noff analyses to show that the carbinols are intermediate in this reaction.

3. These ethers decompose readily to form benzalcrotonolactone, the structure of which has been proved.

4. No *sym*-ethers are isolable (though there is evidence for their transitory existence) from the reaction between ethyl 5-halogenofuroates and phenylmagnesium bromide, but diphenylmethylenecrotonolactone is produced.

5. The principal proof of structure for diphenylmethylenecrotonolactone, by alkaline cleavage, provides a means of structure assignment to ethyl 4,5-dibromo- and 4,5-dichloro-2-furoate; because *asym*-diphenylacetone is formed from the α-halogeno-γ-diphenylmethylenecrotonolactones which in turn are formed from the esters by Grignardization.

6. Since neither the α,β-dibromo- and α,β-dichloro-(diphenylmethylene)-crotonolactones from the ethyl trihalogenofuroates nor β-chloro-γ-(diphenylmethylene)-crotonolactone give *asym*-diphenylacetone on alkaline cleavage, the structure of Hill's ethyl χ-dichlorofuroate must be ethyl 3,5-dichlorofuroate.

AMES, IOWA RECEIVED JANUARY 5, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Preferential Cleavage of Radicals in Organobismuth and Organomercury Compounds[1]

BY HENRY GILMAN* AND HARRY L. YALE[2]

This investigation was prompted by three reported studies. First, a series of unsymmetrical organobismuth compounds, $R_2R'Bi$, has been prepared,[3] and these compounds have a much greater stability than might have been predicted. Second, it has been shown that some typical metal–metal interconversion reactions are reversible:[4] $R'M' + R^2M^2 \rightarrow R'M^2 + R^2M'$. Third, the series formulated by placing the organic radicals in the order of decreasing ease of cleavage from organolead, organotin and organomercury compounds by means of *n*-butyllithium does not agree with similar series based upon cleavage of RM compounds with other cleaving agents.[5]

Unsymmetrical Organobismuth Compounds.—When an $R_2R'Bi$ compound was treated with *n*-butyllithium there was a preferential replacement of R or R′. In most cases, both R and R′ were cleaved. For example, when diphenyl-α-naphthylbismuth and one equivalent of *n*-butyllithium were allowed to react for ten minutes in diethyl ether, there was obtained, subsequent to carbonation, 21.6% of α-naphthoic acid and 1.7% of benzoic acid.

$$(C_6H_5)_2BiC_{10}H_7\text{-}\alpha + n\text{-}C_4H_9Li \longrightarrow C_6H_5Li + \alpha\text{-}C_{10}H_7Li \xrightarrow[(2)\ H_2O]{(1)\ CO_2} C_6H_5CO_2H + \alpha\text{-}C_{10}H_7CO_2H$$

In this significant experiment, the ratio $2C_6H_5:1\alpha\text{-}C_{10}H_7$ was not a determining consideration, for if this were the case a greater percentage of phenyl groups should have been cleaved. The predominant cleavage of the α-naphthyl radical might have been predicted on the basis of the general series of radicals obtained by the cleavage of unsymmetrical organometallic compounds by hydrogen chloride.[6] Also, Challenger and Allpress[7] have shown that the α-naphthyl radical is cleaved preferentially in the following reaction.

$$(C_6H_5)_2BiC_{10}H_7\text{-}\alpha + IBr \longrightarrow (C_6H_5)_2BiBr + \alpha\text{-}C_{10}H_7I$$

However, our observed preferential cleavage of the α-naphthyl radical in the *n*-butyllithium interconversion reaction is apparently exceptional with respect to the HX cleavage of RR′M types.

