give 0.44 g (75%) of **13** as white crystals, mp 189–193° (lit.[7] mp 186°).

Anal. Calcd for $C_2H_5N_3OS$: C, 20.16; H, 4.23; N, 35.27; S, 26.92. Found: C, 20.31; H, 4.39; N, 34.97; S, 26.69.

2-Methyl-2-thiopseudobiuret Hydriodide (10).—To 5.95 g (0.05 mol) of thiobiuret suspended in 50 ml of CH_3CN was added 8.52 g (0.06 mol) of methyl iodide and the mixture was heated under reflux for 0.5 hr. The product, which separated as white shiny plates from the hot medium, was collected from the cooled mixture to give (11.3 g, 87%) of 2-methyl-2-thiopseudobiuret hydriodide, mp 181–183° (from CH_3CN).

Anal. Calcd for $C_3H_8IN_3OS$: C, 13.80; H, 3.09; N, 16.09; S, 12.28. Found: C, 13.87; H, 2.96; N, 16.11; S, 12.20.

Reaction of 10 with Ethyl Alcohol.—A solution of 1.31 g (0.005 mol) of **10** in 25 ml of EtOH was heated under reflux for 24 hr during which time methyl mercaptan was evolved. The solution was then concentrated and cooled giving 0.44 g (85%) of biuret (from EtOH), mp 193–194° (lit.[26] mp 193°); its ir spectrum was identical with the spectrum of an authentic sample.

Reaction of 2-Methyl-2,4-dithiopseudobiuret Hydriodide (11) with Ethyl Alcohol.—A 25-ml EtOH solution of 2-methyl-2,4-dithiopseudobiuret hydriodide (**11**)[10] was heated under reflux for 24 hr. From the concentrated solution was isolated 0.30 g (58%) of biuret.

1-(4-Nitrophenyl)-2-thiourea.—A suspension of 7.2 g (0.04, mol) of 4-nitrophenyl isothiocyanate in 35 ml of MeOH and 15 ml of 28% ammonium hydroxide was warmed on a steam bath for 20 min. The cooled mixture was filtered and the precipitate washed with MeOH to give 6.8 g (85%) 1-(4-nitrophenyl)-2-thiourea, mp 215–218° (lit.[27] mp 189–190°).

Anal. Calcd for $C_7H_7N_3O_2S$: C, 42.63; H, 3.58; N, 21.31; S, 16.26. Found: C, 42.31; H, 3.64; N, 21.31; S, 16.04.

2-Methyl-1-(4-nitrophenyl)-2-thiopseudourea Hydriodide (12).—A suspension of 1.06 g (0.0075 mol) of methyl iodide and 0.98 g (0.005 mol) of 1-(4-nitrophenyl)-2-thiourea in 10 ml of CH_3CN was heated under reflux for 2 hr. The cooled mixture was filtered and the solid was washed with CH_3CN to give 1.45 g (85%) of 2-methyl-1-(4-nitrophenyl)-2-thiopseudourea hydriodide, mp 188–190°.

Anal. Calcd for $C_8H_{10}IN_3O_2S$: C, 28.33; H, 2.97; N, 12.39; S, 9.45. Found: C, 28.10; H, 2.91; N, 12.37; S, 9.83.

Reaction of 12 with Ethyl Alcohol. Formation of 4-Nitrophenylurea.—A 17-ml EtOH solution containing 1.0 g (0.003 mol) of **12** was heated under reflux for 24 hr and cooled. From the solution was isolated 0.3 g (65%) of 4-nitrophenylurea, mp 228–230°, which resolidifies and then remelts at 328–330° (lit.[28] mp 237–238°). The analytical sample was recrystallized from $(CH_3)_2CO$-EtOH.

Anal. Calcd for $C_7H_7N_3O_3$: C, 46.41; H, 3.89; N, 23.20. Found: C, 46.59; H, 3.94; N, 22.94.

From the concentrated mother liquors was also isolated 120 mg (12%) of methyl *N*-(4-nitrophenyl)thiolcarbamate whose ir spectrum was identical with that of the material which was synthesized by the reaction of **12** with H_2O (*cf.* Table II).

Mercaptan Synthesis from 1-Acetyl-2-thiourea (14) and Alkyl Halides.—Each of a series of alkyl halides (*cf.* Table III) was heated under reflux with 1.1 equiv of **14** in ethanol (~1000 ml/mol of halide). After 24 hr, the solvent was removed under reduced pressure and the residue containing the mercaptan, 1-acetylurea, and the unreacted starting materials was transferred to an alumina (activity II) chromatography column by means of petroleum ether (bp 30–60°). Elution of the column with this solvent permitted the passage of only the mercaptan and the unreacted alkyl halide. The yields of the mercaptans were determined iodometrically.

Registry No.—**1**, 614-23-3; **5**, 6966-84-3; **7**, 15146-42-6; **8**, 34277-73-1; **9**, 924-51-6; **10**, 34277-75-3; **12**, 34277-76-4; **13**, 23228-74-2; 1-benzoyl-2-thiobiuret, 34277-78-6; 1-(4-nitrophenyl)-2-thiourea, 3696-22-8; 4-nitrophenylurea, 556-10-5.

Acknowledgments.—We are grateful to Drs. T. E. Fink and J. E. Tomaszewski and A. E. Murray, Jr., for technical assistance.

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[26] J. Theile and E. Uhlfelder, *Justus Liebigs Ann. Chem.*, **303**, 93 (1898).

[27] G. M. Dyson and H. J. George, *J. Chem. Soc.*, **125**, 1702 (1924).

[28] D. G. Crosby and C. Niemann, *J. Amer. Chem. Soc.*, **76**, 4458 (1954).

Halomethyl Metal Compounds. LIII. Reactions of Phenyl(trihalomethyl)mercury Compounds with Thiocarbonyl Derivatives[1]

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Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received November 12, 1971

The reaction of phenyl(bromodichloromethyl)mercury with thiophosgene gave tetrachlorothiirane in excellent yield. This product also was formed in the reaction of this mercury reagent with elemental sulfur; its thermolysis gave tetrachloroethylene and sulfur. Similar reactions of $PhHgCCl_2Br$, $PhHgCClBr_2$, and $PhHgCBr_3$ with thiobenzophenone gave 2,2-dichloro-, 2-bromo-2-chloro-, and 2,2-dibromo-3,3-diphenylthiirane, respectively, in good yield. The first of these underwent extrusion of sulfur on thermolysis, but the second and third lost HBr on being heated to give 2-chloro-3-phenylbenzo[*b*]thiophene and 2-bromo-3-phenylbenzo[*b*]thiophene, respectively. The latter was converted to the Grignard reagent which was hydrolyzed and carboxylated.

