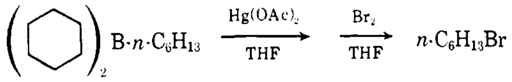
**Table I.** Anti-Markovnikov Hydrobromination of Olefins by Hydroboration–Transmetallation–Bromination Sequence

| Alkene[a] | Product[b] | Yield,[c] % |
|---|---|---|
| 1-Hexene | 1-Bromohexane | 79[d] |
| 1-Octene | 1-Bromooctane | 75 |
| 1-Nonene | 1-Bromononane | 86 |
| 2,4,4-Trimethyl-1-pentene | 2,4,4-Trimethyl-1-bromopentane | 76 |
| 3,3-Dimethyl-1-butene | 3,3-Dimethyl-1-bromobutane | 71 |
| Cyclohexene | Bromocyclohexane | 22[d] |

[a] The hydroboration was carried out as usual using borane in THF solution; see G. Zweifel and H. C. Brown, *Org. React.*, **13**, 1 (1963). [b] The products were characterized by direct comparison of their physical and chemical properties with those reported in the literature. [c] The yields, determined by glpc, are based on starting trialkylborane in a reaction using a 1:1 molar ratio of mercuric acetate to trialkylborane. [d] A 73% yield of *n*-hexylmercuric acetate was isolated when the reaction sequence was interrupted prior to the bromination step. Similarly, a 25% yield of cyclohexylmercuric acetate was obtained.

boranes such as tricyclohexylborane, however, afford greatly diminished yields of secondary bromides.

It is noteworthy that dicyclohexyl-*n*-hexylborane[11] affords a 90% yield of 1-bromohexane when exposed to this transmetallation–bromination sequence. This indicates that primary alkyl groups possess a greater transmetallation facility than secondary alkyl groups in this case.



We have found that the reaction of organoboranes with mercuric salts appears to depend on the ionic character of the salt. The reaction is exceedingly facile with mercuric nitrate, being essentially complete in 10 min at room temperature. The trifluoroacetate and fluoride salts are at least as rapid as mercuric acetate; however, mercuric chloride and bromide failed to react under the same conditions.

A general procedure for the generation of alkyl bromides from organoboranes using the transmetallation sequence is included.

1-Nonene (3.8 g, 30 mmol) in 24 ml of THF is hydroborated in the usual manner[12] with borane in THF. The tri-*n*-nonylborane solution is treated with mercuric acetate (9.56 g, 30 mmol) and refluxed for 4 hr to ensure complete reaction. The mixture is cooled in an ice bath and bromine (6–8 g in 10 ml of $CCl_4$) is added dropwise until the color persists for several minutes. The solvent is removed at reduced pressure and then 40 ml of hexane and 80 ml of water are added. The precipitated mercuric bromide is removed by suction filtration. The organic layer is separated and the aqueous layer is extracted three times with hexane. The combined extracts are dried over magnesium sulfate. After filtration and removal of solvent, distillation of the crude product affords 4.20 g (69%) of 1-bromonane, bp 102–105° (1.8 mm).

We are currently exploring the corresponding iodination and chlorination procedures.[13] In addition, we found that the *in situ* reduction of *n*-nonylmercuric acetate, prepared as described above, using sodium

$$(n\text{-}C_9H_{19})_3B \xrightarrow[\text{THF}]{\text{Hg(OAc)}_2} \xrightarrow[\text{OH}^-\text{–H}_2\text{O}]{\text{NaBH}_4} n\text{-}C_9H_{20}$$

borohydride[14] leads to the formation of *n*-nonane in 72% yield based on trialkylborane, suggesting that the hydroboration–transmetallation–borohydride reduction sequence provides a valuable alternative to the protonolysis procedure for the reductive cleavage of organoboranes.

**Acknowledgment.** We thank the U. S. Army Research Office (Durham) (DA-ARO-31-124-G-889) for generous support of this work.

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[11] H. C. Brown and A. W. Moerikofer, *ibid.*, **84**, 1478 (1962).

[12] See Zweifel and Brown, Table I, footnote *a*.

[13] The halogenation of organomercurials has been reviewed: F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968.

[14] H. C. Brown and P. Geoghegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967).

