98-83-9; 2-phenyl-1-propanol, 1123-85-9; dibutylchloroborane, 1730-69-4; diisobutylchloroborane, 13317-64-1; dicyclopentylchloroborane, 36140-18-8; dibutylbromoborane, 5674-70-4; di-*sec*-butylbromoborane, 13317-63-0; diisobutylbromoborane, 13317-59-4; dihexyliodoborane, 70116-83-5; dicyclopentyliodoborane, 70116-84-6; methyl dibutylborinate, 2344-21-0; methyl di-*sec*-butylborinate, 32705-45-6; methyl diisobutylborinate, 17832-17-6; methyl dicyclopentylborinate, 36140-24-6; cyclopentene, 142-29-0; *cis*-2-butene, 590-18-1; 3,4-dimethyl-3-hexanol, 19550-08-4; 2,3,4,5-tetramethyl-3-hexanol, 36633-44-0; 1-butene, 106-98-9; 5-nonanone, 502-56-7.

Hydroboration. 53. Cyclic Hydroboration of 1,5-Cyclooctadiene with Monohaloborane Complexes. A Simple, Convenient Synthesis of *B*-Halo-9-borabicyclo[3.3.1]nonanes[1]

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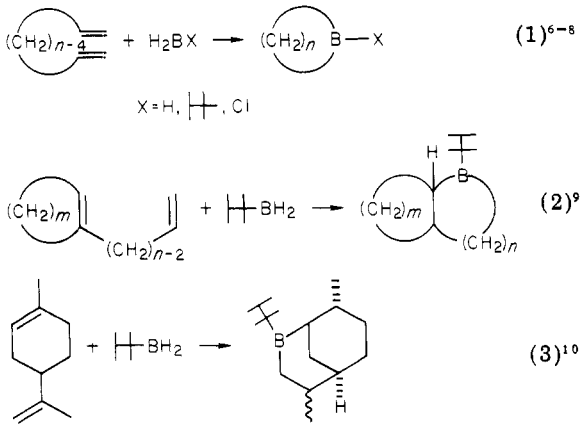
Received December 18, 1978

The hydroboration of 1,5-cyclooctadiene with stable methyl sulfide complexes of monochloro-, monobromo-, and monoiodoboranes ($H_2BX{\cdot}SMe_2$) gives a mixture of *B*-halo-9-borabicyclo[3.3.1]nonane (*B*-X-9-BBN) and its [4.2.1] isomer. The thermodynamically less stable [4.2.1] isomer predominates in the mixture. This can be readily converted to the more stable isomer *B*-X-9-BBN by gentle heating. The methyl sulfide complexes are isolated as stable crystalline solids. Distillation, following the addition of 1 equiv of the respective boron trihalide, provides *B*-X-9-BBN free from SMe_2. These compounds have been characterized by physical and chemical means. They exhibit promise as synthetic intermediates.

Cyclic hydroboration of dienes and polyenes with a variety of hydroborating agents has become increasingly important during the past few years.[3-5] Such reactions provide a valuable route to organoborane heterocycles (eq 1-3).[6-10] The hydroboration of dienes can lead to boraheterocycles or polymers depending upon the hydroborating agent and the reaction conditions employed. Monosubstituted borane reagents have definite advantages over borane itself in the cyclic hydroboration of dienes, since they give rise to much simpler products.[5] Therefore we examined some of the newly developed monosubstituted borane reagents, viz., monohaloborane complexes, for their utility as cyclic hydroborating agents.



Monochloroborane etherate ($H_2BCl{\cdot}OEt_2$, MCBE, **1**) proved to be a versatile reagent for the synthesis of 1-boracycloalkanes via cyclic hydroboration of α,ω-acyclic dienes.[8] Recently, stable methyl sulfide adducts of monochloroborane ($H_2BCl{\cdot}SMe_2$, MCBS, **2a**),[11] monobromoborane ($H_2BBr{\cdot}SMe_2$, MBBS, **2b**),[11] and monoiodoborane ($H_2BI{\cdot}SMe_2$, MIBS, **2c**)[12] were prepared and characterized. They are more stable and more convenient than **1** as hydroborating agents and have provided the first general synthesis of dialkylhaloboranes.[13,14] Therefore, it was felt desirable to explore the usefulness of these reagents for the cyclic hydroboration of representative dienes. Since the hydroboration of 1,5-cyclooctadiene (COD) has been previously studied with tetraethyldiborane ($Et_4B_2H_2$),[15] borane-tetrahydrofuran ($BH_3{\cdot}THF$),[16] thexylborane (⊢BH_2),[7] and borane-methyl sulfide ($BH_3{\cdot}SMe_2$),[17] it appeared ideal for a study of the cyclic hydroboration characteristics of the monohaloborane complexes.

