We report here such a reaction and its utility in organic syntheses. The donor properties of triphenylphosphine are well known, and we have found that the preparation of halocarbenes from halomethanes, either by the alkoxide method[2] or by the alkyllithium method,[5] when carried out in the presence of triphenylphosphine, gives triphenylphosphinehalomethylene reagents[6], *e.g.*

$$CH_2Cl_2 + n\text{-BuLi} + (C_6H_5)_3P \longrightarrow (C_6H_5)_3P{=}CHCl + LiCl + C_4H_{10}$$

Addition of hydrogen bromide to the yellow solution of triphenylphosphinechloromethylene, prepared by adding 0.1 mole of *n*-butyllithium in ether to 0.11 mole of triphenylphosphine and 0.13 mole of methylene chloride in ether at $-30°$, precipitated a mixture of $[(C_6H_5)_3PH]Br$ and $[(C_6H_5)_3PCH_2Cl]Br$. The precipitated solids were dissolved in water, causing quantitative decomposition of triphenylphosphonium bromide to HBr and triphenylphosphine. Filtration of the latter was followed by precipitation of $[(C_6H_5)_3PCH_2Cl][B(C_6H_5)_4]$, m.p. 189–192° (dec.) (Calcd. for $C_{43}H_{37}ClPB$: C, 81.84; H, 5.91; Cl, 5.62. Found: C, 82.03; H, 6.17; Cl, 5.37) by addition of aqueous sodium tetraphenylborate to the filtrate. It was determined in this manner that triphenylphosphinechloromethylene had been formed in about 65% yield. A separate experiment using $[(C_6H_5)_3PCH_2Cl]Br$, purified by recrystallization from 2-propanol–ether (m.p. 209–211°. Calcd. for $C_{19}H_{17}ClBrP$: C, 58.26; H, 4.38; Cl, 9.05; Br, 20.40. Found: C, 58.47; H, 4.31; Cl, 8.6; Br, 20.3. Picrate, m.p. 192–194°. Calcd. for $C_{25}H_{19}O_7N_3ClP$: C, 55.61; H, 3.55; Cl, 6.56. Found: C, 55.60; H, 3.76; Cl, 6.32) in aqueous solution at comparable *p*H showed that the $[(C_6H_5)_3PCH_2Cl]^+$ ion is precipitated quantitatively by sodium tetraphenylborate. When phenyllithium was used as the base in the chlorocarbene generation, triphenylphosphinechloromethylene resulted in yields of *ca.* 40%. Dibromo- and dichlorocarbene could also be trapped in this manner to give triphenylphosphinedihalomethylene reagents.

Triphenylphosphinehalomethylenes undergo the Wittig reaction,[7] thus providing a new general synthesis of substituted vinyl chlorides and vinylidene chlorides and bromides. Treatment of solutions of triphenylphosphinechloromethylene with aldehydes and ketones using standard Wittig reaction conditions resulted in the expected substituted vinyl chlorides. A mixture of the *cis* and *trans* isomers was obtained when an aldehyde or unsymmetrical ketone was used. As an example may be given the preparation of 1-chloro-2-phenyl-1-propene[8] in 46% yield, based on methylene chloride, by the reaction of $(C_6H_5)_3P{=}CHCl$ with acetophenone. Gas chromatographic analysis showed that both possible geometrical isomers were present in 1:1.15 ratio; no assignment of structure was attempted. Triphenylphosphinechloromethylene may also be prepared by treatment of the triphenylchloromethylphosphonium bromide described above with phenyllithium in ether. The reagent prepared in this manner reacted with acetophenone to give 1-chloro-2-phenyl-1-propene in yields of 80–90%. The lower yield of the chloroölefin obtained when $(C_6H_5)_3P{=}CHCl$ was used in the solution in which it was generated by trapping of chloromethylene may be due to the presence of unreacted triphenylphosphine which interferes in isolation of the chloroolefin by distillation.

Some of the other conversions carried out include: cyclohexanone to chloromethylenecyclohexane; methyl isobutyl ketone to 1-chloro-2,4-dimethyl-1-pentene; diethyl ketone to 1-chloro-2-ethyl-1-butene and acetophenone to 1,1-dibromo-2-phenyl-1-propene (*via* CBr_2 generated using potassium *tert*-butoxide).

Extension of this reaction to the preparation of other phosphinemethylene reagents and the application of these reagents in organometallic syntheses such as those we have reported recently[9] is in progress.

We are grateful to the National Science Foundation for a predoctoral fellowship awarded to one of us (S.O.G.) and to the Quartermaster Research and Engineering Command for support of this work.