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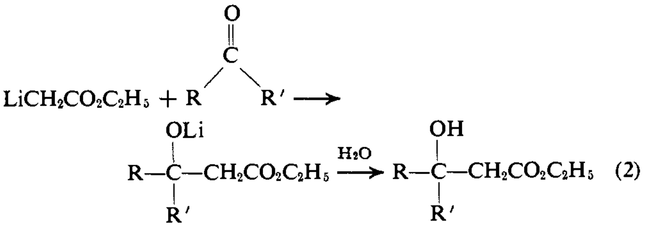
## The Preparation of Lithio Ethyl Acetate. A Simple Procedure for the Conversion of Aldehydes and Ketones to β-Hydroxy Esters

*Sir:*

Addition of ethyl acetate to a solution of lithium bis(trimethylsilyl)amide in tetrahydrofuran at −78° results in essentially quantitative formation of lithio ethyl acetate,[1] I. At the same low temperature, I reacts

$$LiN[Si(CH_3)_3]_2 + CH_3CO_2C_2H_5 \longrightarrow HN[Si(CH_3)_3]_2 + LiCH_2CO_2C_2H_5 \quad (1)$$

almost instantly with aldehydes or ketones to give, after hydrolysis, excellent yields of the corresponding β-hydroxy esters (eq 2).



$$LiCH_2CO_2C_2H_5 + RC(=O)R' \longrightarrow R\text{—}\overset{\displaystyle OLi}{\underset{\displaystyle R'}{C}}\text{—}CH_2CO_2C_2H_5 \xrightarrow{H_2O} R\text{—}\overset{\displaystyle OH}{\underset{\displaystyle R'}{C}}\text{—}CH_2CO_2C_2H_5 \quad (2)$$

Solutions of lithio ethyl acetate are stable indefinitely at −78°, but decompose rapidly if allowed to warm to 0°. Thus a solution prepared according to eq 1 remains colorless at −78° and quenching with water after 4 hr gives 95% recovery of ethyl acetate. However, warming a solution to 0° produces an immediate deep yellow color and quenching gives only 2% recovery of ethyl acetate.

Previous workers[3] have shown that sodium bis(trimethylsilyl)amide converts ethyl acetate to sodio ethyl acetate. This anion is much less stable than the corresponding lithium derivative. Thus, quenching a tetrahydrofuran solution of sodium bis(trimethylsilyl)-

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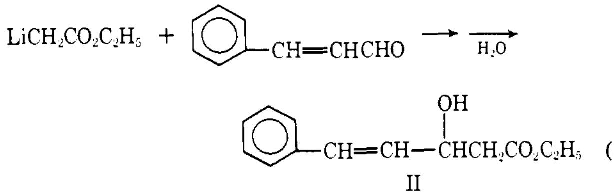
[1] Lithio ethyl acetate has previously been made by the addition of ethyl bromoacetate to butyllithium in a hexane–ether solvent at −75°.[2] However, quenching of such solutions with water indicates the conversion to I is less than 15%.

[2] W. M. Jones and R. S. Pyron, *Tetrahedron Lett.*, 479 (1965).

[3] C. R. Kruger and E. G. Rochow, *J. Organometal. Chem.*, **1**, 476 (1964).

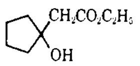
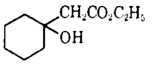
amide at −78° 2 min after addition of ethyl acetate gives only 60% recovery of ethyl acetate while quenching after 1 hr gives only 20% recovery.

The synthetic potential of I is indicated by its reaction with cinnamaldehyde to produce a 94% isolated yield of II (eq 3). The yields of β-hydroxy esters from other aldehydes and ketones are equally good as shown in Table I. This method for preparing β-hydroxy esters not only gives much higher yields than the usual Reformatsky procedure[4,5] but is much less time consuming as indicated by the following procedure for the conversion of cinnamaldehyde into II. A dry 100-ml flask equipped with septum inlet and magnetic stirrer was flushed with nitrogen. A solution of lithium bis(trimethylsilyl)amide in tetrahydrofuran[7] (25 ml of a 1.0 *M* solution) was injected and the flask immersed in a Dry Ice–acetone bath. Ethyl acetate (2.42 ml, 25 mmol) was added dropwise over a period of 2 min and the solution was stirred for an additional 15 min to complete the formation of I. Cinnamaldehyde (2.95 ml, 25 mmol) was then injected and after 5 min the solution was hydrolyzed by injection of 5 ml of 20% hydrochloric acid. The solution was allowed to reach room temperature. Addition of pentane to the separated organic phase followed by cooling gave 5.17 g (94% yield) of ethyl-3-hydroxy-5-phenyl-4-pentanoate, II, mp 38–39°.[9]



II (3)

Table I. Conversion of Carbonyl Compounds into β-Hydroxy Esters by Reaction with Lithio Ethyl Acetate

| Carbonyl compd | Product | Yield, %[a] |
|---|---|---|
| Butanal | $CH_3(CH_2)_2CHOHCH_2CO_2C_2H_5$ | 80 |
| Benzaldehyde | $C_6H_5CHOHCH_2CO_2C_2H_5$ | (80) |
| Cinnamaldehyde | $C_6H_5CH{=}CHCHOHCH_2CO_2C_2H_5$ | (94) |
| Acetone | $(CH_3)_2COHCH_2CO_2C_2H_5$ | 90 |
| Cyclopentanone |  | 93 |
| Cyclohexanone |  | 91 |

[a] Glpc yields, isolated yields in parentheses.

