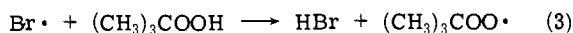


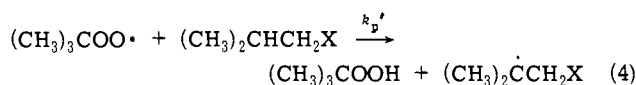
propagation reactions. The sensitivity of an autoxidation to $\text{Br}\cdot$ is illustrated by the observation that the oxidizability of **1** is increased by a factor of ~ 100 by the addition of 0.04 *M* HBr .

The rate of autoxidation of **1** in the presence of $(\text{CH}_3)_3\text{COOH}$ (0.5 to 2 *M*) does not depend on the partial pressure of oxygen indicating that reaction 1 is not important in this system. This is not unexpected because at such large hydroperoxide concentrations any bromine atoms that are formed should undergo chain transfer with the hydroperoxide to regenerate peroxy radicals.



This was confirmed by the observation that catalysis of the oxidation of **1** by HBr was eliminated by 2 *M* $(\text{CH}_3)_3\text{COOH}$ (vide Table I).

The only rate controlling propagation reaction in this system is, therefore



and the propagation rate constant that is measured is k_p' .

Measurements of homopropagation rate constants at 30° for organic substrates with unactivated C-H's (e.g., isobutane **3**) and organic substrates with α -bromo and α -chloro substituents (e.g., isopropyl bromide **4** and isopropyl chloride **5**) is not possible because kinetic chain lengths are too short.¹¹ A propagation rate constant of $0.003 \text{ M}^{-1} \text{ sec}^{-1}$ for the autoxidation of **3** has, however, been estimated¹¹ while rate constants for reaction of **4** and **5** with $(\text{CH}_3)_3\text{COO}\cdot$ have been calculated to be $\sim 0.0006 \text{ M}^{-1} \text{ sec}^{-1}$.¹¹

The reactivity of compounds **1** to **5** to $(\text{CH}_3)_3\text{COO}\cdot$ decreases in the order $1 > 2 \sim 3 > 4 \sim 5$ whereas on purely electronic grounds the reactivity order should be $3 > 1 \sim 2 > 4 \sim 5$. Thus a CH_2Br group activates an adjacent C-H bond relative to a CH_3 group because anchimeric assistance from the β -bromine overshadows the deactivating effect expected from electron withdrawal by the bromine. The similarity between the rate constants for **3** and **2** implies that the deactivating effect of a β -chloro substituent is almost exactly balanced by the accelerating effect from anchimeric assistance.

We have previously concluded¹¹ that rate constants for reaction of organic compounds with $(\text{CH}_3)_3\text{COO}\cdot$ at 30° correlate with the strength of the weakest bond in the molecule ($D[\text{R-H}]$) by the empirical equation

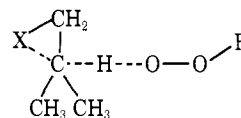
$$\log(k_p'/\text{M}^{-1} \text{ sec}^{-1}) = 15.4 - 0.2D[\text{R-H}]$$

with $D[\text{R-H}]$ in kilocalories per mole. As values of k_p' for **1** and **2** would be expected to fit this relationship **1** must have a tertiary C-H bond that is $\sim 7 \text{ kcal mol}^{-1}$ weaker than **4** and $\sim 4 \text{ kcal mol}^{-1}$ weaker than **3**, while the tertiary C-H's in **2** and **3** have approximately the same strength.

The estimated stabilizing effect of a CH_2Br substituent relative to a CH_3 substituent of 4 kcal mol^{-1} is in reasonable agreement with the estimate of $2.5 \text{ kcal mol}^{-1}$ obtained by Cain and Solly¹² from a kinetic study of the thermolysis of 1-bromomethyl- and 1-methyl-4-chlorobicyclo[2.2.0]hexanes and the estimate of 3 kcal mol^{-1} made by Skell and Shea¹³ from a study of the brominations of 1-bromobutane and propane.