Additional studies under the same conditions gave the following results in check experiments: diphenyl-*p*-chlorophenylbismuth, 30.7 and 28.1% *p*-chlorobenzoic acid, 3.4 and 10.0% benzoic acid; di-*p*-tolyl-*p*-chlorophenylbismuth, 30.7 and 25.6% *p*-chlorobenzoic acid, 7.3 and 8.0% *p*-toluic acid; di-*p*-chlorophenyl-α-naphthylbismuth, 23.5 and 20.2% *p*-chlorobenzoic acid and 22.9 and 22.4% α-naphthoic acid; and di-*p*-chlorophenyl-*o*-tolylbismuth, 42.2 and 34.5% *p*-chlorobenzoic acid and no *o*-toluic acid. While these experiments may be considered as exploratory and the results approximations, the differences in yields are sufficiently large to indicate the following order of decreasing labilities: (*p*-chlorophenyl, α-naphthyl), phenyl, *p*-tolyl, *o*-tolyl. The order of decreasing labilities of these five radicals in the hydrogen chloride cleavage of unsymmetrical organomercury com-

---

* Harvard University Ph.D. 1918.

[1] This paper was submitted to the Editor in May, 1941, and was accepted for publication which, however, was delayed during the war at the suggestion of the U. S. Government. Paper XL in the series: "Relative reactivities of organometallic compounds." The preceding paper is Gilman and Kirby, THIS JOURNAL, **63**, 2046 (1941).

[2] Present address: Squibb Institute for Medical Research, New Brunswick, New Jersey.

[3] Gilman and Yablunky, THIS JOURNAL, **63**, 207 (1941).

[4] Gilman and Jones, *ibid.*, **63**, 1439 (1941).

[5] Gilman, Moore and Jones, *ibid.*, **63**, 2482 (1941).

[6] Gilman, "Organic Chemistry," John Wiley and Sons, New York, 1943, pp. 519–520, 1071–1072.

[7] Challenger and Allpress, *J. Chem. Soc.*, **107**, 16 (1915). It has been noted, however, that the α-naphthyl group is held *more* firmly than is phenyl on the basis of the competitive cleavage of symmetrical R_3Bi compounds by halogens [Challenger and Allpress, *J. Chem. Soc.*, **119**, 913 (1921); Stilp, Inaugural Dissertation, University of Rostock, 1910] and thiophenol (unpublished studies).

pounds is: α-naphthyl, *o*-tolyl, *p*-tolyl, phenyl, *p*-chlorophenyl.[8a]

Symmetrical Organobismuth Compounds.—An approximate measure of the relative labilities of radicals was obtained by measuring the rates of cleavage of a series of symmetrical organobismuth compounds by *n*-butyllithium under equivalent conditions. Thus, in check experiments, tri-*p*-chlorophenylbismuth gave 44.7 and 48.8% *p*-chlorobenzoic acid; tri-*p*-bromophenylbismuth, 41.8 and 40.8% *p*-bromobenzoic acid; tri-*p*-fluorophenylbismuth, 40.0 and 42.8% *p*-fluorobenzoic acid; triphenylbismuth, 3.3 and 5.8% benzoic acid; tri-*p*-tolylbismuth, 2.2 and trace *p*-toluic acid; tri-*p*-ethoxyphenylbismuth, 1.9 and 1.5% *p*-ethoxybenzoic acid; and tri-α-naphthylbismuth, 1.3% α-naphthoic acid. Trimesitylbismuth, tri-*o*-tolylbismuth and tri-*o*-chlorophenylbismuth gave no acidic products. The, order of decreasing ease of cleavage, therefore, was found to be: (*p*-chlorophenyl, *p*-bromophenyl, *p*-fluorophenyl), phenyl, *p*-tolyl, (*p*-ethoxyphenyl, α-naphthyl), (mesityl, *o*-tolyl, *o*-chlorophenyl). This series which is again at variance with the series obtained by the hydrogen chloride cleavage of RR'M compounds, is in essential agreement with the smaller series obtained by the *n*-butyllithium reaction with unsymmetrical organobismuth compounds. The notable exception is the α-naphthyl radical, and a possible explanation for this discrepancy is suggested later.