The addition of CX_2 (X = halogen), either as the free carbene or *via* a carbenoid reagent, to the C=C and C=C bonds is well known.[5] Some examples are known of such additions to the C=N bond[6] and to the C=O bond,[7] but CX_2 addition to the C=S bond has been restricted to a few examples involving difluorocarbene derived from pyrolysis of perfluoropropylene oxide (eq 1).[8] Addition of dichloro- or dibromocarbene, or of an appropriate "dihalocarbenoid," to any kind of C=S bond had not been reported.

Various diazoalkanes are known to react with thio-

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[1] (a) Preliminary communication: D. Seyferth and W. Tronich, *J. Amer. Chem. Soc.*, **91**, 2138 (1969). (b) Part LII of this series: D. Seyferth and H. Shih, *Organometal. Chem. Syn.*, in press.

[2] Postdoctoral Research Associate, 1968–1969.

[3] Postdoctoral Research Associate, 1971–1972.

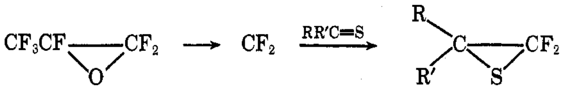
[4] National Institutes of Health Postdoctoral Fellow, 1969–1970.

[5] W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964; "Carbene, Carbenoide und Carbenanaloge," Verlag Chemie, Weinheim/Bergstr., Germany, 1969.

[6] (a) E. H. Fields and J. M. Sandri, *Chem. Ind. (London)*, 1216 (1959); (b) A. G. Cook and E. H. Fields, *J. Org. Chem.*, **27**, 3686 (1962); (c) P. K. Kadaba and J. O. Edwards, *ibid.*, **25**, 1431 (1960); (d) K. Ichimura and M. Ohta, *Tetrahedron Lett.*, 807 (1966); *Bull. Chem. Soc. Jap.*, **40**, 1933 (1967); (e) D. Seyferth and W. Tronich, *J. Organometal. Chem.*, **21**, P3 (1970).

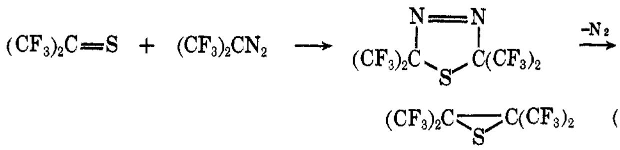
[7] (a) E. P. Moore, Jr., U. S. Patent 3,338,978 (1967); *Chem. Abstr.*, **68**, 114045c (1968); (b) W. Mahler, *J. Amer. Chem. Soc.*, **90**, 523 (1968); (c) R. B. Minasyan, E. M. Rokhlin, N. P. Gambaryan, Yu. V. Zeifman, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 761 (1965); (d) D. Seyferth and W. Tronich, *J. Organometal. Chem.*, **18**, P8 (1969); (e) D. Seyferth and W. E. Smith, *ibid.*, **26**, C55 (1971); (f) C. W. Martin and J. A. Landgrebe, *J. Chem. Soc. D*, 15 (1971).

[8] (a) W. R. Brasen, H. N. Chipps, C. G. Bottomley, M. W. Farlow, and C. G. Krespan, *J. Org. Chem.*, **30**, 4188 (1965); (b) F. C. McGrew, U. S. Patent 3,136,744 (1964); *Chem. Abstr.*, **61**, 4312*b* (1964).



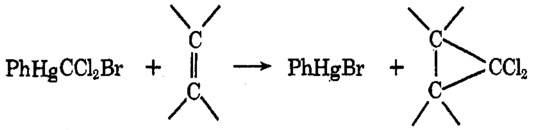
(1)

carbonyl compounds to give thiiranes (episulfides),[9] but recent work has shown that these products are formed *via* an intermediate thiadiazoline (eq 2).[10]



(2)

Our application of phenyl(trihalomethyl)mercury reagents to the synthesis of *gem*-dihalocyclopropanes had been very successful (eq 3),[11] and we became interested in the possible use of these reagents (especially of $PhHgCCl_2Br$, $PhHgCClBr_2$, and $PhHgCBr_3$) in the synthesis of three-membered heterocyclic systems.



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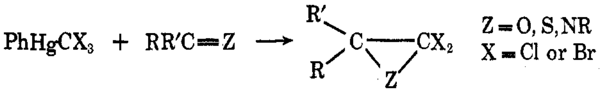
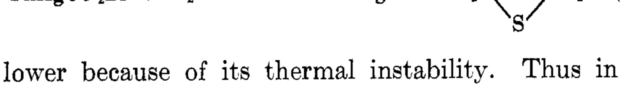


In view of the advantages associated with the use of the phenyl(trihalomethyl)mercury compounds (compared with other dihalocarbene-generating systems),[11b] we felt that such a study would have a good chance for success. We report here the results of our investigations of reactions of these organomercury reagents with selected thiocarbonyl compounds.

Results and Discussion

We chose to study the reactions of our phenyl(trihalomethyl)mercury reagents with thiophosgene and thiobenzophenone, feeling that these should serve adequately as representative members of the class of thiocarbonyl derivatives.

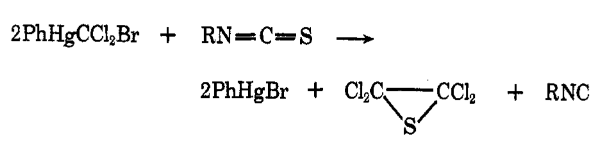
Thiophosgene.—Phenyl(bromodichloromethyl)mercury was found to react with a twofold excess of thiophosgene in benzene at 70–75° to give phenylmercuric bromide (88%) and tetrachlorothiirane (96% by glc) (eq 4). Isolated yields of the latter invariably were lower because of its thermal instability. Thus in a reaction carried out on a 33.5-mmol scale (at 60° for 4 hr) phenylmercuric bromide was obtained in 90% yield, but the yield of tetrachlorothiirane isolated by distillation was only 57%.