We believe that the enhanced reactivity of a H atom β to a bromine and chlorine substituent to $t\text{-ROO}\cdot$ provides un-

equivocal support for the bridged radical postulate favored by Skell and coworkers.² This means that the transition state for reaction 4 contains a stabilizing contribution from¹⁴



References and Notes

- (1) Issued as NRCC No. 14539.
- (2) (a) P. S. Skell and K. J. Shea, *Isr. J. Chem.*, **10**, 493 (1972); (b) *Free Radicals*, **2**, 809 (1973).
- (3) (a) D. D. Tanner, D. Darwish, M. W. Mosher, and N. J. Bunce, *J. Am. Chem. Soc.*, **91**, 7398 (1969); (b) D. D. Tanner, H. Yabuuchi, and E. V. Blackburn, *ibid.*, **93**, 4802 (1971); (c) D. D. Tanner, M. W. Mosher, N. C. Das, and E. V. Blackburn, *ibid.*, **93**, 5846 (1971); (d) D. D. Tanner, J. E. Rowe, T. Pace, and Y. Kpsugi, *ibid.*, **95**, 4705 (1973).
- (4) K. U. Ingold, *Free Radicals*, **1**, 37 (1973).
- (5) J. A. Howard, *Adv. Free-Radical Chem.*, **4**, 49 (1972); *Free Radicals*, **2**, 3 (1973).
- (6) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **47**, 3809 (1969); J. A. Howard and J. H. B. Chenier, *Int. J. Chem. Kinet.*, **6**, 527 (1974).
- (7) C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *J. Am. Chem. Soc.*, **77**, 3233 (1955).
- (8) All of the oxygen absorbed by **1** and **2** could be titrated for as hydroperoxide. 1-Bromo-2-methyl-2-hydroperoxypropane and 1-chloro-2-methyl-2-hydroperoxypropane were identified, after reduction with a slight excess of triphenylphosphine, as the bromo- and chlorohydrins. For example, **1** (9.24 *M*) containing AIBN (0.18 *M*) absorbed 0.035 *M* of oxygen in 70 hr. An aliquot liberated I_2 (0.032 *M*) from acidified KI at room temperature. Reduction of a further aliquot with Ph_3P (0.035 *M*) produced 1-bromo-2-methylpropanol (0.03 *M*), which was identified by comparison with an authentic sample⁹ by GLC.
- (9) H. O. House, *J. Am. Chem. Soc.*, **77**, 5083 (1955).
- (10) (a) J. E. Bennett, D. M. Brown and B. Mile, *Trans. Faraday Soc.*, **66**, 386 (1970); (b) J. A. Howard and J. E. Bennett, *Can. J. Chem.*, **50**, 2374 (1972).
- (11) S. Korcek, J. H. B. Chenier, J. A. Howard, and K. U. Ingold, *Can. J. Chem.*, **50**, 2285 (1972).
- (12) E. N. Cain and R. K. Solly, *J. Chem. Soc., Chem. Commun.*, 148 (1973).
- (13) P. S. Skell and K. J. Shea, *J. Am. Chem. Soc.*, **94**, 6500 (1972).
- (14) CIDNP signals observed during the thermolysis of benzoyl- β -bromopropionyl peroxide imply that β -bromoalkyl radicals are not symmetrically bridged.¹⁵
- (15) J. H. Hargis and P. B. Shevlin, *J. Chem. Soc., Chem. Commun.*, 179 (1973).
- (16) NRCC Summer Student 1974.

