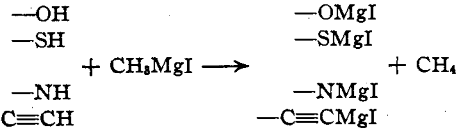
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

# Relative Reactivities of Organometallic Compounds. XVI. Detection of the —SH Group

BY HENRY GILMAN AND JOSEPH F. NELSON

The Tschugaeff–Zerewitinoff[1] analysis makes it possible to determine, qualitatively and quantitatively, active or acidic hydrogens by measurement of the volume of methane evolved when a weighed amount of sample is treated with an excess of methylmagnesium iodide.



$$\begin{array}{l}—OH\\—SH\\ \\—NH\\—C\equiv CH\end{array} + CH_3MgI \longrightarrow \begin{array}{l}—OMgI\\—SMgI\\ \\—NMgI\\—C\equiv CMgI\end{array} + CH_4$$

A study of other organometallic compounds indicates that it may be possible, by use of appropriate organometallic compounds, to effect selective or preferential reactions with specific active hydrogen types. We are reporting at this time the use of triethylbismuth and tetraethyllead for detecting the —SH group.

## Experimental Part

**Materials.**—A convenient method for the preparation of triethylbismuth is one patterned after the procedure of Schaefer and Hein[2] for the preparation of trimethylbismuth. To an ethylmagnesium bromide solution prepared from 1.4 moles of ethyl bromide in 400 cc. of ether, was added slowly and with rapid stirring 200 g. of an ether solution containing 0.4 mole of bismuth chloride. Because of the inflammability of triethylbismuth all operations were carried out in a nitrogen atmosphere. Heat was applied until the reaction was complete, and a large quantity of gray precipitate formed.

Most of the ether was then removed by fractionation through an efficient column, a hot water-bath being used. Triethylbismuth, like some other organometallic compounds, undergoes a ready ether distillation, and a fractionating column reduces the carry-over of triethylbismuth. The remaining ether and triethylbismuth were then distilled off at 4 mm. pressure into a 250-cc. modified Claisen flask cooled by an ether–dry ice mixture. In this distillation an oil-bath was used, and the external temperature was raised gradually to 170° near the end of the distillation. Abrupt and excessive heating should be avoided.

The ether was finally distilled from the distillate, and the triethylbismuth then collected at about 123° (150 mm.). The yield was 88%.

The tetraethyllead and the several compounds studied were purified by customary procedures.

**Procedure.**—The usual Zerewitinoff apparatus and technique were used, 5 cc. of *n*-butyl ether or of 1,4-dioxane being added to the 0.2–0.4 g. sample. After flushing out the side-bulb with nitrogen, 5 cc. of a 25% (by volume) solution of triethylbismuth in *n*-butyl ether was run into the side-bulb through a bent pipet provided with a stopcock. The main bulb was then flushed with nitrogen and attached to the gas buret.[3] The bulb was then immersed for a few minutes in a water-bath kept at 25°, and the system closed to the atmosphere. A water-bath containing boiling water was then applied and the water kept boiling for a definite time (see Table I), after which the contents of the bulb were cooled quickly and the original water-bath applied to bring the temperature to 25°. Temperature, volume and pressure readings were made fifteen minutes after heating was discontinued. Blanks, averaging 0.3 cc., were made, and this volume was deducted from the total volume measured. The same procedure was used in the tetraethyllead studies. All experiments were checked. The results given in Table I are averages, and the numerical values represent the fractional amount of the active hydrogen that reacted in the time given.

**Tetraethyllead and Thiophenol.**—In order to determine the number of ethyl groups that can be cleaved, 2 g. (0.018 mole) of thiophenol in 5 cc. of *n*-butyl ether was added to 0.629 g. (0.00194 mole) of tetraethyllead in 5 cc. of *n*-butyl ether, and the solution kept at 100° for six hours with occasional shaking. Gas was evolved quite rapidly at first, and of the 132.8 cc. finally collected only about 10 cc. was evolved in the last three hours. In a check experiment, 126.4 cc. of gas was collected, and these two volumes correspond to 3.07 and 3.20 ethyl groups, respectively.