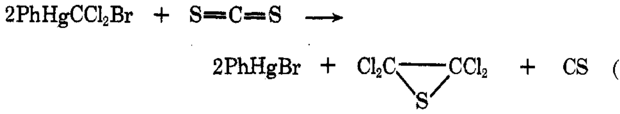
(4)

During the course of another project, three other routes to tetrachlorothiirane were discovered. The remarkable reaction of elemental sulfur with phenyl(bromodichloromethyl)mercury in benzene at 70° to give this compound in 34% yield when 2 molar equiv of $PhHgCCl_2Br$ per gram-atom of sulfur were used is of special interest. A reaction sequence involving conversion of the sulfur to thiophosgene by reaction with CCl_2 or $PhHgCCl_2Br$ followed by CCl_2 addition to the C=S bond thus formed seems reasonable. However, nothing is known concerning the course of the $PhHgCCl_2Br–S_8$ reaction and a better understanding of this novel process would be desirable.

The reactions of phenyl(bromodichloromethyl)mercury with isothiocyanates and with carbon disulfide also result in formation of tetrachlorothiirane (eq 5 and 6). In both cases thiophosgene is formed first and then reacts further with the mercurial. Details of these two reactions have been reported.[12]



(5)



(6)

Tetrachlorothiirane, a new compound, is a malodorous liquid which also is a lachrymator. It appears to be stable at room temperature and analytically pure samples could be obtained by glc. However, larger samples isolated by distillation or preparative glc invariably were contaminated with small quantities (up to 10%) of tetrachloroethylene, the volatile product of its thermal decomposition. The fragmentation of tetrachlorothiirane in the mass spectrometer at 70 eV gave the expected chlorinated equivalents of the principal species observed in the mass spectrum of thiirane itself. Desulfurization of tetrachlorothiirane also could be accomplished by treatment with phosphorus trichloride in slight excess at room temperature or with triphenylphosphine in diethyl ether. The latter reaction is complicated; only low yields of triphenylphosphine sulfide were obtained and only trace yields of tetrachloroethylene. Instead, much polymeric material appeared to be formed. Reaction with diethylamine in benzene at 50° gave no volatile products; only yellow-brown nonvolatiles which could not be crystallized were produced. Anhydrous hydrogen chloride was without effect on tetrachlorothiirane at room temperature, but chlorination at room temperature resulted in desulfurization, giving hexachloroethane as the organic product. Further study of the chemistry of tetrachlorothiirane should be of interest but is beyond the scope of this investigation.

Thiobenzophenone.—The reaction of equimolar quantities of phenyl(bromodichloromethyl)mercury and thiobenzophenone required about 3 hr at 70°. During this time the blue color of the thiobenzophenone was not discharged completely; however, phenylmercuric bromide was filtered off in 98% yield. 2,2-Dichloro-3,3-diphenylthiirane was formed in this reaction in 75% yield (eq 7). This product is a known compound,

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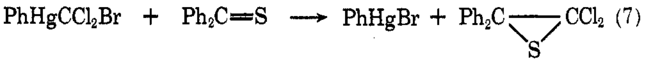
[9] (a) H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, **3**, 833 (1920); (b) A. Schönberg and S. Nickel, *Ber.*, **64**, 2323 (1931); (c) A. Schönberg and E. Frese, *Chem. Ber.*, **96**, 2420 (1963); (d) W. J. Middleton and W. H. Sharkey, *J. Org. Chem.*, **30**, 1384 (1965).

[10] W. J. Middleton, *J. Org. Chem.*, **34**, 3201 (1969).

[11] (a) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, *J. Amer. Chem. Soc.*, **87**, 4259 (1965); (b) D. Seyferth, *Accounts Chem. Res.*, **5**, 65 (1972).

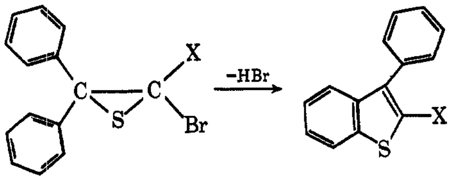
[12] D. Seyferth, R. Damrauer, H. Shih, W. Tronich, W. E. Smith, and J. Y.-P. Mui, *J. Org. Chem.*, **36**, 1786 (1971).



$$\mathrm{PhHgCCl_2Br + Ph_2C{=}S \longrightarrow PhHgBr + Ph_2C\underset{S}{-}CCl_2} \quad (7)$$

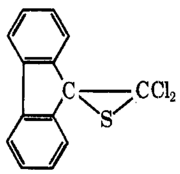
having been prepared by Staudinger and Siegwart[9a] by reaction of diphenyldiazomethane with thiophosgene. The behavior of 2,2-dichloro-3,3-diphenylthiirane on being heated (200° for 4 hr) was similar to that of tetrachlorothiirane; formed were 1,1-dichloro-2,2-diphenylethylene and sulfur.

The reactions of $PhHgCClBr_2$ and $PhHgCBr_3$ with thiobenzophenone also were investigated. In both cases similar reactions occurred, giving 2-bromo-2-chloro-3,3-diphenylthiirane and 2,2-dibromo-3,3-diphenylthiirane, respectively. These, however, were less stable than 2,2-dichloro-3,3-diphenylthiirane and were difficult to purify. Of special interest is that their thermolysis takes takes an entirely different course, as shown in eq 8. The appropriate 2-halo-3-phenylbenzo[*b*]thiophene (I) was produced in good yield in each case. Such a mode of decomposition of phenyl-substituted thiiranes had been reported already by earlier workers. Staudinger and Siegwart[13] found that the thiiranes II and III decomposed *via* sulfur extrusion but that IV decomposed at 100° with loss of hydrogen chloride, giving a product which was presumed to be 2,3-diphenylbenzo[*b*]thiophene. Schönberg and Vargha[14] described a similar decomposition of other substituted thiiranes (eq 9). It was suggested (but not proven) that this decomposition proceeded *via* the sulfenyl chloride intermediate V. In support of this suggestion, we note the recent report of the decomposition of an appropriate sulfenyl chloride in this fashion (eq 10).[15] Another possibility is that ring opening of the thiirane gives the thio acid chloride and that this is the intermediate which forms the benzo[*b*]thiophene (eq 11). The ionic species VI should be accessible both from the thio acid chloride and from the sulfenyl bromide; so it also is possible that both ring-opened species are formed in the course of the thiirane decomposition, as shown in eq 11. In indirect support of this idea, it may be noted that analogous aziridines[16] and oxiranes[7d] undergo similar ring opening upon thermolysis (eq 12 and 13).



