibromophenylethylene <i>cis</i> -1.2- dibromophenylethylene | 15 | $90^{a,b}$ 10 ^b | 134–135/22 Isomerizes by de | 134-136/22 ^[22] estillation ^[22] |
| 3. | Phenylacetylene | 1,1,2,2-tetrabromophenylethane | 30 | 78° | 74-76 | $72^{[11]}$ |
| 4. | 1-Phenylpropyne | trans-1,2-dibromo-1-phenylpropene | 15 | $84^{a,b}$ | 117/120/3 | $118 - 120/3^{[22]}$ |
| 5. | Dinhenvlacetvlene | <i>cis</i> -1,2-dibromo-1-phenylpropene <i>trans</i> -1.2-dibromodinhenvlethvlene | 15 | 16° | 210-212 | $210^{[20]}$ |
| | | cis-1,2-dibromodiphenylethylene | | 17^{d} | 68-70 | $66-68^{[20]}$ |
| ^a Purifica ^b Yield w | tion was carried out by v vas determined by GC and | acuum distillation. d NMR. | | | | |
| ^c Product | t was recrystallized from | aqueous methanol. | | | | |
| Product | t was recrystauized from | acetic acid. | | | | |

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The products were identified by comparison of their NMR spectra and physical data with those of authentic samples.

General Procedure for Bromination with ZnBr₂ and Pb(OAc)₄

Method A

To a vigorously stirred solution of dry $ZnBr_2$ (1.13 g, 5 mmol) in CHCl₃ (25 mL) was added Pb(OAc)₄ (1.11 g, 2.5 mmol). Stirring continued for 5 min while a solution of the alkene or the alkyne (2 mmol) in CHCl₃ (5 mL) was added all at once. The mixture was stirred for the specified reaction time and then filtered by suction. The filtrate was washed with aqueous sodium metabisulfite and water. It was dried (Na₂SO₄) and evaporated in vacuo to give the dibromide. The yields were measured by GC and H NMR.

Method B

Lead tetraacetate (1.11 g, 2.5 mmol) was added portionwise over 5 min to a vigorously stirred solution of the alkene or the alkyne (2 mmol) and dry $ZnBr_2$ (1.13 g, 5 mmol) in CHCl₃ (25 mL). The mixture was stirred for the specified reaction time and then filtered by suction. The filtrate was worked up as in Method A.

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