Results and Discussion

Hydroboration of COD with $BH_3{\cdot}THF$ proceeds in a cyclic fashion forming a mixture of two isomeric bicyclic boron compounds, 9-borabicyclo[3.3.1]nonane (1,5 adduct) and its [4.2.1] isomer (1,4 adduct) (eq 4).[16] The relative amounts of these isomers vary with the hydroborating agent used. The monohaloborane complexes also provide a mixture of the two isomers, although the isomer distribution is quite different from those realized with borane itself.

Hydroboration with Monochloroborane Etherate (1). This reagent hydroborates COD cleanly in ethyl ether at 0 °C (eq 5). Following the removal of the solvent,

(1) Partly presented at the Joint Central-Great Lakes Regional Meeting of the American Chemical Society, May 24-26, Indianapolis, Ind., 1978.
(2) Graduate research assistant on Grant GM 10937-15 from the National Institutes of Health.
(3) H. C. Brown and E. Negishi, *Pure Appl. Chem.*, **29**, 527 (1972).
(4) E. Negishi, S. U. Kulkarni, and H. C. Brown, *Heterocycles*, **5**, 883 (1976).
(5) H. C. Brown and E. Negishi, *Tetrahedron*, **33**, 2331 (1977).
(6) P. L. Burke, Ph.D. Thesis, Purdue University, 1973.
(7) H. C. Brown and E. Negishi, *J. Am. Chem. Soc.*, **94**, 3567 (1972).
(8) H. C. Brown and M. Zaidlewicz, *J. Am. Chem. Soc.*, **98**, 4917 (1976).
(9) H. C. Brown and E. Negishi, *Chem. Commun.*, 594 (1968).
(10) H. C. Brown and C. D. Pfaffenberger, *J. Am. Chem. Soc.*, **89**, 5475 (1967).
(11) H. C. Brown and N. Ravindran, *Inorg. Chem.*, **16**, 2938 (1977).
(12) K. Kinberger and W. Siebert, *Z. Naturforsch., B*, **30**, 55 (1975).
(13) H. C. Brown, N. Ravindran, and S. U. Kulkarni, *J. Org. Chem.*, preceding paper in this issue.
(14) (a) H. C. Brown and N. Ravindran, *J. Org. Chem.*, **42**, 2533 (1977); (b) *Synthesis*, 695 (1977).
(15) R. Köster, G. Griaznov, W. Larbig, and P. Binger, *Justus Liebigs Ann. Chem.*, **672**, 1 (1964).
(16) E. F. Knights and H. C. Brown, *J. Am. Chem. Soc.*, **90**, 5280 (1968).
(17) H. C. Brown, A. K. Mandal, and S. U. Kulkarni, *J. Org. Chem.*, **42**, 1392 (1977).

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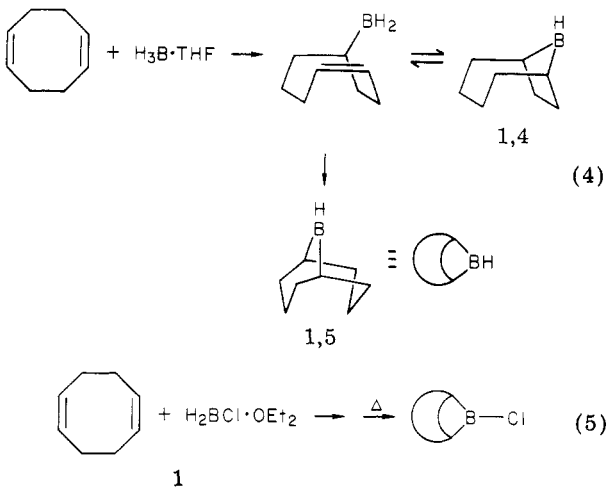
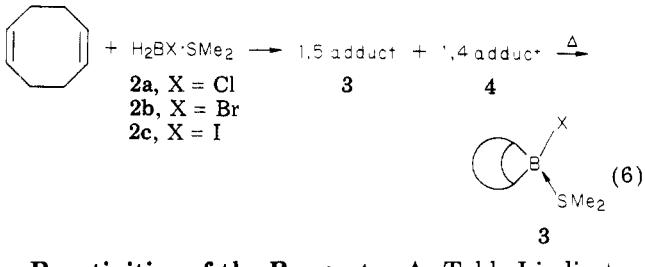