(8)

X = Cl, Br   I



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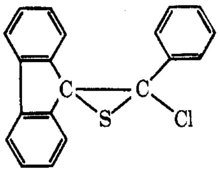

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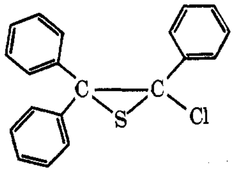

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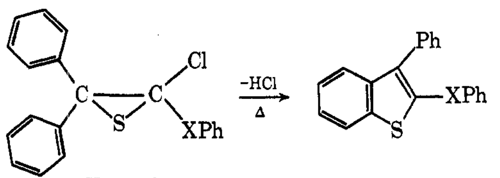
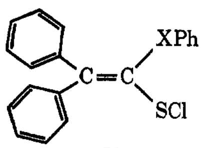


(9)

X = O, S



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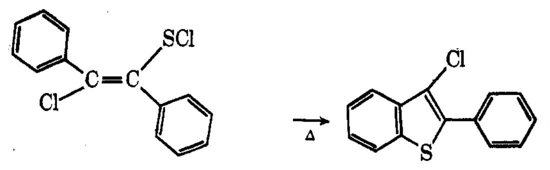
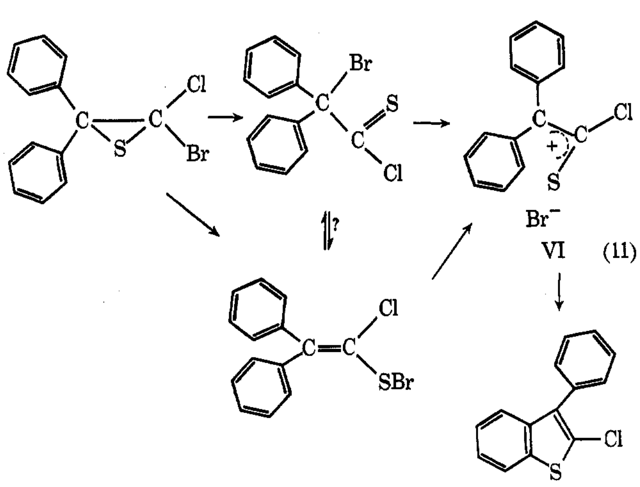


(10)

(prepared *via* $PhC{\equiv}CPh + SCl_2$)



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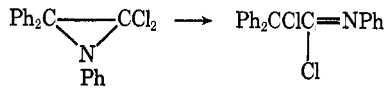
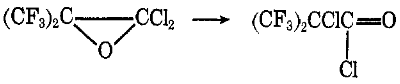
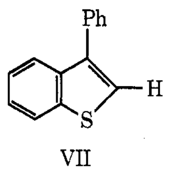


$$\mathrm{Ph_2C\underset{\underset{Ph}{N}}{-}CCl_2 \longrightarrow Ph_2CCl\underset{Cl}{C}{=}NPh} \quad (12)$$

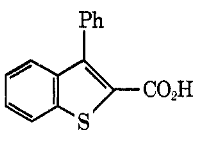


$$\mathrm{(CF_3)_2C\underset{O}{-}CCl_2 \longrightarrow (CF_3)_2CCl\underset{Cl}{C}{=}O} \quad (13)$$

2-Bromo-3-phenylbenzo[*b*]thiophene (I, eq 8) was converted to the Grignard reagent in THF solution. Hydrolysis of this reagent gave 3-phenylbenzo[*b*]thiophene (VII), while its carboxylation produced 2-carboxy-3-phenylbenzo[*b*]thiophene (VIII). The formation of VII by hydrolysis of the Grignard reagent from I (X = Br) serves to confirm the structure of I (X = Br) and, by interference, of I (X = Cl). We obtained VII as a colorless oil, in agreement with the report by Rao and Tilak[17] that 3-phenylbenzo[*b*]thiophene is an oil and 2-phenylbenzo[*b*]thiophene is a solid, mp 171–



VII



VIII

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[13] H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, **3**, 840 (1920).

[14] A. Schönberg and L. v. Vargha, *Justus Liebigs Ann. Chem.*, **483**, 176 (1930); *Ber.*, **64**, 1390 (1931).

[15] T. J. Barton and R. G. Zika, *J. Org. Chem.*, **35**, 1729 (1970).

[16] (a) H. W. Heine and A. B. Smith, *Angew. Chem.*, **75**, 669 (1963); (b) R. E. Brooks, J. O. Edwards, G. Levey, and F. Smyth, *Tetrahedron*, **22**, 1279 (1966).

[17] D. S. Rao and B. D. Tilak, *J. Sci. Ind. Res.*, **18B**, 77 (1959); *Chem. Abstr.*, **54**, 1484f (1960).

172°.[18] In confirmation of the report by Rao and tilak,[17] we found that VII underwent acid-catalyzed thermal rearrangement to give 2-phenylbenzo[*b*]thiophene.

Conclusions.—This study has shown that phenyl(trihalomethyl)mercury compounds react with thiocarbonyl compounds to add CX_2 to the C=S bond to give thiiranes. The exact nature of this addition process is not known. One mechanistic extreme involves a two-step process, decomposition of the organomercury reagent to give a dihalocarbene which subsequently adds to the C=S bond. Such an addition could either occur as a concerted cycloaddition or as a process in which an ylide intermediate, $R_2C{=}\overset{+}{S}{-}\overset{-}{C}X_2$, is formed prior to ring closure to the thiirane. At the other extreme is a noncarbene process in which a direct interaction between the organomercurial and the thiocarbonyl compound is involved in the CX_2 transfer.[19]

This research, which had purely exploratory synthetic objectives, has brought the first synthesis of tetrachlorothiirane, an interesting new compound whose chemistry remains largely unexplored. It has made available a new route to 1,1-dihalo-2,2-diarylthiiranes and as an added dividend has provided what may be a fairly general entry to 3-aryl-2-halobenzo[*b*]thiophenes. The latter have a reactive "handle" in the 2 position which allows further transformations. The reactions described in this report thus provide new examples of the wide-ranging synthetic utility of the phenyl(trihalomethyl)mercury reagents.