In a series of comparable experiments, diphenylmercury gave 29.4 and 22.8% benzoic acid; di-*p*-chlorophenylmercury, 51.1% *p*-chlorobenzoic acid (40 ml. ether used as solvent) and 67.8% *p*-chlorobenzoic acid (60 ml. ether used as solvent); phenyl-*p*-chlorophenylmercury, 57.5 and 50.9% *p*-chlorobenzoic acid, 4.0 and 4.9% benzoic acid; di-*p*-tolylmercury, 28.2% *p*-toluic acid (40 ml. ether) and 41.5% *p*-toluic acid (60 ml. ether); and trimesitylmercury, 72.5% β-isodurylic acid. On the basis of this work, the order of decreasing ease of cleavage with symmetrical and unsymmetrical mercurials was: mesityl, *p*-chlorophenyl, *p*-tolyl, phenyl. Here, too, the *p*-chlorophenyl radical is definitely out of line, since in the hydrogen chloride cleavage it follows the phenyl radical.

Factors Affecting Metal–Metal Interconversion. (a) **Solubility.**—From tri-α-naphthylbismuth and *n*-butyllithium, under the general conditions used with the R_3Bi compounds, the yield of α-naphthoic acid was 1.2%. Tri-α-naphthylbismuth is insoluble in diethyl ether, and this may account for the slow rate of reaction. However, with the ether soluble unsymmetrical bismuth compounds containing the α-naphthyl radical, this group showed itself to have a lability equal to that of the *p*-chlorophenyl radical. With the exception of this reaction with tri-α-naphthylbismuth, all the other bismuth compounds were completely dissolved in the ether prior to the addition of the *n*-butyllithium. As noted above, in the reaction between *n*-butyllithium and the sparingly soluble di-*p*-tolylmercury or di-*p*-chlorophenylmercury, if the volume of ether was increased there was an increase in M-M interconversion. (b) **Solvent.** When tri-α-naphthylbismuth was dissolved in a mixture of benzene and diethyl ether and reacted with *n*-butyllithium, the yield of α-naphthoic acid was decreased from 1.3 to 0.6%. In benzene–petroleum ether as a mixed solvent, tri-*p*-chlorophenylbismuth and di-*p*-chlorophenyl-*o*-tolylbismuth did not undergo metal–metal interconversion. These reactions demonstrate the inhibitory effect of benzene and of petroleum ether in this reaction, and reveal the important role played by a solvent like diethyl ether. Somewhat related solvent effects have been reported in halogen metal interconversions.[9] (c) **Steric Effects.** Tri-*o*-tolylbismuth, tri-*o*-chlorophenylbismuth and trimesitylbismuth, even though completely dissolved in diethyl ether, gave no cleavage with *n*-butyllithium. Steric factors are probably involved with these compounds as well as related organobismuth compounds which interfered with the color test for some organobismuth and other RM compounds.[10] However, dimesitylmercury and *n*-butyllithium gave 72.5% cleavage under conditions where trimesitylbismuth was apparently not affected.

General Considerations.—The numerous experiments described leave no doubt that the series of radicals obtained by the *n*-butyllithium cleavage is quite different from the series obtained by hydrogen chloride cleavage. Actually, the two series are in many respects inverted counterparts. However, there are some radicals, like *p*-chlorophenyl and *p*-bromophenyl, which are wholly out of line. In this connection, it was shown[8b] that in the hydrogen chloride scission of phenyl-*p*-fluorophenylmercury, the *p*-fluorophenyl radical was cleaved somewhat more readily than the phenyl radical. Qualitatively, our experiments with *n*-butyllithium and R_3Bi compounds support this finding; but quantitatively, we found that the *p*-fluorophenyl radical is distinctly more labile than the phenyl radical.