thermal isomerization and distillation affords *B*-chloro-9-borabicyclo[3.3.1]nonane (*B*-Cl-9-BBN) as a colorless liquid. However, *B*-Cl-9-BBN obtained by this method is contaminated with 3–5% of *B*-OEt-9-BBN arising from the cleavage of ether during workup. Secondly, we cannot follow an analogous procedure to obtain *B*-bromo- and *B*-iodo-9-BBN's since the corresponding monohaloborane etherates ($H_2BX{\cdot}OEt_2$ (X = Br, I)) are unstable. These problems could be avoided by using the recently developed more stable methyl sulfide complexes of monohaloboranes ($H_2BX{\cdot}SMe_2$, **2**).

Hydroboration with Monohaloborane–Methyl Sulfides (2). MCBS (**2a**) and MBBS (**2b**) hydroborate COD cleanly and completely in 1 h at 25 °C in CH_2Cl_2 solution. The corresponding reaction with MIBS (**2c**) is slower and it is desirable to reflux the reactants in CH_2Cl_2 for 3 h to achieve rapid completion of the reaction (Table I). The reaction can also be conveniently carried out under neat conditions by carefully mixing the reactants (**2a–c** and COD). The initial hydroboration product is a mixture of two isomeric bicyclic boron compounds, *B*-halo-9-borobicyclo[3.3.1]nonane (1,5 adduct, **3**) and its [4.2.1] isomer (1,4 adduct, **4**). Thermal isomerization affords pure *B*-X-9-BBN·SMe_2 (**3**) in good yields (eq 6).



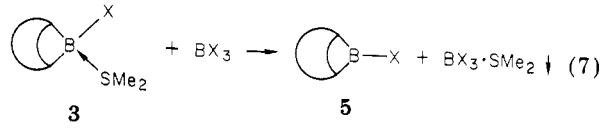
Reactivities of the Reagents. As Table I indicates, BH_3·THF, $ThBH_2$·THF, and MCBE hydroborate COD under mild conditions (0 °C, 1 h). On the other hand, MCBS and MBBS require more drastic conditions (25 °C, 1 h). MIBS is even less reactive, requiring 3 h at 40 °C for completion of hydroboration.

It has been reported that ^{11}B NMR chemical shifts of borane–ligand complexes are, at least approximately, indicative of the strengths of the donor–acceptor complexes.[11,18] More tightly bound complexes have larger upfield shifts. It can be generalized from the available data that the ease of hydroboration of a given olefin with a complexed borane reagent depends on the strength of the donor–acceptor complex. The complexes with weaker coordinate bonds hydroborate more easily than those with stronger ones. Therefore, the larger the upfield chemical shift of a complex in ^{11}B NMR, the tighter the complex and the more difficult is the hydroboration.[19] This generalization is supported by the present study.

Regiochemistry of Hydroboration. The isomer distribution in the hydroboration of COD with the monohaloborane reagents (**1**, **2a–c**) is surprisingly more comparable to that realized with thexylborane[7] than with BH_3·THF[16] (Table I). Thus these reagents direct hydroboration mainly toward the formation of the kinetic product, i.e., **4**. This presumably results from steric influences operating during cyclic hydroboration.