Experimental Section

General.—All reactions were carried out under an atmosphere of dry argon or prepurified nitrogen using flame-dried glassware. Carefully dried solvents were used in all reactions. Nmr spectra were recorded using a Varian Associates A-60 or T-60 spectrometer. Chemical shifts are given in δ units, downfield from internal TMS. Infrared spectra were recorded using a Perkin-Elmer 237B, 337, or 257 grating infrared spectrophotometer. Gas-liquid partition chromatography (glpc) was used for yield determinations and collection of liquid samples. Commercial stainless steel columns were employed with either an F & M Model 700, 720, or 5754 gas chromatograph. Yields were determined by the internal standard procedure. The standard apparatus used in these reactions of phenyl(trihalomethyl)mercury compounds consisted of a three-necked flask of appropriate size equipped with a reflux condenser (topped with a gas inlet tube), a thermometer, and a magnetic stirring assembly. The phenyl(trihalomethyl)mercurials were prepared by our improved THF procedure.[20] The progress of the reactions involving these reagents was followed using thin layer chromatography.[11a]

Reaction of Phenyl(bromodichloromethyl)mercury with Thiophosgene.—The standard apparatus was charged with 4.41 g (10 mmol) of $PhHgCCl_2Br$, 2.30 g (20 mmol) of thiophosgene (Aldrich), and 25 ml of dry benzene. The reaction mixture was stirred and heated under nitrogen for 1 hr at 70–75°. The resulting suspension was chilled to 10° and filtered under nitrogen through a Schlenk tube to remove 3.2 g (88%) of phenylmercuric bromide, mp 274–279°. The filtrate was trap-to-trap distilled after 5.7 g of *n*-dodecane had been added as a "chaser" (at 0.1 mm, pot temperature below 70°). Glpc analysis of the distillate (6-ft Dow Corning DC-200 silicone oil on Chromosorb W, 135°) showed that tetrachlorothiirane had been formed in 81% yield.

Experiments were carried out on a larger scale in order to accumulate more of this compound. In a typical reaction, 33.5 mmol each of the mercury reagent and freshly distilled thiophosgene in 60 ml of benzene were stirred and heated at 60° for 4 hr. After filtration of PhHgBr (90%), the filtrate was trap-to-trap distilled at 0.1 mm (pot temperature to 50°). The resulting distillate was redistilled using an 8-in. Vigreux column, first at room temperature and approximately 0.2 mm to remove most of the benzene and subsequently at 25° and 0.1 mm to obtain the product, 3.79 g (57%), $n^{25}{}_D$ 1.5665, in analytical purity. The compound has an unpleasant odor and is an intense lachrymator. Glc analysis (as above) showed the presence of a minor ($\sim$5%) impurity, identified as tetrachloroethylene.

Anal. Calcd for C_2Cl_4S: C, 12.14; Cl, 71.66; S, 16.20. Found: C, 12.12; Cl, 71.05; S, 16.08.

The product was isolated as a colorless to faint yellow liquid which became yellow on long standing. A boiling point determination by slow distillation gave 36–38° (0.1 mm). Its ir spectrum (film) showed bands at 1145 (vs), 1110 (w), 920 (w), 910 (w), 835 (w), 815 (vs), 770 (vw), 750 (vs), 745 (w), 705 (vw), 675 (vs), 670 (w), and 650 cm^{-1} (vw). The fragmentation of tetrachlorothiirane in the mass spectrometer at 70 eV gave the chlorinated equivalents of the principal species observed in the mass spectrum of thiirane itself:[21] $C_2Cl_4S^+$ (17.5), $C_2Cl_3S^+$ (29.8), $C_2Cl_2S^+$ (62.9), CCl_2S^+ (3.2), C_2ClS^+ (12.3), $CClS^+$ (100.0), Cl_2S^+ (0.58), S^+ (3.2), $C_2Cl_4{}^+$ (78.8), $C_2Cl_3{}^+$ (46.2), $C_2Cl_2{}^+$ (26.8), C_2Cl^+ (8.7), $CCl_3{}^+$ (21.0), $CCl_2{}^+$ (23.5), and CCl^+ (21.7).

Reaction of Phenyl(bromodichloromethyl)mercury with Sulfur.—The standard apparatus was charged with 10 mmol of the mercury compound and 5 mg-atoms (0.16 g) of yellow sulfur (S_8) in 30 ml of benzene. The reaction mixture was stirred and heated at 70° for 1 hr. Phenylmercuric bromide was filtered off in 93% yield. The filtrate was concentrated at 30° (14 mm) and the residue, a yellow semisolid, was trap-to-trap distilled at 0.05 mm (to 30°). Glpc analysis of the distillate indicated the presence of tetrachlorothiirane in 34% yield.

Chemical Properties of Tetrachlorothiirane. A. Thermolysis.—Tetrachlorothiirane (260 mg) was placed in a vacuum-sealed tared flask and entirely immersed in an oil bath at 130° for 24 hr. All volatiles were trap-to-trap distilled at 0.1 mm to leave 105 mg of a viscous orange residue, a mixture of elemental sulfur (burns with blue flame and odor of SO_2) and polymer. The distillate (155 mg) was analyzed by glc (6-ft DC-200, at 85°). Only one component, tetrachloroethylene, was present, and this represents an isolated yield of 71%. The product was identified on the basis of its glpc retention time and mass spectrum.

B. Desulfurization with Phosphorus Trichloride.—Tetrachlorothiirane (431 mg, 2.17 mmol) and 497 mg (3.62 mmol) of PCl_3 were stirred under nitrogen at room temperature for 3 days. Glc analysis was difficult; on an Apiezon L column there was no separation between $PSCl_3$ and tetrachloroethylene; on a DC-200 column slight separation was observed. On a polar General Electric Co. XF-1112 cyanoethylsilicone rubber gum column adequate separation of these products occurred. However, PCl_3 was partially retained in the column and gave irregular peaks. Also, $POCl_3$ appeared, even though the reaction mixture was protected from the air. In any case, smooth conversion to only two products, $PSCl_3$ and C_2Cl_4, was indicated. These products were present in equivalent amounts (DC-200 column analysis) and were identified by means of their glpc retention times and their ir spectra.