J. H. Bernard Chenier, J. Paul-Alain Tremblay¹⁶
James A. Howard*

Division of Chemistry, National Research Council
Ottawa, Ontario, Canada

Received October 3, 1974

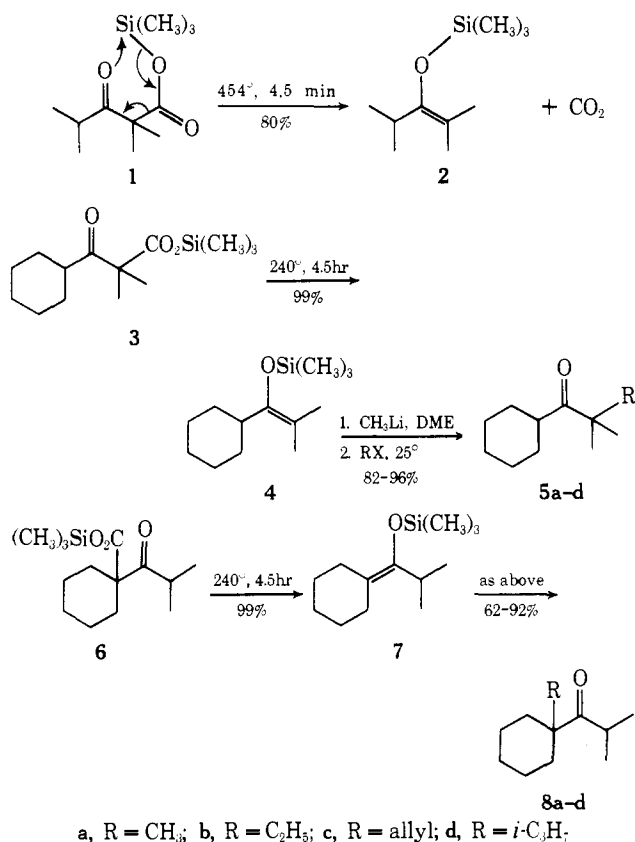
Regiospecific Synthesis of Trimethylsilyl Enol Ethers via Silatropic Rearrangements

Sir:

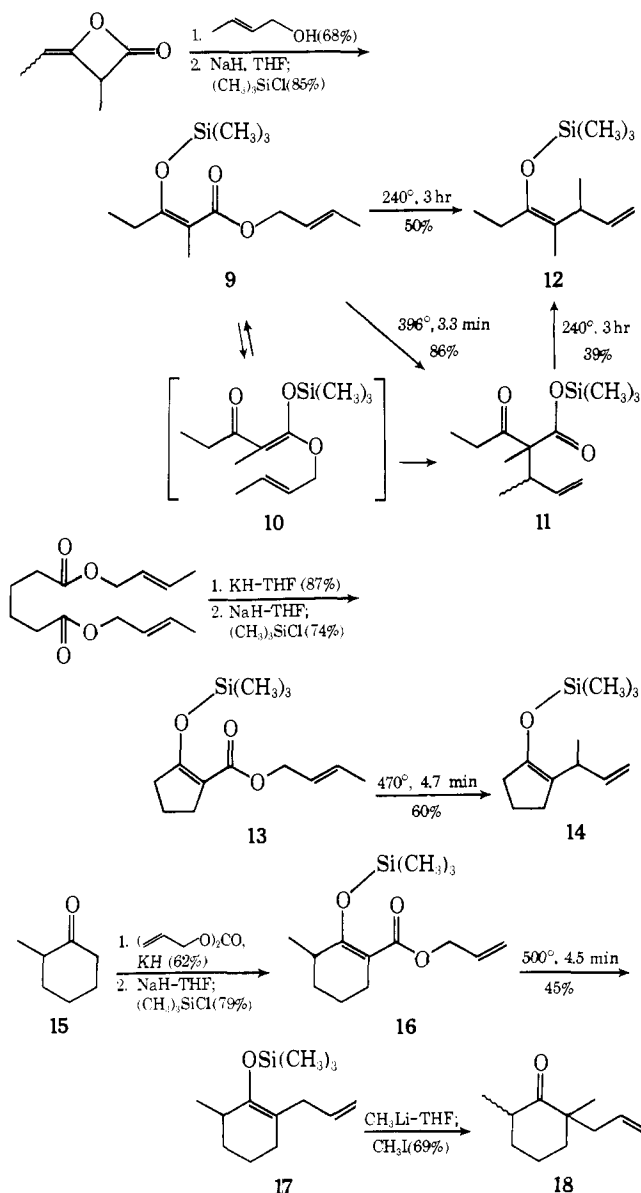
Trimethylsilyl enol ethers are proving to be versatile intermediates in organic synthesis. In addition to serving as convenient precursors for the formation and alkylation of specific enolate anions,¹ trimethylsilyl enol ethers undergo oxidative functionalization reactions with strong electrophiles to give heterosubstituted carbonyl compounds,² oxidative cleavage with ozone,^{3a} Schmidt-type rearrangement with sulfonyl azides,^{3b} cyclopropanation with iodomethyl zinc iodide,^{3c} titanium tetrachloride catalyzed aldol condensation with acetals, aldehydes, and ketones,⁴ and acylation with acid chlorides^{2a} and isocyanates.⁵ The principal method for the preparation of trimethylsilyl enol ethers has been silylation of enolate anions, the scope of which is defined by the procedures for the regiospecific generation of enolate anions.⁶ We wish to report that thermal silatropic rearrangements,⁷ formally analogous to known prototropic pro-