Thermal Isomerization. Isomerization of **4** to the thermodynamically more stable isomer **3** can be achieved by heating the reaction mixture at 140 °C for 1 h after removal of the solvent. Pure crystalline 1:1 addition complexes, *B*-Cl-9-BBN·SMe_2 (**3a**), *B*-Br-9-BBN·SMe_2 (**3b**), and *B*-I-9-BBN·SMe_2 (**3c**) are readily obtained by recrystallization from hexane.[20]

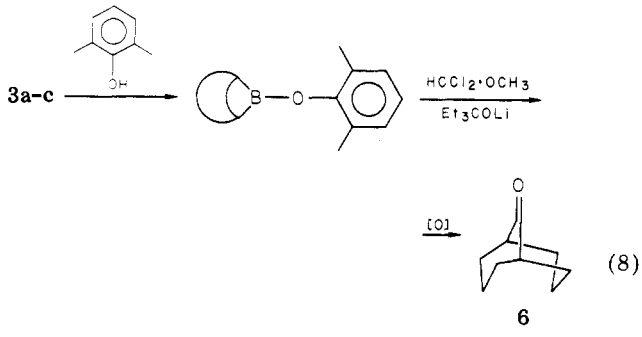
Uncomplexed *B*-X-9-BBN (**5**) can be prepared by the addition of 1 equiv of the corresponding boron trihalide followed by distillation (eq 7).[21] The yields and physical properties of **3** and **5** are listed in Table II.



Characterization of *B*-X-9-BBN. Oxidation of **3** and **5** with alkaline hydrogen peroxide provides pure *cis*-1,5-cyclooctanediol in 90–95% yield by GLC. The methanolysis of **3** according to known procedures[14] gives *B*-methoxy-9-BBN in good yields.

The ^1H and ^{11}B NMR spectral data (Table II) for compounds **3** and **5** are in good agreement with those expected on the basis of the Lewis acidities of the boron centers. The Lewis acidities of **5a–c** are expected to be in the order B–Cl < B–Br < B–I.[11,22] Consequently, the ^{11}B chemical shifts should be increasingly downfield in this order. Also as we move along the series of methyl sulfide complexes (**3a–c**), progressively stronger coordinate bonds are formed, as reflected in the increasing downfield shifts of the Me protons in the ^1H NMR spectra and the upfield shift of boron resonances in the ^{11}B NMR spectra (Table II).

Conclusive proof for the structure of the *B*-X-9-BBN compounds is provided by their conversion to bicyclo[3.3.1]nonan-9-one (**6**) via the DCME reaction (eq 8).[23]



(18) H. C. Brown and S. U. Kulkarni, *Inorg. Chem.*, **16**, 3090 (1977).

(19) An exception to this statement is $HBBr_2{\cdot}SMe_2$. See H. C. Brown and N. Ravindran, *J. Am. Chem. Soc.*, **99**, 7097 (1977).

(20) It is necessary to add at least 25 mol % of SMe_2 during crystallization in order to compensate for any loss during isomerization.

(21) In the preparation of **5a** a considerable amount of $BCl_3{\cdot}SMe_2$ is present in the distillate. This can be avoided by separating the solid from the pentane extract prior to distillation.

(22) M. J. Bula and J. S. Hartman, *J. Chem. Soc., Dalton Trans.*, 1047 (1973).

Table I. Regiochemistry in the Hydroboration of 1,5-Cyclooctadiene with Various Reagents[a]

reagent	^{11}B NMR δ	reaction conditions: solvent	temp, °C	time, h	isomer distribution,[d] %: 1,4	1,5	yield,[e] %
H_3B·THF	−1.1	THF	0	1	28	72	91
thexylborane	24	THF	0	1	80	20	
MCBE	4.2	OEt_2	0	1	78	22	98
MCBS	−6.7	CH_2Cl_2	0-25[b]	1	80	20	97
MBBS	−10.5	CH_2Cl_2	0-25[b]	1	82	18	97
MIBS	−20.5	CH_2Cl_2	25-40[c]	3	73	27	89

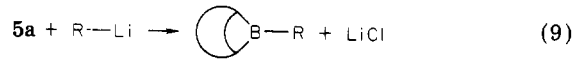
[a] The values for H_3B·THF[16] and thexylborane[7] are included for comparison. [b] Reagents were mixed at 0 °C and then stirred at 25 °C for 1 h. [c] The reagents were mixed at 25 °C and refluxed for 3 h. [d] Determined by oxidation and GLC analysis of the bis(trimethylsilyl) ethers of the diols.[17] [e] The overall yield of the mixture of diols determined by GLC using an SE-30 column.

