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## Editor's Note

Professor Arthur Becket Lamb has had a long and distinguished career, and by far the major portion has been in intimate association with the Department of Chemistry of Harvard University. He received the degrees of Master of Arts in 1903 and Doctor of Philosophy in 1904 at Harvard and was instructor in electrochemistry there during the academic year 1905–06. There followed six years at New York University, but since 1912, with the exception of the years during World War I, Professor Lamb has been continuously associated with Harvard. He has been Professor of Chemistry, Director of the Chemistry Laboratories, and Dean of the Graduate School of Arts and Sciences. Harvard chemistry and Professor Lamb are inextricably associated in the minds of chemists.

It has seemed appropriate, therefore, that each article in this issue which is dedicated to Professor Lamb should have as author either one Harvard chemist, past, present, or future or some particular friend of Professor Lamb. The enthusiasm with which this suggestion was greeted gave ample proof of the great affection in which Professor Lamb is held not only by Harvard chemists but by all chemists.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

# Decomposition of 5-Halogeno-2-furylmethyl Ethers to Benzalcrotonolactones

BY HENRY GILMAN,* R. A. FRANZ, A. P. HEWLETT AND GEORGE F WRIGHT†

In spite of early failures in reactions between furfural and Grignard reagents,[1] which probably were caused by the presence of water, later workers were able successfully to prepare alkyl or aryl furylcarbinols by this method.[2] None of these chemists had difficulty in the preparation of dialkyl or diaryl furylcarbinols from ethyl furoate and the appropriate Grignard reagent. All of the carbinols were reasonably stable compounds.

No such successes attended the reactions between 5-bromo-(I: R, $R^1$, $R^2$ = H; X = Br) or 5-chlorofurfural (I: R, $R^1$, $R^2$ = H; X = Cl) and phenylmagnesium bromide. While unstable compounds could be isolated by close attention to neutrality during the hydrolyses (the use of aqueous ammonium chloride gave the best results) they were not alcohols. Elemental and Zerewitinoff analyses together with molecular weight determinations on the chloro compound indicated that they were bis-α-(5-halogeno-2-furyl)-benzyl ethers, (III: $R^1$, $R^2$, $R^3$ = H; X = Br or Cl) which must have been formed by loss of water from the ephemeral alcohol.

This process was demonstrated by a preparation from 5-chlorofurfural and phenylmagnesium bromide which was carried out in di-*n*-butyl ether. An aliquot of the ether solution, after careful hydrolysis, gave about the same amount of gas in the Zerewitinoff determination as did a comparable preparation of 2-furylphenylcarbinol. The (chlorofuryl)-phenylcarbinol, (II: $R^1$, $R^2$, $R^3$ = H; X = Cl), could not be isolated in a state of purity, however, and a trace of acetic acid would cause it to decompose with observable loss of water to form the *sym*-ether.

This behavior is undoubtedly due to the strong

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* Harvard University Ph.D. 1918.