The sulfur containing organometallic products obtained from the several compounds will be reported later.

The gas obtained from tetraethyllead and *p*-thiocresol was analyzed and shown to be ethane.

## Discussion of Results

Organometallic compounds of lesser reactivity than the Grignard reagent almost always give low values in active hydrogen analyses. This applies not only to diethylzinc[4] but to organometallic compounds containing cadmium, mercury, boron, aluminum and tin. However, even though the results obtained with the lesser reactive RM types are only partially quantitative, they are of definite diagnostic value. Furthermore, when there is selective substitution of hydrogen by

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(1) Tschugaeff, *Ber.*, **35**, 3912 (1902); Zerewitinoff, *ibid.*, **40**, 2023 (1907); **41**, 2233 (1908); *Z. anal. Chem.*, **50**, 680 (1911). See also Kobler, Stone and Fuson, THIS JOURNAL, **49**, 3181 (1927).

(2) Schaefer and Hein, *Z. anorg. Chem.*, **100**, 297 (1917).

(3) All traces of air are not removed by this procedure. As a consequence, the reagent becomes cloudy, but this appears to be without effect on the result. The ready clouding of triethylbismuth by oxygen suggests the use of triethylbismuth as a delicate test for traces of oxygen. Fortunately, for the purposes of such a test, triethylbismuth is unaffected by moisture.

(4) Haurowitz, *Mikrochemie*, **6**, 88 (1929).

TABLE I

TRIETHYLBISMUTH AND TETRAETHYLLEAD WITH SOME ACTIVE HYDROGEN COMPOUNDS

Average active hydrogen based on heating at 100° for various times.

| | $(C_2H_5)_3Bi$ | | $(C_2H_5)_4Pb$ | | |
|---|---|---|---|---|---|
| | 30 min. | 120 min. | 10 min. | 30 min. | 60 min. |
| —SH Compounds | | | | | |
| *n*-Butyl mercaptan | 0.54 | | 0.15 | 0.23 | |
| *n*-Heptyl mercaptan | .56 | 0.63 | .45 | .61 | |
| Benzyl mercaptan | .50 | | .57 | .67 | |
| Thiophenol | .74 | | | .75 | 0.75 |
| *p*-Thiocresol | .67 | | .55 | .72 | |
| Thio-β-naphthol | .50 | | .37 | .49 | |
| 1-Mercaptobenzothiazole[a] | .44 | | .06 | .16 | .27 |
| Thioacetic acid | .59 | | .49 | .57 | |
| —OH compounds | | | | | |
| Water[a] | 0.0 | | | | 0.0 |
| *n*-Butyl alcohol | .0 | | | | .01 |
| Formic acid[b] | | | | 0.12 | .27 |
| Acetic acid | .02 | 0.11 | | .02 | .04[e] |
| Chloroacetic acid | .06 | .22 | | .52 | .68 |
| Dichloroacetic acid | .21 | .61 | | .70 | .80 |
| Trichloroacetic acid | .42 | .74 | | .72 | .76 |
| Butyric acid | .01 | | | | .01 |
| Maleic acid[a] | .09[c] | | | .68 | .78 |
| Benzoic acid | .02[d] | | | .06 | .17 |
| Phenol | .01 | | | | .01 |
| 2,4-Dibromophenol | | | | | .02 |
| 2,4-Dinitrophenol | | | | | .09 |
| 2,4,6-Trinitrophenol | .06 | | | .48 | .55[a] |
| *p*-Hydroxyazobenzene | .0 | | | | .0 |
| Vanillin | | | | | .0 |
| 1,2,3-Trihydroxybenzene[a] | | | | | .02 |
| Acetoxime | | | | | .0 |
| Acetophenone oxime | .0 | | | | |
| —NH compounds | | | | | |
| Aniline | 0.0 | | | 0.0 | 0.0 |
| 2-Amino-4-phenylthiazole[a] | .01 | | | .01 | .01 |
| Benzamide[a] | .00 | | | .01 | .02 |
| Thiourea[a] | .0 | | | | .02 |
| *s*-Diphenylthiourea[a] | .05 | .09 | | .05 | .06 |
| Miscellany | | | | | |
| Phenylacetylene | 0.0 | | | 0.0 | 0.0 |
| Acetylacetone | .01 | | | | |
| Azobenzene | .0 | | | .01 | .01 |
| Nitrobenzene | .0 | | | | |
| 1,2-Dinitrobenzene | | | | .0 | .0 |
| 1,3-Dinitrobenzene | .0 | | | | |
| 1,3,5-Trinitrobenzene | .04 | | | .0 | .0[f] |
| Ethyl disulfide | | | | | .0 |