There is no reason why the series obtained by hydrogen chloride cleavage should agree with the series obtained by the *n*-butyllithium reactions. A possible explanation for the difference may lie in the general reversibility of M-M interconversions, and the apparent irreversibility[11] of the hydrogen chloride cleavage reactions. The pres-

---

[8] (a) A recent comprehensive reference on the cleavage of unsymmetrical organomercury compounds is Kharasch, Legault and Sprowls, *J. Org. Chem.*, **3**, 409 (1938). Earlier literature citations on this reaction may be traced back from this article; (b) Kharasch, Pines and Levine, *ibid.*, **3**, 347 (1938); (c) Kharasch and Flenner, THIS JOURNAL, **54**, 674 (1932).

[9] Gilman and Moore, THIS JOURNAL, **62**, 1843 (1940).

[10] Gilman and Yablunky, *ibid.*, **63**, 839 (1941).

[11] Adkins, *J. Chem. Education*, **9**, 1865 (1932); see, also, Kharasch, Reinmuth and Mayo, *ibid.*, **11**, 82 (1934); and Calingaert, Soroos and Shapiro, THIS JOURNAL, **63**, 947 (1941).

ent findings add support to the idea that different series may be expected with different cleaving agents and also with different central metallic elements in the RM compounds.

Experimental

Two typical metal–metal interchange reactions (one for $R_2R'Bi$ and the other for $RR'Hg$) are described in detail.

Reaction between Di-*p*-chlorophenyl-*o*-tolylbismuth and *n*-Butyllithium.—Two and sixty-two hundredths grams (0.005 mole) di-*p*-chlorophenyl-*o*-tolylbismuth in 45 ml. of ether were treated with 0.005 mole of *n*-butyllithium. The total volume was 65 ml. After stirring at room temperature for ten minutes the reaction mixture was poured on crushed Dry Ice, and allowed to stand for about a day to permit the butylbismuth compound formed to oxidize.[12] The mixture was then extracted thoroughly with 25 ml. of 10% potassium hydroxide solution. The alkaline extract was boiled with a little Norit and filtered. Acidification of the clear filtrate gave 0.33 g. (42.2%) of acid, m. p., 233–234°. A mixed m. p. with *p*-chlorobenzoic acid was 234–235°. The aqueous filtrate from the chlorobenzoic acid was extracted with ether, the ether extracts were dried, and distilled. The residue which would not distill from the water-bath, was subjected to vacuum distillation at 15 mm. and heated by an external bath at 100–110°. Some valeric acid distilled, but no residue of *o*-toluic acid remained in the flask.

.From the original ether layer there was recovered 0.85 g. (32.4%) of unreacted di-*p*-chlorophenyl-*o*-tolylbismuth, m. p. 103.5°, and the mixed m. p. with an authentic sample of the bismuth compound was 103.5°.

If the recovered unreacted bismuth compound is considered, the yield of *p*-chlorobenzoic acid was 62.4%.

Preparation of Di-*p*-chlorophenylmercury.—The complex, p-$ClC_6H_4N_2Cl \cdot HgCl_2$, was prepared according to the directions of Nesmeyanov,[13] and decomposed by adding slowly to a suspension of copper bronze in acetone at 0°. After allowing the mixture to stand for a day, the acetone was evaporated and the residual solid thoroughly extracted with chloroform in a Soxhlet extractor. The chloroform was then distilled to give a 69.2% yield of *p*-chlorophenylmercuric chloride. Nesmeyanov reported a 46% yield.

Di-*p*-chlorophenylmercury was obtained in 80.4% yield by treatment of the *p*-chlorophenylmercuric chloride with hydrazine.[14]

Preparation of Phenyl-*p*-chlorophenylmercury.—To 3.47 g. (0.01 mole) *p*-chlorophenylmercuric chloride in 100 ml. of boiling 95% ethanol was added a mixture of 1.2 g. (0.01 mole) phenylboric acid in 20 ml. of ethanol and 5 ml. of 20% sodium hydroxide solution, also at the boiling point. Reaction occurred instantly and the mixture, after cooling to room temperature, was diluted with 250 ml. of water and the mixture extracted with ether. The ether extract was washed with 10 ml. of 25% sodium hydroxide solution, then twice with water, and dried over anhydrous calcium chloride. Evaporation of the ether gave 3.12 g. (80.3% yield) of phenyl-*p*-chlorophenylmercury, m. p. 190–215°, after crystallization from chloroform–ethanol.