C. Chlorination.—Tetrachlorothiirane (752 mg) in 20 ml of CCl_4 was stirred at room temperature while the solution was saturated with an excess of chlorine in a sealed system. The solution was stirred for 3 days, after which time the resulting orange solution was distilled to remove unconverted chlorine and solvent at 2 mm. The remaining white residue was sublimed *in vacuo* (heat lamp) to give 592 mg of white crystals, mp 174–176°. Recrystallization from ether at −78° gave pure hexachloroethane: mp 185–186° (sealed tube); mmp with authentic material, 184–186° (sealed tube); "Handbook of Chemistry and Physics" mp 187°.

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(18) The structure of 2-phenylbenzo[*b*]thiophene has been proven by independent synthesis and by degradation: J. E. Banfield, W. Davies, N. W. Gamble, and S. Middleton, *J. Chem. Soc.*, 4791 (1956). (The structure of 3-phenylbenzo[*b*]thiophene also was confirmed by independent synthesis.[17]) Melting points as high as 176° have been reported: G. M. Badger, N. Kowanko, and W. H. F. Sasse, *ibid.*, 2969 (1960).

(19) Note the evidence in favor of such a process in the case of the reaction of $PhHgCCl_2Br$ with benzophenone.[7f]

(20) D. Seyferth and R. L. Lambert, Jr., *J. Organometal. Chem.*, **4**, 127 (1965).

(21) E. Gallegos and R. W. Kiser, *J. Phys. Chem.*, **65**, 1177 (1961).

Reactions of Phenyl(trihalomethyl)mercury Compounds with Thiobenzophenone. A. Phenyl(bromodichloromethyl)mercury.—The standard apparatus was charged with 4.41 g (10 mmol) of the mercurial and 10 mmol (1.98 g) of thiobenzophenone[22] in 50 ml of dry benzene. The resulting blue solution was stirred and heated at 70° under nitrogen for 3 hr. During this time the blue color of the thiobenzophenone was not completely discharged, but tlc indicated complete consumption of the organomercury reagent. The reaction mixture was cooled and filtered to remove 3.5 g (98%) of phenylmercuric bromide, mp 275–278°. The filtrate was concentrated at 50° (14 mm) to leave a solid residue. Unconverted thiobenzophenone was washed out from the latter by treatment with cold ethanol, leaving yellow crystals (2.1 g, 75%) of 2,2-dichloro-3,3-diphenylthiirane, mp 88–90° dec. Two recrystallizations from ethanol gave 1.7 g of fine, faintly yellow needles, mp 88.5–89.5° dec. 2,2-Dichloro-3,3-diphenylthiirane prepared by reaction of diphenyldiazomethane and thiophosgene was reported to have mp 89–90° dec.[9a] The ir spectrum (Nujol) showed the following bands below 1600 cm^{-1}: 1595 (w), 1580 (w), 1485 (m), 1445 (s), 1335 (w), 1310 (w), 1225 (w), 1100 (m), 1070 (m), 1030 (m), 1000 (w), 930 (m), 895 (w), 810 (s), 770 (s), 745 (m), 720 (s), 705 (s), and 690 cm^{-1} (s).

B. Phenyl(dibromochloromethyl)mercury.—The organomercury reagent (10 mmol) and thiobenzophenone (10 mmol) in 40 ml of benzene were stirred and heated at 40° for 3 days. The initially blue solution became gray-violet during this time. Filtration gave PhHgBr (90%). The filtrate was evaporated at reduced pressure (pot temperature to 50°) to leave a colored solid residue. Extraction of unconverted thiobenzophenone left a yellow residue (2.8 g, 86%), which was recrystallized (with difficulty) from ethanol to give 2.4 g (74%) of pale yellow crystals, mp 80–81° dec, of 2-bromo-2-chloro-3,3-diphenylthiirane: ir (Nujol) 1595 (w), 1580 (w), 1485 (w), 1445 (s), 1330 (w), 1095 (m), 1075 (m), 1045 (w), 1030 (w), 1000 (w), 925 (m), 890 (w), 810 (m), 770 (s), 720 (s), 710 (s), 700 (s), 690 (s), and 680 cm^{-1} (s).

Anal. Calcd for $C_{14}H_{10}ClBrS$: C, 51.65; H, 3.09. Found: C, 51.36; H, 3.36.

C. Phenyl(tribromomethyl)mercury.—The same procedure as described in B was used in the reaction of 10 mmol each of $PhHgCBr_3$ and thiobenzophenone in 40 ml of benzene. The crude product (3.3 g, 89%) had mp 74–76° dec. Material recrystallized twice from ethanol had mp 76–77° dec. In another preparation the crude product was dissolved in hot methanol and filtered through Celite. On cooling, yellow needles of 2,2-dibromo-3,3-diphenylthiirane crystallized: ir (Nujol) 1600 (w), 1585 (w), 1490 (m), 1445 (s), 1155 (w), 1095 (m), 1080 (w), 1030 (w), 1000 (w), 920 (w), 795 (w), 770 (s), 755 (s), 715 (m), 705 (s), 690 (m), and 680 cm^{-1} (s).

Anal. Calcd for $C_{14}H_{10}Br_2S$: C, 45; H, 2.73. Found: C, 45.64; H, 3.04.

Thermolysis of the 2,2-Dihalo-3,3-diphenylthiiranes. A. 2,2-Dichloro-3,3-diphenylthiirane.—A 585-mg sample was stirred in a sealed flask in a 200° oil bath for 4 hr. The resulting brown oil was extracted with four 5-ml portions of boiling hexane under nitrogen, leaving behind undissolved polymers and sulfur. Refrigeration of the combined hexane extracts precipitated some sulfur. The filtered solution was evaporated at reduced pressure and the residue was triturated under nitrogen with several small portions of Dry Ice cooled ether. The remaining white solid was dried *in vacuo*, giving 352 mg of 1,1-dichloro-2,2-diphenylethylene, mp 79–80° (lit.[23] mp 79–80°); ν(C=C) 1610 cm^{-1}.