[a] Dioxane was used as a solvent for these compounds. In all other cases, di-*n*-butyl ether was used. [b] An 87–90% solution of formic acid was used. The gas evolved with tetraethyllead was shown to be ethane. Also the gas from trichloroacetic acid and tetraethyllead was practically pure ethane. [c] Heating for sixty minutes gave 0.13 active hydrogen. [d] Heating for sixty minutes gave 0.03 active hydrogen. [e] Heating for one hundred and twenty minutes gave 0.14 active hydrogen. [f] Heating for ninety minutes gave no active hydrogen.

metal it appears reasonable to expect preferential replacement reactions with the intermediate metallic compounds. For example, acylation and alkylation of a compound containing both —SH and —NH groups may be largely confined to the —SH group after the compound is first treated with triethylbismuth or tetraethyllead.

There is a broad correlation between acidities of weakly acid organic compounds and relative reactivities of organometallic compounds. For example, the weakly acidic hydrogen in benzene is replaced by a metal when the highly reactive alkyl-alkali compounds are used, but not when the moderately reactive Grignard reagents are used. The reaction of —SH but not generally of —OH with triethylbismuth or tetraethyllead appears as a particularly striking exception, for some of the —OH compounds (Table I) which do not react are definitely more acidic than the —SH compounds which undergo substitution of hydrogen by metal. Acidities do play some part even in the substitutions considered, and one illustration from the results reported is the increase in rate of reaction observed with acetic and the chloroacetic acids.[5] For example, with triethylbismuth the number of active hydrogens observed after heating at 100° for two hours is: acetic acid, 0.11; chloroacetic acid, 0.22; dichloroacetic acid, 0.61; and trichloroacetic acid, 0.74. Incidental to the reaction of carboxylic acids with tetraethyllead it should be stated that silica gel is an effective catalyst for replacing one ethyl group to give $(C_2H_5)_3PbOCOR$ compounds,[6] and that three ethyl groups may be removed as ethane by the action of acetic acid at high temperature (250–260°).[7] In the Experimental Part we have reported the replacement of more than three ethyl groups from tetraethyllead by heating with thiophenol at 100°. Historically it is interesting to note that long years ago Dünhaupt[8] obtained bismuth sulfide from triethylbismuth and hydrogen sulfide.

Azo and nitro goups interfere with active hydrogen determinations by the Grignard re-

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(5) If acidities play a significant role one might predict that tellurophenol will cleave organotin and possibly organogermanium compounds.

(6) Browne and Reid, THIS JOURNAL, **49**, 830 (1927).

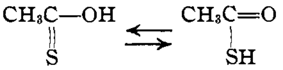
(7) Jones and Werner, *ibid.*, **40**, 1257 (1918).

(8) Dünhaupt, *Ann.*, **92**, 371 (1854).

agent.[9] Triethylbismuth and tetraethyllead, however, do not evolve gas with such groups. The small volume of gas evolved from triethylbismuth and 1,3,5-trinitrobenzene is just about the experimental limit of accuracy.