cesses, afford new regiospecific routes to various types of trimethylsilyl enol ethers.⁸

Trimethylsilyl β -keto esters **1**, **3**, and **6** were prepared as described by Kuo, Yahner, and Ainsworth,⁸ i.e., acylation of the required carboxylic acid dianion followed by silylation. Pyrolysis of **1** (flow pyrolysis in a hot tube at 454°; contact time 4.5 min), **3**, and **6** (neat liquid pyrolysis at 240° for 4.5 hr) effected decarboxylation and the production of trimethylsilyl enol ethers **2**, **4**, and **7** in high yields.^{9,10} This overall transformation is, of course, analogous to the ready prototropic decarboxylation of β -keto acids to enols.¹¹⁻¹³ The regiospecificity of the reaction is indicated by the absence of any detectable (<3-5%) cross contamination between regioisomers **4** and **7**. Enol ethers **4** and **7** were cleaved with methyllithium and the resulting lithium enolate anions allowed to react with a series of alkyl halides (CH₃I, C₂H₅I, allyl-Br, and *i*-C₃H₇I). High yields of regiospecifically pure alkylated ketones (**5a**, 96%; **5b**, 89%; **5c**, 95%; **5d**, 82%; **8a**, 92%; **8b**, 88%; **8c**, 87%; **8d**, 62%) were obtained in all cases except the relatively slow isopropylation of the enolate from **7** which afforded a small amount (11%) of the regioisomer **5d**.

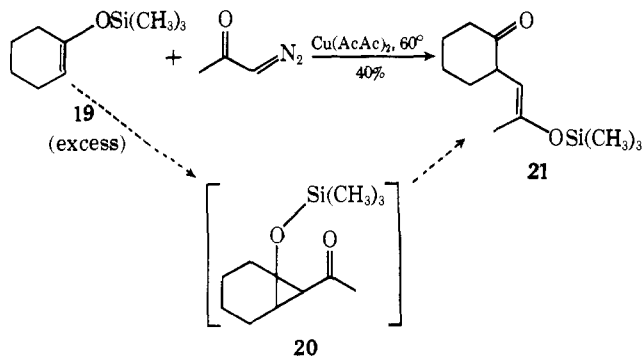


The thermal decarboxylation of allylic β -keto esters to α -allylated ketones with allylic transposition (Carroll reaction)¹⁴ has proven useful in synthesis.¹⁵ We have been able to effect a silatropic Carroll reaction by pyrolytic decarboxylation of trimethylsilyl enol ethers (**9**, **13**, and **16**)¹⁶ of allylic β -keto esters to allylated trimethylsilyl enol ethers (**12** (cis + trans), **14** and **17**; ir 1660-1665 (C=C—O), 1625-1630 (C=C) cm⁻¹). The three allyl β -keto esters were prepared by three different methods (diketene alcoholysis, Dieckmann cyclization, and diallyl carbonate condensation, respectively) in order to demonstrate the scope of this trimethylsilyl enol ether synthesis. The pyrolyses were carried out either by passage through a column of glass helices with nitrogen flow (~400-500°, 3-5 min contact time) or as the neat liquid (240°, 3 hr).