We are presently exploring in greater detail the synthetic uses of lithio ethyl acetate. In addition, we are studying the conversion of other esters to the corresponding lithium derivatives.

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[4] R. L. Shriner, *Org. React.*, **1**, 20 (1942).

[5] Hauser, *et al.*,[6] have shown that ethyl acetate may be condensed with carbonyl compounds in liquid ammonia using 2 equiv of lithium amide. However, the yields of product are disappointing in many cases. Thus benzaldehyde gives only a 32% yield of the β-hydroxy ester.

[6] W. R. Dunnavant and C. R. Hauser, *J. Org. Chem.*, **25**, 503 (1960).

[7] Solutions of lithium bis(trimethylsilyl)amide in hexane were prepared by a procedure outlined by Amonoo-Neizer, *et al.*[8] The hexane was then evaporated and replaced by tetrahydrofuran.

[8] E. H. Amonoo-Neizer, R. A. Shaw, D. O. Skovlin, and B. C. Smith, *J. Chem. Soc.*, 2997 (1965).

[9] Saponification and dehydration gave 5-phenylpentadienoic acid, mp 165–166°, lit.[6] mp 165–166°.

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## Stereospecific Formation of 1,2-Dioxetanes from *cis*- and *trans*-Diethoxyethylenes by Singlet Oxygen

*Sir:*

To the two modes of reaction of singlet oxygen, conjugate addition to dienes and allylic hydroperoxide formation,[1] a third mode, formation of 1,2-dioxetanes, has recently been added.[2] This reaction requires alkenes specially activated, as by amino[2a] or alkoxy[2f–i] groups, and the absence of very active allylic hydrogen in the molecule. Dioxetanes, whether prepared from singlet oxygen[2g–i] or by cyclization of halohydroperoxides,[3] have been observed to decompose cleanly to carbonyl compounds with chemiluminescence.[4] We report here evidence supporting stereospecific *cis* addition of singlet oxygen to vinylene diethers to give isolable dioxetanes as products.

*cis*-Diethyoxyethylene (**1**), freed from its *trans* isomer by preparative vapor phase chromatography, 0.211 g, was dissolved in 7 ml of fluorotrichloromethane (Freon 11) which had been dried over molecular sieves. The solution, containing $10^{-4}$ *M* tetraphenylporphin, was held in an acetone–Dry Ice bath at −78° in a dewar with Pyrex windows and irradiated through a Corning uv filter with a 500-W lamp for 25 min in a stream of oxygen. Under these conditions white crystals began to form in 15–20 min, and soon filled the vessel. The crystalline dioxetane **2** was isolated by removing the Freon under vacuum through a sintered glass disk. A small sample of the product, on warming to room temperature, melted and exploded.

When the photooxidation of **1** was monitored by nmr, the ethylenic singlet of **1** at δ 5.12 gave way to a new singlet at δ 5.91. At the same time the methylene quartet of the ethyl group initially at δ 3.73 in **1** was further split because of the proximity of the new asymmetric carbon atom in **2**, the signal in **2** being centered at δ 3.88. The 100-MHz nmr spectrum of **2** is shown in Figure 1. The position of the methyl triplet was

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[1] C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968), and references therein.

[2] (a) C. S. Foote and J. W.-P. Lin, *Tetrahedron Lett.*, **29**, 3267 (1968); (b) J. Huber, *ibid.*, **29**, 3271 (1968); (c) W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, **91**, 3396 (1969); (d) W. Fenical, D. R. Kearns, and P. Radlick, *ibid.*, **91**, 7771 (1969); (e) G. Rio and J. Berthelot, *Bull. Soc. Chim. Fr.*, **10**, 3609 (1969); (f) R. S. Atkinson, *Chem. Commun.*, 177 (1970); (g) P. D. Bartlett, paper presented at the International Symposium on Singlet Oxygen, New York Academy of Sciences, New York, N. Y., Oct 23, 1969; (h) P. D. Bartlett, G. D. Mendenhall, and A. P. Schaap, *Ann. N. Y. Acad. Sci.*, in press; (i) S. Mazur and C. S. Foote, *J. Amer. Chem. Soc.*, **92**, 3225 (1970).

[3] K. R. Kopecky, J. H. van de Sande, and C. Mumford, *Can. J. Chem.*, **46**, 25 (1968).

[4] (a) K. R. Kopecky and C. Mumford, *ibid.*, **47**, 709 (1969); (b) E. H. White, J. Wiecko, and D. R. Roswell, *J. Amer. Chem. Soc.*, **91**, 5194 (1969).