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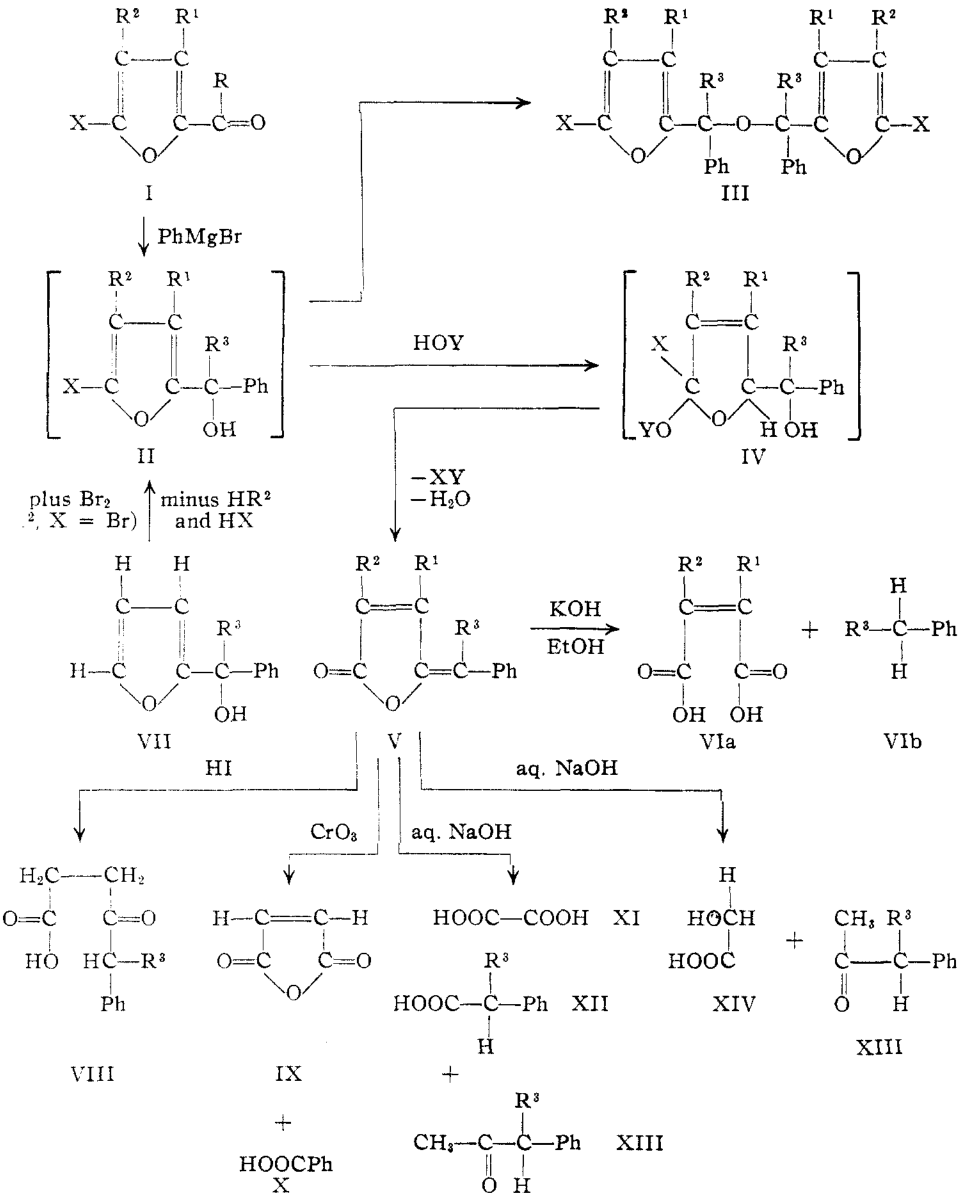
[1] W. J. Hale, W. D. McNally and C. J. Pater, *Am. Chem. J.*, **35**, 68 (1906).

[2] F. N. Peters and R. Fischer, THIS JOURNAL, **52**, 2079 (1930).



electron attracting tendency of the 5-halogeno-2-furyl group which makes these mixed diarylcarbinols resemble less electronegatively substituted triarylcarbinols with respect to lability at the oxygen linkage. Indeed, the unsubstituted furyl group seems to have a strong influence in this respect, since it was found that diphenylfuryl carbinol was converted to the very insoluble bis-diphenylfurylmethyl ether by reflux with 10% aqueous acetic acid. Such lability has not been observed with triphenylcarbinol.

Although the α-(5-halogeno-2-furyl)-benzyl ethers were thus more stable than the alcohols, they tended to decompose spontaneously (bromo-less stable than chloro-) unless they were maintained under conditions where autocatalytic reaction due to mineral acid was prevented. The decomposition could be promoted by reflux in ethanol, or more conveniently and in good yield by solution in *concd.* sulfuric acid or acetyl chloride. The product of this decomposition has been shown to be γ-benzalcrotonolactone, (V: $R^1$, $R^2$, $R^3$ = H).

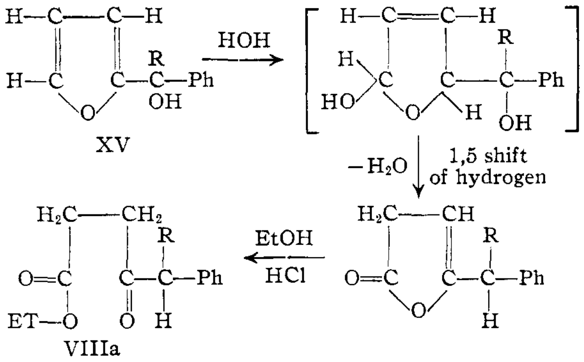
The proof of structure for this lactone involves first, reduction by hydriodic acid to δ-phenyllevulinic acid, (VIII: $R^3$ = H). Secondly, oxidation with chromic anhydride in acetic acid yields both maleic anhydride, (IX), and benzoic acid, (X).