Table II. Synthesis of *B*-Halo-9-borabicyclo[3.3.1]nonane Derivatives and Their Characterization

SMe_2 complex 3	yield,[a] %	physical properties of 3: mp, °C	^{1}H NMR[b] δ	^{11}B NMR[c] δ	uncomplexed species	yield,[d] %	physical properties of 5: bp, °C (mm)	^{11}B NMR δ	yield[e] of 6, %
3a	88	104-105	2.26	18.5	5a	81	37-40 (0.3)	78.6	71 (83)
3b	91	128-129	2.30	12.8	5b	97	64-65 (1.0)	83.0	68 (88)
3c	65	133-134	2.30	12.4	5c	75	70-72 (0.4)	82.0	(71)

[a] Isolated yields based on COD and H_2BX·SMe_2. [b] Chemical shift for SMe_2 protons. [c] With reference to BF_3·OEt_2; positive sign indicates downfield from BF_3·OEt_2. For this sign convention see *J. Organomet. Chem.*, **131**, C43 (1977). [d] Isolated yields based on 3. [e] Prepared by the DCME reaction from 3; the values in the parentheses indicate GLC yields.

Applications. The *B*-X-9-BBN compounds exhibit interesting possibilities for synthetic work. For example, **5a** has already been employed for the preparation of *B*-alkyl-9-BBN's which are not available via hydroboration (eq 9)[24] and also for the preparation of *B*-methylamino-9-BBN (eq 10).[25] *B*-Br-9-BBN (**5b**) has demonstrated its utility as a selective ether cleavage agent and is far superior to BBr_3 as such.[26]



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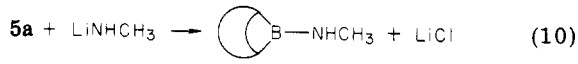

(10)

Conclusions

Although the cyclic hydroboration of COD was previously achieved by various reagents, the present study establishes the value of the H_2BX·SMe_2 reagents for such cyclic hydroboration. The reagents achieve a different regiochemistry, giving larger amounts of the thermodynamically less stable isomer. This phenomenon may throw light on the importance of electronic and steric factors in cyclic hydroboration. In addition, this study opens a way to the possible synthesis of hitherto difficultly synthesized bicyclic carbon structures involving the bicyclo[4.2.1]-nonane system. This study also makes available a general and convenient method for the preparation of *B*-X-9-BBN, highly promising synthetic intermediates. The full scope of the application of these reagents for the preparation of other derivatives of 9-BBN and for the selective ether cleavage reaction are yet to be explored. These developments are highly promising for the future application of the H_2BX·SMe_2 reagents and for the COD derivatives that they produce.

Experimental Section

General Comments. General procedures for the manipulation of air-sensitive materials have been described elsewhere.[27] All of the reactions were carried out under the atmosphere of dry nitrogen. The hydroboration reactions were carried out in a round-bottomed flask equipped with a septum inlet, magnetic stirring bar, and a connecting tube.[27]

The reagents MCBE,[28] MCBS,[11] MBBS,[11] and MIBS[12] were prepared according to the reported procedures. 1,5-Cyclooctadiene from Cities Service Co. was distilled over $LiAlH_4$; SMe_2 and CH_2Cl_2 from Aldrich, pentane from Phillips, and Et_2O from Mallinckrodt were stored over molecular sieves before use.

The ^{1}H NMR spectra were recorded on a Varian T-60 (60 MHz) instrument with Me_4Si (δ 0) as an internal standard. ^{11}B NMR spectra were recorded on an XL-100 instrument with BF_3·OEt_2 as an external standard (a positive sign indicates a downfield shift from the standard). Physical constants and the spectral data are given in Table II.

Preparation of *B*-Cl-9-BBN·SMe_2 (3a). In a 500-mL reaction flask cooled in an ice bath, 10.5 mL of **2a** (100 mmol, neat liquid is 9.5 M) was dissolved in 177 mL of CH_2Cl_2. The mixture was stirred as 12.3 mL (100 mmol) of COD was added dropwise. The contents of the flask were then brought to 25 °C and stirred for an additional hour. The solvent was pumped off and the resulting viscous mass was heated to 140 °C (using a reflux condenser to avoid loss of SMe_2) for 1 h in an oil bath. Recrystallization from hexane containing 5.0 mL of SMe_2 provided 19.2 g (88% yield) of crystalline product, mp 104–105 °C.