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(5) G. L. Closs and L. E. Closs, THIS JOURNAL, **81**, 4996 (1959); W. T. Miller, Jr., and C. S. Y. Kim, *ibid.*, **81**, 5008 (1959).

(6) G. Wittig and W. Haag, *Chem. Ber.*, **88**, 1654 (1955), with this end in mind, added diazomethane to triphenylphosphine in ether solution, but stable $(C_6H_5)_3P{=}N{-}N{=}CH_2$ was formed instead of $(C_6H_5)_3P{=}CH_2$.

(7) G. Wittig and U. Schöllkopf, *Chem. Ber.*, **87**, 1318 (1954); see also U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1959).

(8) B.p. 102–105° at 14 mm. Calcd. for C_9H_9Cl: C, 70.82; H, 5.94. Found: C, 70.81; H, 5.95,

(9) S. O. Grim and D. Seyferth, *Chem. and Ind. (London)*, 849 (1959).

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RECEIVED JANUARY 22, 1960

CONDITIONS FOR STEREOSPECIFIC OLEFIN-MERCAPTAN RADICAL ADDITIONS

Sir:

Non-stereospecificity in radical-olefin addition reactions is the generally accepted pattern, certain additions involving hydrogen bromide being the only established exceptions.[1,2,3,4,5] Although mercaptans add to alkenes with high specific reaction velocities[6] (10^6 l. mole^{-1} sec.$^{-1}$), there have been a number of reports on non-stereospecificity for olefin-mercaptan additions.[7,8,9] We confirm this pattern for the reaction of CH_3SD with the *cis*- and *trans*-2-butenes at $-70°$. Under reaction conditions producing only minor amounts of olefin

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(1) For reviews of the earlier literature, C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957; and P. S. Skell, R. C. Woodworth and J. H. McNamara, THIS JOURNAL, **79**, 1253 (1957).

(2) P. S. Skell and R. G. Allen, *ibid.*, **80**, 5997 (1958).

(3) P. S. Skell and R. G. Allen, *ibid.*, **81**, 5383 (1959).

(4) H. L. Goering and D. W. Larsen, *ibid.*, **81**, 5937 (1959).

(5) N. A. Le Bel (Abstracts Boston Meeting 1959, 4-O) described non-stereospecific reaction of HBr with norbornene. Also, private communication from Prof. P. I. Abell indicates that in the 1-bromo-1-cycloalkenes (C_4,C_6,C_7), additions of hydrogen bromide are not stereospecific.

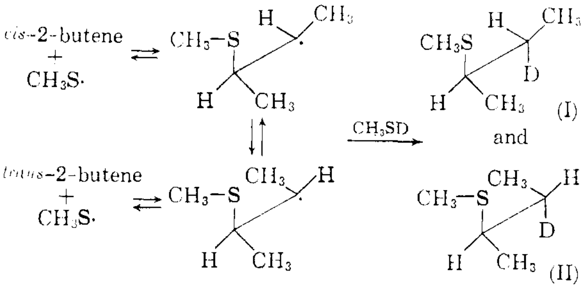
(6) C. Sivertz, *J. Phys. Chem.*, **63**, 34 (1959).

(7) F. G. Bordwell and W. A. Hewett, THIS JOURNAL, **79**, 3493 (1957).

(8) H. L. Goering, D. I. Relyea and D. W. Larsen, *ibid.*, **78**, 348 (1956).

(9) S. J. Cristol and R. P. Arganbright, *ibid.*, **79**, 6039 (1957).

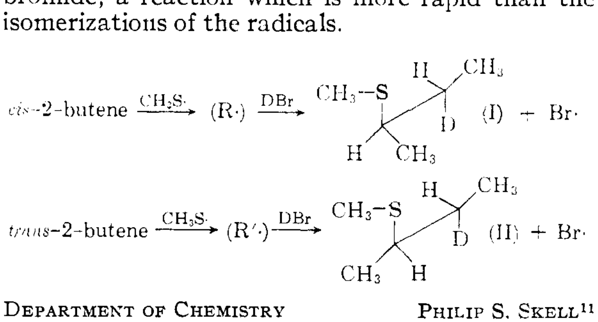
isomerization, the products are the same mixture of *erythro-* and *threo-*3-deuterio-2-methylthiobutane starting with either olefin. Rationalization of these observations requires an open chain radical which isomerizes more rapidly than the transfer of a deuterium atom from CH_3SD.