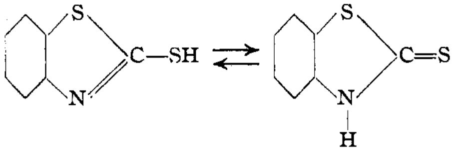
On general grounds triethylbismuth may be preferred to tetraethyllead because it not only gives high values for —SH groups but also is less interfered with by —OH groups. The inflammability and lesser accessibility of triethylbismuth is to be contrasted with the toxicity and accessibility of tetraethyllead.

Some of the results are interesting from the point of view of tautomerism. The replacement of hydrogen by metal noted with thioacetic acid establishes the presence of an —SH group, but throws no light on the equilibrium



$$\underset{\text{S}}{\overset{}{\text{CH}_3\underset{\|}{\text{C}}\text{—OH}}} \rightleftharpoons \text{CH}_3\underset{|}{\text{C}}{=}\text{O} \atop \quad\quad\quad\quad\quad \text{SH}$$

Thioenolization is probably affected by the RM compounds used to establish the presence of active hydrogen groups. What may be a pertinent illustration are the results with 1-mercaptobenzothiazole.



Both triethylbismuth and tetraethyllead show the presence of an —SH group. However, tri-*n*-propylboron which reacts with —SH groups but not with the —NH group, gives no reaction with 1-mercaptobenzothiazole. Slight thioenolization is shown by *s*-diphenylthiourea but not by thiourea.

Some solvents may have special enolizing effects.[10]

## Summary

Triethylbismuth and tetraethyllead can be used for the detection of the —SH group. These organometallic compounds do not react with the hydrogens in —NH and —C≡CH groups; they do not react with simple —OH groups, although some strong carboxylic acids undergo generally limited reactions; and there is no interference by azo or nitro groups.

The RM compounds may be useful to establish the existence of thioenolization in compounds like thioacetic acid.

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[9] Gilman and Fothergill, THIS JOURNAL, **50**, 867 (1928); Gilman, Fothergill and Towne, *ibid.*, **52**, 405 (1930).

[10] Clutterbuck, Raistrick and Reuter, *Biochem. J.*, **29**, 300 (1926).

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# The Passivity of Iron in Chromic Acid Solutions[1]

BY W. H. CONE AND H. V. TARTAR

In a previous paper[2] the authors described some experiments which showed that iron could be made active in chromic acid solutions if a sufficiently reduced pressure were maintained at the time of placing the iron in the solution. Subsequent experiments have shown that this effect of reduced pressure was associated with the presence of some sulfate ion in the solution. Experiments on iron in chromic acid solutions with and without phosphate or sulfate ion under varying conditions of temperature and pressure are described in this paper. Pertinent data on the adsorption of oxygen by iron are also given.

**Materials and Apparatus.**—Pure chromium trioxide ($CrO_3$) was prepared from potassium dichromate and sulfuric acid. The crystals were washed with concentrated nitric acid until free of sulfate and then dried at 80° to remove the nitric acid.

The data reported in this paper were obtained using No. 30 iron wire, for standardizing, Fe 99.84%. Some experiments were made with iron of varying purity without any appreciable effect on the results.

Preliminary tests showed that a reduction of pressure after the iron was placed in the chromic acid solution did not produce activity. Consequently in finding the pressure at which the iron became active, it was necessary to use a fresh piece of the metal each time the pressure was changed. To facilitate changing the sample of iron without changing the pressure, a special apparatus was constructed, Fig. 1. When the pressure in the system had been adjusted to the desired value a sample of iron wire was fed from the spool into the electrode vessel by means of the motor-driven feed rolls. The potential of the wire was determined by connecting to a potentiometer through a saturated calomel half cell. A nearly saturated potassium

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[1] Original manuscript received July 27, 1936.

[2] Cone and Tartar, THIS JOURNAL, **56**, 48 (1934).