The preparation of **3b** is carried out in the same way. In the case of **3c** it was necessary to reflux for 3 h to complete the hydroboration reaction. The initial product is dark, but on crystallization from hexane (twice), it can be obtained as pale brown needles.[29]

Preparation of Uncomplexed *B*-Br-9-BBN (5b). To a well-stirred suspension of 10.0 g (38.1 mmol) of **3b** in 50 mL of pentane was added 3.62 mL (38.1 mmol) of BBr_3 dropwise. After 1 h the solvent was pumped off and **5b** was distilled under vacuum, keeping the oil bath below 100 °C (melting point of BBr_3·SMe_2 107 °C). A colorless liquid, 7.4 g (97% yield), bp 64–65 °C (1.0 mmHg) was obtained.

The preparation of **5c** involves the same procedure. However, in the case of **5a**, it is necessary to separate BCl_3·SMe_2 from the

(23) B. A. Carlson and H. C. Brown, *Synthesis*, 776 (1973).
(24) G. W. Kramer and H. C. Brown, *J. Organomet. Chem.*, **73**, 1 (1974).
(25) G. W. Kramer and H. C. Brown, *J. Organomet. Chem.*, **132**, 9 (1977).
(26) M. V. Bhatt, *J. Organomet. Chem.*, **156**, 221 (1978).
(27) H. C. Brown, G. W. Kramer, A. B. Levy, and M. M. Midland, "Organic Syntheses via Boranes", Wiley-Interscience, New York, N.Y., 1975; see Chapter 9.
(28) H. C. Brown and N. Ravindran, *J. Am. Chem. Soc.*, **98**, 1785 (1976).
(29) The elemental analyses for the SMe_2 complexes (**3a–c**) are comparable to those reported in H. C. Brown and S. U. Kulkarni, *J. Organomet. Chem.*, **168**, 281 (1979).

pentane extract prior to distillation.

Determination of the Rate of Hydroboration. The hydroboration was carried out on 10-mmol scale in the same manner as described for the preparation of **3a**. At definite intervals of time 2.0-mL aliquots were hydrolyzed as described elsewhere.[27] From the volume of hydrogen liberated, the residual active hydride content in the reaction mixture could be calculated.

Oxidation of Initial Hydroboration Product and GLC Analysis. In a 50-mL reaction flask equipped with a reflux condenser, a 4.0-mL aliquot (2.0 mmol) was introduced with a syringe. Then 10 mL of THF and 2 mL of water were added. The flask was cooled in ice bath and 2 mL (6 mmol) of 3 N NaOH solution was added, followed by a dropwise addition of 1.0 mL (8 mmol) of 30% hydrogen peroxide. After the initial vigorous reaction subsided, the flask was maintained at 50 °C for 2 h. The aqueous layer was saturated with anhydrous potassium carbonate, and the organic layer was used for GLC analysis, in order to determine the relative amounts of 1,4- and 1,5-cyclooctanediols. Whenever the yield of these diols was to be determined, an internal standard, usually *n*-tetradecane, was added during the oxidation step.

Two drops of the THF solution from the oxidation experiment were taken in a vial, and 0.1 mL of dry pyridine and 0.1 mL (excess) of *N,O*-bis(trimethylsilyl)acetamide (BSA) were added. The mixture was thoroughly shaken and heated for 5 min. The resulting solution containing the silyl derivatives of the diols was analyzed by GLC. A 6 ft × $^1/_8$ in. column packed with 5% SE-30 deposited on Varaport-30 was used to estimate the overall yield of the diol mixture and an 18 ft × $^1/_8$ in. column packed with 5% neopentylglycol adipate on Varaport-30 was employed for the separation of the silyl derivatives of the isomeric diols.