A likely mechanism for these thermal rearrangements involves three separate steps: a presumably fast and reversible silatropic rearrangement to the trimethylsilyl ketene acetal (e.g., **9** \rightleftharpoons **10**),¹³ Claisen rearrangement to the trimethylsilyl β -keto ester (**10** \rightarrow **11**),¹⁷ and finally silatropic decarboxylation (**11** \rightarrow **12**).¹² In fact, β -keto ester **11** could be isolated in 86% yield from pyrolysis of **9** and separately decarboxylated to the final product (**12**) as indicated in the scheme. Although the yields in the pyrolyses are only moderate (45-60%), the silatropic Carroll reaction nevertheless provides a relatively simple, regiospecific synthesis of allyl-substituted trimethylsilyl enol ethers. Since the lithium enolate from silyl enol ether **17** could be methylated regiospecifically to give 2-allyl-2,6-dimethylcyclohexanone (**18**, 69%), the overall transformation (**15** \rightarrow **18**) from 2-methylcyclohexanone constitutes a new method for regiospecific geminal dialkylation of ketones.¹⁸

The copper-catalyzed carbenoid addition of α -diazo ketones and esters to enol acetates leads to acetoxycyclopropyl carbonyl compounds which undergo retro-aldol ring opening to 1,4-dicarbonyl compounds upon hydrolysis.¹⁹ We have found that the reaction of diazoacetone with the trimethylsilyl enol ether of cyclohexanone (**19**) in the presence of cupric acetylacetonate^{19c} affords silyl enol ether **21**, pre-



sumably by way of cyclopropyl ketone **20** which then undergoes a silatropic retro-aldol reaction.²⁰ Although the sensitivity of enol ether **21** hampered purification, its structure was established by spectral data (ir 1705 (C=O), 1675 (C=C—O), 850 (Si—C) cm^{-1} ; NMR 4.61 (d, $J = 8$ Hz, C=CH), 1.63 (s, CH_3), 0.17 (s, $\text{Si}(\text{CH}_3)_3$) and hydrolysis to the known 2-acetyl cyclohexanone.²¹

Acknowledgment. We wish to thank the National Science Foundation and the National Institutes of Health for partial support of this research.