The procedure described above is an adaptation of a general method by Friedlina and co-workers.[15] Kharasch and Flenner[8c] prepared phenyl-*p*-chlorophenylmercury from C_6H_5HgX and p-ClC_6H_4MgBr and from the *p*-chlorophenylmercuric halide and C_6H_5MgBr, and reported that the product in either case melted at 190–210°. They did not recrystallize the compound. Kharasch, Pines and Levine[8b] prepared the same compound later by essentially the same methods and reported a melting point of 165–205°. The crude product prepared by the method described above melted at 120–165°, and progressive crystallizations from benzene–petroleum ether gave melting points of 190–210°, and 220–227°. One crystallization of the crude product from chloroform–ethanol gave a colorless product melting at 190–215°. Metal–metal interconversions were carried out with three different products: (1) the crude product, (2) the compound after two crystallizations from benzene–petroleum ether (m. p., 220–227°), and (3) the chloroform–ethanol crystallization product. The mixture of acids obtained after reaction in the usual way with *n*-butyllithium followed by carbonation after ten minutes were: from (1), 93.8% *p*-chlorobenzoic acid, 6.2% benzoic acid; from (2), 91% *p*-chlorobenzoic acid, 9.0% benzoic acid; and from (3), 95.5% *p*-chlorobenzoic acid, 4.5% benzoic acid. It would appear that no marked changes occurred in the recrystallization of the unsymmetrical mercurial even though the melting points indicate a slowly increasing concentration of the higher melting di-*p*-chlorophenylmercury (m. p., 243–244°).

Reaction between Di-*p*-chlorophenylmercury and *n*-Butyllithium.—Two and twelve-hundredths grams (0.005 mole) of di-*p*-chlorophenylmercury in 40 ml. of ether were treated with 0.005 mole of *n*-butyllithium with vigorous stirring. The reaction mixture first turned red and then faded to a pale pink after several minutes. The mixture was carbonated after ten minutes by pouring on crushed Dry Ice. The residue which remained in the reaction flask weighed 0.77 g. (36.3%) and was unreacted di-*p*-chlorophenylmercury which had not dissolved. The carbonated mixture was extracted with 25 ml. of 10% potassium hydroxide solution, made slightly acid with hydrochloric acid, and then alkaline by the addition of solid sodium bicarbonate. The alkaline solution was filtered and the clear filtrate was acidified. The yield of acid was 0.4 g. (51.7%) m. p., 233–234°; and a mixed m. p., with authentic *p*-chlorobenzoic acid, was 233–234°.

From the ether an additional 0.1 g. of unreacted mercurial was recovered. The total recovery was 0.87 g. (41.4%).

If the recovered unreacted mercurial is considered, the yield of acid was 86.8%.

Summary

A study has been made of some factors affecting the cleavage of both symmetrical and unsymmetrical organobismuth and organomercury compounds by interconversion reactions with *n*-butyllithium.

The series of radicals obtained in this manner does not agree with the general series of radicals obtained by the hydrogen chloride cleavage of unsymmetrical RM compounds.

AMES, IOWA RECEIVED MAY 25, 1949

---

[12] Gilman, Yablunky and Svigoon, THIS JOURNAL, **61**, 1170 (1939).

[13] Nesmeyanov, *Ber.*, **62**, 1010 (1929).

[14] Gilman and Barnett, *Rec. trav. chim.*, **55**, 563 (1936). Hein and Wagler, *Ber.*, **58**, 1499 (1925), obtained an 81% conversion by the use of copper and pyridine.

[15] Friedlina, Nesmeyanov and Kocheshkov, *Ber.*, **68**, 565 (1935).