B. 2-Bromo-2-chloro-3,3-diphenylthiirane.—A solution of 1.6 g (4.9 mmol) of the thiirane in 10 ml of dry benzene was stirred and heated at reflux under nitrogen for 24 hr. During this time the originally yellow solution became brown. The solvent was removed at reduced pressure and the residual oil was distilled using a short-path distillation apparatus to give a colorless oil, boiling range 160–170° (0.05 mm), yield 0.9 g (75%, based on eq 8). Two recrystallizations at low temperature from a minimum amount of pentane gave white crystals, mp 39–40°, of 2-chloro-3-phenylbenzo[*b*]thiophene.[24] This compound also could be purified by glc (6-ft Carbowax W on Chromosorb W at 175°): ir (molten film) 3105 (sh), 3090 (sh), 3070 (s), 3035 (m), 1960 (w), 1910 (w), 1670 (w), 1610 (m), 1580 (w), 1540 (w), 1490 (s), 1460 (m), 1450 (s), 1435 (s), 1345 (s), 1320 (m), 1315 (w), 1285 (w), 1270 (s), 1190 (w), 1180 (w), 1165 (m), 1140 (w), 1080 (m), 1040 (s), 1020 (s), 975 (w), 950 (w), 930 (m), 915 (s), 860 (w), 850 (w), 825 (w), 810 (w), 780 (s), 775 (s), 760 (s), 740 (s), 725 (s), 705 (s), 670 (m), and 650 cm^{-1} (m).

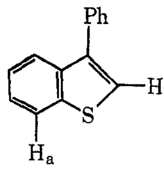
Anal. Calcd for $C_{14}H_9ClS$: C, 68.71; H, 3.71; Cl, 14.48; S, 13.10. Found: C, 68.40; H, 3.63; Cl, 14.51; S, 13.01.

C. 2,2-Dibromo-3,3-diphenylthiirane.—A solution of 940 mg of the thiirane in 10 ml of dry benzene was stirred at reflux under nitrogen for 24 hr, during which time HBr evolution was evident. The solvent was removed at reduced pressure and the violet residue was extracted with two 10-ml portions of hot hexane, leaving undissolved a small amount of black polymer. The yellow hexane solution was evaporated and the residue (665 mg, 91% crude) was sublimed at 110° (0.03 mm), giving 530 mg of pale yellow crystals, mp 62–69°. Recrystallization from pentane gave an analytically pure sample, mp 73–74°, of 2-bromo-3-phenylbenzo[*b*]thiphene: ir (Nujol) 1595 (w), 1570 (w), 1525 (w), 1425 (s), 1330 (m), 1260 (m), 1155 (w), 1130 (w), 1070 (m), 1030 (w), 990 (s), 940 (w), 920 (w), 890 (w), 860 (w), 850 (w), 765 (s), 755 (s), 735 (s), 715 (m), and 700 cm^{-1} (s).

Anal. Calcd for $C_{14}H_9BrS$: C, 58.14; H, 3.14; Br, 27.64; S, 11.09. Found: C, 58.39; H, 3.21; Br, 27.68; S, 11.11.

In another experiment, the intermediate thiirane was not isolated. A solution of 40 mmol of thiobenzophenone and 52 mmol of $PhHgCBr_3$ in 200 ml of dry benzene was stirred under nitrogen in an oil bath kept at 45° for 4 days, at the end of which time the blue color had been discharged. The brown solution was filtered to remove 13.4 g of phenylmercuric bromide (72%, based on the mercurial). The filtrate was heated at reflux with the exclusion of atmospheric moisture for 28 hr. The solvent was removed at reduced pressure and the black residue was extracted with three 50-ml portions of hot hexane. The hexane extracts were concentrated and the remaining oil was short-path distilled to give a semisolid oil, boiling range 110° (0.07 mm)–140° (0.03 mm). The distillate was dissolved in 200 ml of pentane, treated with activated charcoal, filtered through Celite, and concentrated to 70 ml. Refrigeration gave a first crop of 3.78 g, mp 72–74°. A second crop of 1.34 g was obtained on concentrating the mother liquor to 20 ml, mp 70–73°. Total yield of 5.12 g represented at 45% yield.

Reduction of 2-Bromo-3-phenylbenzo[*b*]thiophene to 3-Phenylbenzo[*b*]thiophene.—This reduction was carried out to confirm the structure of the 2,2-dibromo-3,3-diphenylthiirane pyrolysis product. The Grignard reagent was prepared by heating at reflux a THF solution (12 ml) of 1.157 g (4.0 mmol) of 2-bromo-3-phenylbenzo[*b*]thiophene with 120 mg (5.0 mg-atom) of magnesium for 22 hr under nitrogen. The reaction mixture was hydrolyzed by addition of 1 ml of concentrated HCl diluted with 5 ml of water. The resulting mixture was evaporated at reduced pressure until the THF was removed. The residue was extracted twice with hexane and the extracts were dried (Na_2SO_4) and evaporated to leave 880 mg of product as a yellow oil. Short-path distillation gave 740 mg of pure product as a colorless oil (88%) at 103–108° (0.02 mm): $n^{25}{}_D$ 1.6789; ir (neat) 3040 (m), 3000 (m), 1600 (m), 1520 (w), 1480 (m), 1440 (m), 1420 (s), 1345 (m), 1300 (w), 1255 (w), 1210 (w), 1140 (w), 1070 (w), 1060 (w), 1020 (w), 940 (w), 910 (w), 830 (m), 790 (w), 765 (s), 750 (m), 730 (s), and 700 cm^{-1} (s); nmr (CCl_4) δ 7.6–8.0 (multiplet, area 2, a and b) and 7.1–7.6 ppm (multiplet, area 8).



Anal. Calcd for $C_{14}H_{10}S$: C, 79,96; H, 4.79; S, 15.25. Found: C, 80.01; H, 4.83; S, 15.24.

The 3-phenylbenzo[*b*]thiophene thus obtained (354 mg) and a very small drop of concentrated H_2SO_4 were placed in a sealed flask under nitrogen and heated at 200–210° for 22 hr. Only a hard, black residue remained on the bottom of the flask, but

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[22] "Organic Syntheses," Collect. Vol. IV, N. Rabjohn, Ed., Wiley, New York, N. Y., 1963, p 927.

[23] A. Baeyer, *Ber.*, **6**, 223 (1873).

[24] The isomeric 3-chloro-2-phenylbenzo[*b*]thiophene has mp 67°.[15]

crystals of 2-phenylbenzo[*b*]thiophene had sublimed to the top of the flask. These were recrystallized from 10 ml of absolute ethanol, giving 110 mg of white plates, mp 170–171°. Another recrystallization raised the melting point to 171.5–172° (lit.[17] mp 171–172°, lit.[15] 172–173°; note also footnote 18).