References and Notes

- (1) (a) G. Stork and P. F. Hudrlik, *J. Am. Chem. Soc.*, **90**, 4462, 4464 (1968); (b) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969); H. O. House, M. Gall, and H. D. Olmstead, *ibid.*, **36**, 2361 (1971); (c) H. O. House, "Modern Synthetic Reactions", W. H. Benjamin, Menlo Park, Calif., 1972, Chapter 9.
- (2) (a) α -Phenylthio ketones with phenyl sulfonyl chloride, S. Murai, Y. Kuroki, K. Hasegawa, and S. Tsutsumi, *J. Chem. Soc., Chem. Commun.*, 946 (1972); (b) α -sulfonyl ketones with sulfonyl chlorides, Y. Kuroki, S. Murai, N. Sonoda, and S. Tsutsumi, *Organomet. Chem. Synth.*, **1**, 465 (1972); J. K. Rasmussen and A. Hassner, *Tetrahedron Lett.*, 2783 (1973); (c) α -oximino ketones with nitrosyl chloride, J. K. Rasmussen and A. Hassner, *J. Org. Chem.*, **39**, 2558 (1974); (d) α -halo ketones with halogens, R. H. Reuss and A. Hassner, *ibid.*, **39**, 1785 (1974); (e) α -trimethylsilyloxy ketones with peracid, A. G. Brook and D. M. Macrae, *J. Organomet. Chem.*, **77**, C19 (1974); G. M. Rubottom, M. A. Vazquez, and D. R. Pelegrina, *Tetrahedron Lett.*, 4319 (1974).
- (3) (a) R. D. Clark and C. H. Heathcock, *Tetrahedron Lett.*, 2027 (1974); (b) R. A. Wohl, *Helv. Chim. Acta*, **56**, 1826 (1973); (c) C. Girard and J. M. Conia, *Tetrahedron Lett.*, 3327 (1974); S. Murai, T. Aya, T. Renge, I. Ryu, and N. Sonoda, *J. Org. Chem.*, **39**, 858 (1974), and references cited therein.
- (4) T. Mukaiyama, K. Narasaka, and K. Banno, *Chem. Lett.*, 1011 (1973); *J. Amer. Chem. Soc.* **96**, 7503 (1974). T. Mukaiyama and M. Hayashi, *Chem. Lett.*, 15 (1974).
- (5) I. Ojima, S. Inaba, and Y. Nagai, *Tetrahedron Lett.*, 4271 (1973); *Chem. Lett.*, 1069 (1974).
- (6) For example, kinetic and thermodynamic generation of ketone enolate anions with bases, and conjugate reduction of (or conjugate addition to) α,β -unsaturated ketones, see ref 1 and the following: (a) R. K. Boeckman, Jr., *J. Am. Chem. Soc.*, **96**, 6179 (1974); (b) G. Stork and J. Singh, *ibid.*, **96**, 6181 (1974); (c) M. Tanabe and D. F. Crowe, *J. Chem. Soc., Chem. Commun.*, 564 (1973); (d) M. Rathke and D. F. Sullivan, *Synth. Commun.*, **3**, 67 (1973); (e) C. Ainsworth, F. Chen, and Y-N. Kuo, *J. Organomet. Chem.*, **46**, 59 (1972); (f) one alternative method is the thermal rearrangement of trimethylsilyloxyvinylcyclopropanes, B. M. Trost and M. J. Bogdanowicz, *J. Am. Chem. Soc.*, **95**, 5311 (1973).
- (7) For leading references to silatropic rearrangements, see J. Slutsky and H. Kwart, *J. Am. Chem. Soc.*, **95**, 8678 (1973).
- (8) Y-N. Kuo, J. A. Yahner, and C. Ainsworth, *J. Am. Chem. Soc.*, **93**, 6321 (1971).
- (9) Ainsworth and coworkers reported that trimethylsilyl dimethylbenzoylacetate (**3** with the six-membered ring aromatic) decarboxylated upon distillation to afford the corresponding trimethyl silyl enol ether.⁸ The decarboxylation of silyl malonates has also been reported: U. Schmidt and M. Schwochau, *Tetrahedron Lett.*, 875 (1967).
- (10) All new compounds were characterized by appropriate ir and NMR spectral data and, with the exception of **21**, either a satisfactory combustion analysis or exact mass determination by high resolution mass spectrometry.
- (11) (a) K. J. Pedersen, *J. Am. Chem. Soc.*, **51**, 2098 (1929); (b) *ibid.*, **58**, 240 (1936); (c) F. H. Westheimer, *Proc. Chem. Soc., London*, 253 (1963); (d) R. G. Button and P. J. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 557 (1973), and pertinent references cited therein.
- (12) Although this reaction is depicted in the scheme as a concerted 1,5-migration of the trimethyl silyl group,^{8,11a,b,c} alternative mechanisms are possible.^{11d}
- (13) (a) T. J. Pinnavaia, W. T. Collins, and J. J. Howe, *J. Am. Chem. Soc.*, **92**, 4544 (1970); (b) H. Shanan-Atidi and Y. Shvo, *Tetrahedron Lett.*,