In the liquid phase at −78°, product analyses for the reaction of HBr, CH_3SH and *cis*-2-butene (1:2:1) yielded an apparent relative rate of hydrogen atom transfer to $CH_3\text{-}CHX\text{-}\dot{C}H\text{-}CH_3$ of $k_{\text{HBr}}/k_{\text{CH}_3\text{SH}} = 1.94$. Thus it was deemed advisable to examine the stereospecificity of CH_3SD additions in the presence of DBr. Under these conditions the formation of the 3-deuterio-2-bromobutanes is stereospecific, as it is in the absence of methyl mercaptan.[3] *The 3-deuterio-2-methylthiobutanes are also produced by stereospecific trans additions, cis-* and *trans-*2-butenes yielding *threo* (I) and *erythro* (II) products, respectively. Evidence for structure and purity was obtained through syntheses of the thioethers by reactions of CH_3SNa with pure *erythro-* and *threo-*3-deuterio-2-bromobutanes, inversions at C-2 being assumed. Examination of infrared spectra provides no evidence of isomer intercontamination for the radical additions.[10]

These results require that (1) DBr be the sole transfer agent with radicals $CH_3\text{-}CHX\text{-}\dot{C}H\text{-}CH_3$, and (2) equilibration $Br\cdot + CH_3SD \rightarrow DBr + CH_3S\cdot$ be more rapid than additions of Br· and $CH_3S\cdot$ to these olefins.

Steric control of mercaptan addition is achieved by the rapid reaction of the diastereomerically related 3-methylthio-2-butyl radicals with hydrogen bromide, a reaction which is more rapid than the isomerizations of the radicals.



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RECEIVED JANUARY 5, 1960

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[10] Throughout, vapor phase chromatography homogeneous samples were examined neat. Less than 5% intercontamination might have escaped detection.

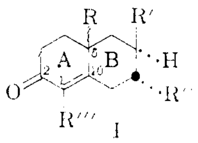
[11] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. AF 49(638)-457.

STEREOCHEMISTRY OF THE LITHIUM-AMMONIA REDUCTION OF α,β-UNSATURATED KETONES

Sir:

It has been proposed that the reduction of an α,β-unsaturated ketone with lithium in ammonia leads to the more stable epimer at the β-carbon atom.[1] Results in this Laboratory have led us to reëxamine these conclusions. We will illustrate the argument by reference to the reduction of octalones such as I. The transition state for protonation of the intermediate anion II must have considerable tetrahedral character at the β-carbon atom (C_{10}): if the β-carbon atom were still trigonal in the transition state for protonation (*cf.* II) approach of the proton source would be at least as easy to give a *cis* as a *trans* product and considerable quantities of *cis* decalones would be expected. This is contrary to experience. Even though the transition state has considerable tetrahedral character at C_{10}, the developing orbital at that carbon will be expected to overlap continually with the double bond, *i.e.*, must remain perpendicular to it (*cf.* III and IV). This leads to introduction of the C_{10} hydrogen *axially to ring A*. It is in the recognition of the necessity of continual overlap of the β-orbital with the enolate double bond that the picture differs from that previously suggested.[1]

We are thus led to the following rule: In reduction of an octalone system with lithium in ammonia the product will be the more stable of the two isomers (*cis* or *trans*) *having the newly introduced hydrogen axial to the ketone ring*. The conformation of the *cis* form of a β-decalone which is not permitted in the transition state (*cf.* V) is in many



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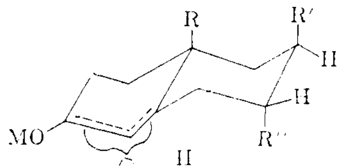

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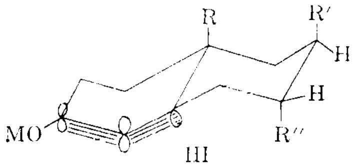
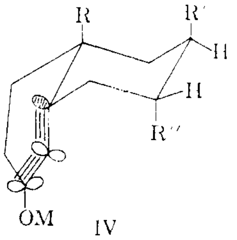
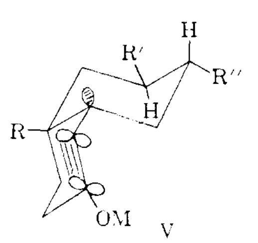


III



IV



V

cases more stable than the conformation of the *trans* isomer, whereas the permitted *cis* form is in general less stable than the *trans*. The product of the reduction of an octalone such as I will thus often be exclusively the *trans*-β-decalone even when the *cis*-decalone would be expected to be the more stable isomer.

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[1] D. H. R. Barton and C. H. Robinson, *J. Chem. Soc.*, 3045 (1954).