Preparation of Bicyclo[3.3.1]nonan-9-one (6). In a 500-mL reaction flask 10.9 g (50 mmol) of **3a** was dissolved in 50 mL of CH_2Cl_2 at room temperature and 21.7 mL of a 2.3 M solution (50 mmol) of 2,6-dimethylphenol in CH_2Cl_2 was added dropwise with stirring. After 0.5 h, the solvent was completely pumped off and 25 mL of dry THF was added. The flask was then cooled in ice bath, and 6.3 g (5.0 mL, 55 mmol) of α,α-dichloromethyl methyl ether was added, followed by slow, dropwise addition of 62.5 mL of a 1.6 M solution of lithium triethylcarboxide (100 mmol) in hexane. The reaction mixture was stirred for 2 h at room temperature. To this flask were added 40 mL of ethanol, 8.0 g of solid sodium hydroxide, and 10 mL of water. The flask was cooled to 0 °C and 20 mL of 30% hydrogen peroxide was added dropwise, maintaining the temperature below 50 °C. After the initial vigorous reaction subsided, the mixture was heated for 2 h at 50 °C. The aqueous phase was saturated with sodium chloride, the organic phase was removed and washed once with 25 mL of saturated salt solution, and the solvents were removed on a rotary evaporator. The resulting liquid was diluted with 50 mL of pentane, the phenol extracted with 3 N aqueous sodium hydroxide (2 × 25 mL), and the pentane solution washed with 25 mL of saturated salt solution. Pentane was removed under reduced pressure, followed by triethylcarbinol (bp 54–56 °C (16 mmHg)), and the semisolid residue was dissolved in 40 mL of pentane. The solution was cooled to −78 °C. Filtration, followed by washing with cold (−78 °C) pentane, gave 4.9 g (71% yield) of colorless crystals, mp 152–153 °C. On recrystallization from pentane a product, mp 155–156 °C, was obtained (lit.[23] mp 154.5–156.5 °C).

Registry No. **1**, 36594-41-9; **2** (X = Cl), 63348-81-2; **2** (X = Br), 55652-52-3; **2** (X = I), 55652-50-1; **3** (X = Cl)·OEt_2, 70160-57-5; **3** (X = Cl)·SMe_2, 70160-58-6; **3** (X = Br)·SMe_2, 70160-59-7; **3** (X = I)·SMe_2, 70160-56-4; **4** (X = Cl)·OEt_2, 70145-36-7; **4** (X = Cl)·SMe_2, 70145-37-8; **4** (X = Br)·SMe_2, 70145-39-0; **4** (X = I)·SMe_2, 70145-41-4; **5** (X = Cl), 22086-34-6; **5** (X = Br), 22086-45-9; **5** (X = I), 70145-42-5; **6**, 17931-55-4; COD, 111-78-4.

Preparation of Hindered Esters by the Alkylation of Carboxylate Salts with Simple Alkyl Halides

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Sterically hindered esters were prepared in excellent yields by the use of anion-exchange resins in both biphase and triphase systems. In addition, quantitative yields of a variety of esters were obtained by the displacement reactions of simple aliphatic and aromatic potassium carboxylate salts and alkyl halides in acetone or acetone–water mixtures. Esters prepared in quantitative yields include ethyl hexadecanoate in 95% acetone and ethyl 2,-4,6-trimethylbenzoate, 1-methylheptyl 2,4,6-trimethylbenzoate, and ethyl 9,10-epoxyoctadecanoate in pure acetone. The second-order rate constant for the reaction of potassium 2,4,6-trimethylbenzoate with iodoethane in 95% acetone was found to be 2.67×10^{-4} mL^{-1} s^{-1} at 40 °C.

Classical acid-catalyzed esterification methods are of little value in the preparation of sterically hindered esters.[2] The displacement reaction of alkali metal carboxylate salts would seem to be a suitable method for the preparation of these esters. However, there are several reports that this reaction with unactivated halides is not suitable for the preparation of even ordinary esters,[3,4] giving poor yields and conversions along with much elimination.[4] To avoid these supposed problems, hindered esters have been prepared by nucleophilic displacement by carboxylate anions on compounds such as alkyl chlorosulfites,[5] trimethylanilinium salts,[6] triethyloxonium fluoroborates,[7] dimethyl sulfate,[8] and benzyl and allyl halides,[9] all of which

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