- 603 (1971); (c) I. K. Kusnezowa, K. Rühlmann, and E. Gründemann, *J. Organomet. Chem.*, **47**, 53 (1973).
- (14) (a) M. F. Carroll, *J. Chem. Soc.*, 704, 1266 (1940); 507 (1941); (b) W. Kimel and A. C. Cope, *J. Am. Chem. Soc.*, **65**, 1992 (1943).
- (15) For examples see (a) R. K. Hill and M. E. Synerholm, *J. Org. Chem.*, **33**, 925 (1968); (b) N. Wakabayashi, R. M. Waters, and J. P. Church, *Tetrahedron Lett.*, 3253 (1969); (c) W. Hoffmann, H. Pasedach, and H. Pommer, *Justus Liebig's Ann. Chem.*, **729**, 52 (1969); W. Hoffmann, H. Pasedach, H. Pommer, and W. Relf, *ibid.*, **747**, 60 (1971).
- (16) H. Gilman and R. N. Clark, *J. Am. Chem. Soc.*, **69**, 967 (1947); R. West, *J. Org. Chem.*, **23**, 1552 (1958).
- (17) R. E. Ireland and R. H. Mueller, *J. Am. Chem. Soc.*, **94**, 5897 (1972).
- (18) For references to methods for regiospecific geminal dialkylation see R. M. Coates and R. L. Sowerby, *ibid.*, **93**, 1027 (1971); R. M. Coates, H. D. Pigott, and J. Ollinger, *Tetrahedron Lett.*, 3955 (1974).
- (19) (a) H. O. House and C. J. Blankley, *J. Org. Chem.*, **33**, 47 (1968); (b) E. Wenkert, R. A. Mueller, E. J. Reardon, Jr., S. S. Sathe, D. J. Scharf, and G. Tosi, *J. Am. Chem. Soc.*, **92**, 7428 (1970); (c) J. E. McMurry and T. E. Glass, *Tetrahedron Lett.*, 2575 (1971).
- (20) The reaction of ethyl diazoacetate with trimethylsilyl enol ethers yields, after hydrolysis, γ -keto esters. The intermediates in these reactions were not examined: R. Le Goaller and J-L. Pierre, *C.R. Acad. Sci., Ser. C*, **276**, 193 (1973).
- (21) D. P. Brust and D. S. Tarbell, *J. Org. Chem.*, **31**, 1251 (1966).
- (22) A. P. Sloan Foundation Fellow 1971-1973.

Robert M. Coates,*²² L. O. Sandefur, R. D. Smillie

Department of Chemistry, University of Illinois
Urbana, Illinois 61801

Received January 8, 1975

A New Boron Hydride. Tetradecaborane(20)

Sir:

We wish to report the synthesis and novel structure of a stable new boron hydride, tetradecaborane(20). The synthesis of this material in low yield was accomplished by reaction of excess octaborane(12)¹ with potassium nonahydrohexaborate² in diethyl ether solution, solvent removal at room temperature, and treatment of the solid with liquid HCl at -78° . Fractional distillation of the volatile components yielded a mixture (stopping in a 0° trap) of a white solid ($\text{B}_{16}\text{H}_{20}$) and a yellow semicrystalline solid ($\text{B}_{14}\text{H}_{20}$) embedded in a small amount of yellow oily material. The mixture was placed in an oven maintained at 32° , and yellow crystals of $\text{B}_{14}\text{H}_{20}$ slowly formed over a period of several weeks. The yellow $\text{B}_{14}\text{H}_{20}$ was then manually separated from the colorless $\text{B}_{16}\text{H}_{20}$ in the open air. The yield of $\text{B}_{14}\text{H}_{20}$ could not be measured accurately, since only extremely small quantities of this material were obtained, but probably does not exceed 2%.

The mass spectrum of a sample purified in this manner contained a base peak at 162 amu and a parent peak at 174 amu, corresponding to the molecular ion $^{11}\text{B}_{14}\text{H}_{20}$. The 70.6-MHz ^{11}B NMR spectrum of a very dilute solution of $\text{B}_{14}\text{H}_{20}$ in dichloromethane suggested a high degree of molecular symmetry since only five resonances were observed: a low field area 1 doublet at -34.6 ppm ($J_{\text{BH}} = 150$ Hz), two overlapping area 2 doublets at -8.8 ($J_{\text{BH}} = 160$ Hz) and -6.0 ppm ($J_{\text{BH}} = 160$ Hz), and two upfield area 1 doublets at $+10.6$ ($J_{\text{BH}} = 150$ Hz) and $+36.1$ ppm ($J_{\text{BH}} = 160$ Hz).³

A well-formed single crystal of approximately 0.7 mm diameter was utilized in a single-crystal structure determination at -164° . The compound is thermochromic; the crystals became colorless upon cooling although there was no indication of a phase transition. The compound crystallizes in space group $P2_12_12_1$, with $a = 13.119$ (4), $b = 9.976$ (3), and $c = 8.963$ (3) Å (at -164°) and with $\rho_{\text{calc}} = 0.971$ g/cm³ for $Z = 4$.

The structure was solved using direct methods. The initial E map showed all 14 boron atoms. A difference Fourier located the 20 hydrogen atoms. Anisotropic least-squares