It is easier to write a possible mechanism by which this benzalcrotonolactone is formed from the non-isolable halogenofurylmethylphenylcarbinols than from the corresponding *sym*-ethers. Indeed it is reasonable to assume that the ethers, which form with great ease, are as readily split to the parent alcohols. There is no assurance that this is true but it does not alter the following argument.

It may be presumed that the bromo- or chlorofuryl-phenylcarbinol (II: $R^1$, $R^2$, $R^3$ = H; X = Cl or Br) has the tendency in common with other furans to add the elements of water, sulfuric acid or acetic acid (designated as HOY where OY is hydroxyl, bisulfate or acetate) across the 1,4 conjugated dienic ring to give IV.[3] Loss of XY (hydrogen halide, halogenosulfonic acid or acetyl chloride) from this intermediate, as well as water, would then yield benzalcrotonolactone.

It might be expected that this series of reactions could be demonstrated also with the tertiary alcohols derived from ethyl 5-halogenofuroate (I: R = OEt; $R^1$, $R^2$ = H; X = Cl or Br) and phenylmagnesium bromide, but in this instance the carbinols were too unstable for isolation under any conditions yet applied. The product from either ethyl 5-chlorofuroate (48% yield) or ethyl 5-bromofuroate (56% yield) was found to be γ-(diphenylmethylene)-crotonolactone, (V: $R^1$, $R^2$ = H; $R^3$ = phenyl). The same yield (56%) was obtained when 5-bromofuryl phenyl ketone was treated with phenylmagnesium bromide.

This lactone, previously unknown, could be reduced to a compound which was proven to be δ,δ-diphenyllevulinic acid, (VIII: $R^3$ = phenyl). The acid was identified with the hydrolysis product of the ester formed by the method of Tchichibabin[4] from diphenylfurylcarbinol (XV: R = phenyl) and ethanolic hydrogen chloride. The reliability of this synthesis of δ-substituted levulinic acids was demonstrated by a similar synthesis of δ-phenyllevulinic acid, from furylphenylcarbinol (XV: R = H) *via* the ethyl ester (VIIIa: R = H).



A further demonstration for the structure of δ,δ-diphenyllevulinic acid was effected through the alcoholic alkaline cleavage by which Orekhoff[5] converted 1,1,3-triphenylpropanone-2 to diphenylmethane and phenylacetic acid. In like manner ethanolic potassium hydroxide converted δ,δ-diphenyllevulinic acid to diphenylmethane and succinic acid.

This alkaline cleavage could likewise be applied to γ-(diphenylmethylene)-crotonolactone. In this case the products were diphenylmethane, (VIb: $R^3$ = phenyl), and fumaric acid, (VIa: $R^1$, $R^2$ = H) when ethanolic potassium hydroxide was used. On the other hand scission with aqueous sodium hydroxide produced *asym*-diphenylacetone (XIII: $R^3$ = phenyl); the other product, glyoxylic acid, (XIV), was evidently destroyed.

In a preliminary communication,[6] the conversion of a dihalogenated ethyl furoate to a monohalogenated (diphenylmethylene)-crotonolactone was cited as evidence for revision of the structure of Hill's so-called 3,5-dibromofuroic acid to 4,5-dibromofuroic acid. This work is reported in detail in the present paper. The product obtained in 53% yield from ethyl 4,5-dibromo-2-furoate and phenylmagnesium bromide is designated as α-bromo-γ-(diphenylmethylene)-crotonolactone (V: $R^1$ = H; $R^2$ = Br; $R^3$ = phenyl) because cleavage with 5% aqueous sodium hydroxide gave oxalic acid, (XI), *asym*-diphenylacetone (XIII, $R^3$ = phenyl) and diphenylacetic acid (XII: $R^3$ = phenyl) as products.