No rearrangement of 2-phenylbenzo[*b*]thiophene took place in the absence of an acid catalyst, and the starting material was recovered unchanged.

Preparation of 2-Carboxy-3-phenylbenzo[*b*]thiophene.—The Grignard reagent was prepared as above from 868 mg (3.0 mmol) of 2-bromo-3-phenylbenzo[*b*]thiophene and 100 mg (4.0 mg-atoms) of magnesium in 9 ml of dry THF. The nitrogen atmosphere was replaced with dry tank carbon dioxide and the solution was heated at reflux for 25 hr under positive CO_2 pressure. The solution was evaporated at reduced pressure and the residue was treated with 2 ml of concentrated HCl in 15 ml of water. Extraction with two 15-ml portions of diethyl ether followed. The ether solution was extracted with three 10-ml portions of saturated sodium bicarbonate solution, which gave an aqueous suspension of the product sodium salt. The combined bicarbonate layers were acidified with dilute HCl and extracted with three 20-ml portions of ether. The combined ether extracts were dried and evaporated and the remaining yellow powder was recrystallized from 15 ml of 70% aqueous ethanol. A first crop of 394 mg, mp 198–199°, and a second crop of 121 mg were obtained, a total yield of 68%. Recrystallization from 50% aqueous ethanol gave an analytical sample, mp 199.0–199.5°, with prior softening at about 175°: ir (Nujol) 2550 (broad, OH), 1650 (s), 1520 (s), 1485 (m), 1340 (m), 1295 (s), 1250 (m), 1180 (w), 1125 (w), 1080 (m), 1050 (w), 920 (m), 860 (w), 780 (w), 755 (s), 745 (m), 740 (s), 715 (m), and 700 cm^{-1} (s).

Anal. Calcd for $C_{15}H_{10}O_2S$: C, 70.84; H, 3.96; S, 12.61. Found: C, 70.68; H, 4.29; S, 12.49.

Registry No.—VII, 14315-12-9; VIII, 29491-86-9; phenylmercuric bromide, 1192-89-8; tetrachlorothiirane, 22706-41-8; 2,2-dichloro-3,3-diphenylthiirane, 34281-40-8; 2-bromo-2-chloro-3,3-diphenylthiirane, 34281-41-9; 2,2-dibromo-3,3-diphenylthiirane, 34281-42-0; 2-chloro-3-phenylbenzo[*b*]thiophene, 34281-43-1; 2-bromo-3-phenylbenzo[*b*]thiophene, 34281-44-2.

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Selective Hydrogenation of α,β-Unsaturated Carbonyl Compounds *via* Hydridoiron Complexes

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A reagent generated *in situ* from iron pentacarbonyl and a small amount of base in moist solvents serves as a new, efficient agent for selective hydrogenation of α,β-unsaturated carbonyl compounds (ketones, aldehydes, esters, and lactones, etc.) under mild reaction conditions. The characteristics and the possible mechanisms of the reduction are described.

The reduction of α,β-unsaturated carbonyl compounds (eq 1) has been effected *chemically* by dissolving alkali metals such as Li, Na, and K in liquid ammonia (Birch conditions),[1] and amalgamated zinc in hydrochloric acid (Clemmensen conditions).[2] Because such reductions require strongly basic or acidic conditions, which often cause undesired side reactions, their synthetic utility has been restricted. Sodium borohydride also has been employed in certain cases, but lacks general utility.[3] The homogeneous, transition metal catalyzed reduction of unsaturated compounds, most of which proved to involve metal hydride complexes, is the subject of current interest.[4] However, there have so far been few attempts to gain selectivity for homogeneous reduction of α,β-unsaturated carbonyl compounds.[5,6] This paper describes a new, selective reduction of α,β-unsaturated carbonyl compounds by means of iron-based complexes under mild reaction conditions.

$$RCH{=}CHCOR' \longrightarrow RCH_2CH_2COR' \qquad (1)$$

Results and Discussion

Treatment of unsaturated carbonyl derivatives with a reagent generated *in situ* from iron pentacarbonyl [$Fe(CO)_5$] and a small amount of NaOH in 95% CH_3OH at 0–60° under nitrogen atmosphere gave the corresponding saturated derivatives in high yield (condition A). A mixture of ether and H_2O (4:1 v/v) which provides a two-layer reaction system may be used in place of 95% CH_3OH (condition B). Besides NaOH, 1,4-diazabicyclo[2.2.2]octane (DABCO) in moist dipolar solvents such as *N,N*-dimethylformamide (DMF) or *N,N,N′,N′,N″,N″*-hexamethylphosphoric triamide (HMPA) gave satisfactory results (condition C). As exemplified in Table I, this reduction method is applicable to a wide variety of α,β-unsaturated carbonyl compounds including ketones, aldehydes, esters, lactones, etc.

The present procedure, within limits of the experiments examined, possesses the following characteristics: (1) overreductions of the ketonic group into $>CHOH$ or $>CH_2$ groups are negligible; (2) ester

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(1) (a) A. J. Birch, *Quart. Rev., Chem. Soc.*, **4**, 69 (1950); (b) H. Smith, "Organic Reactions in Liquid Ammonia," Interscience, New York, N. Y., 1963; (c) M. Smith in "Reduction," R. L. Augustine, Ed., Marcel Dekker, New York, N. Y., 1968, p 95.

(2) J. G. St. C. Buchanan and P. D. Woodgate, *Quart. Rev., Chem. Soc.*, **23**, 522 (1969).

(3) (a) W. R. Jackson and A. Zurqiyah, *J. Chem. Soc.*, 5280 (1965); (b) K. Iqbal and W. R. Jackson, *J. Chem. Soc. C*, 616 (1968), and references cited therein.

(4) Reviews: (a) Collected papers presented at the symposium on homogeneous catalysis, Liverpool, U. K., Sept 17 and 18, 1968, in *Discuss. Faraday Soc.*, **46** (1968); (b) M. E. Vol'pin and I. S. Kolomnikov, *Russ. Chem. Rev.*, **38**, 273 (1969).

(5) Ru(II)Cl_2 in aqueous HCl exhibited marked selectivity: J. Halpern, J. F. Harrod, and B. R. James, *J. Amer. Chem. Soc.*, **88**, 5150 (1966).

(6) For heterogeneous, *catalytic* hydrogenation systems, see R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, New York, N. Y., 1965, p 60.