There was at least no greater opportunity for isolation of dibromodifurylcarbinol as an intermediate in the formation of α-bromo-γ-(diphenylmethylene)-crotonolactone from ethyl 4,5-dibromo-2-furoate than was observed in the Grignard treatment of ethyl mono-5-bromo-2-furoate. Evidence for the existence of the carbinol was obtained, however, by the bromination of furyldiphenylcarbinol (VII: $R^3$ = phenyl) in carbon tetrachloride. In addition to a trace of α,β-dibromocrotonolactone, there was isolated a 13% yield of α-bromo-γ-(diphenylmethylene)-crotonolactone, (V: $R^1$ = H; $R^2$ = Br; $R^3$ = phenyl). Not only does this point strongly to the existence of the unstable carbinol following Grignard addition, but it also indicates that orientation of substituents in the *beta* position of a 5-bromofuryl nucleus is predominantly at the 4-atom regardless of the orienting influence of the group at the 2 position. Thus ethyl 2-furoate and 2-furyldiphenylcarbinol both seem to dibrominate in the 4 and 5 positions.

The acid called by Hill and Jackson[7] 3,5-dichlorofuroic acid must in reality be 4,5-dichlorofuroic acid. Its ethyl ester, when treated with phenylmagnesium bromide, yields a compound which must be α-chloro-γ-(diphenylmethylene)-crotonolactone, (V: $R^1$ = H; $R^2$ = Cl; $R^3$ = phenyl) since cleavage with 5% aqueous sodium hydroxide yields the same products (oxalic and diphenylacetic acids together with *asym*-diphenylacetone) as were obtained from the bromo-analog.

The chlorination of ethyl furoate by Hill and Jackson yielded three dichloroesters of which the

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[3] G. F Wright and H. Gilman, *Ind. Eng. Chem.*, **40**, 1517 (1948).

[4] A. E. Tchichibabin, *Chimie & industrie*, **II**, 563 (1931), Congres de Chimie.

[5] A. Orekhoff, *Bull. soc. chim.*, **25**, 108 (1919).

[6] H. Gilman, R. J. Vander Wal, R. A. Franz and E. V. Brown, THIS JOURNAL, **57**, 1146 (1935).

[7] H. B. Hill and L. L. Jackson, *Am. Chem. J.*, **12**, 47, 128 (1890).

rare one termed by them ethyl χ-dichlorofuroate must have been the 3,5-dichloro compound. Thus, treatment of the ester with phenylmagnesium bromide yielded a compound which was not identical with α-chloro-γ-(diphenylmethylene)-crotonolactone, although its empirical formula was the same. It differed also in behavior toward alkaline cleavage, because no *asym*-diphenylacetone was formed. On this basis it may be considered to be β-chloro-α-(diphenylmethylene)-crotonolactone, (V: R$^1$ = Cl; R$^2$ = H; R$^3$ = phenyl).

This criterion for the latter structure was substantiated by the fact that neither α,β-dichloro-γ-(diphenylmethylene)-crotonolactone, (V: R$^1$,R$^2$ = Cl; R$^3$ = phenyl) nor its bromo analog (prepared from ethyl 3,4,5-trichloro-2-furoate and 3,4,5-tribromo-2-furoate) gave *asym*-diphenylacetone (XIII: R$^3$ = phenyl) when cleaved with 5% aqueous alkali.

## Experimental

**α-(5-Chloro-2-furyl)-benzyl Ether** (III: R$^1$, R$^2$, R$^3$ = H; X = Cl).—To the ice-cold filtered Grignard reagent prepared from 39.2 g. (0.025 mole) of bromobenzene, 12 g. (0.5 atom) of 30–80 mesh magnesium and 180 cc. of ether under nitrogen atmosphere (RMgX titer, 96%) was added with stirring 26 g. (0.2 mole) of 5-chloro-2-furfural[8] in 100 cc. of ether over two hours. After fifteen minutes of subsequent reflux the whole was poured into 500 g. of ice and 15 g. (0.25 mole) of acetic acid. The ether layer was washed once with water, thrice with 10% aqueous sodium carbonate and, finally, was dried with sodium sulfate. Evaporation of the ether left a residue which was crystallized from petroleum ether (b. p. 50–70°) to melt at 108°. It weighed 17.2 g. or 43% of theoretical. A second crystallization raised the melting point to 114.5° (cor.).

*Anal.* Calcd. for $C_{22}H_{16}O_3Cl_2$: C, 66.2; H, 4.0; Cl, 17.8. Found: C, 66.2; H, 4.4; Cl, 17.9.

The molecular weight was determined by the Rast method as 391 (calcd. 399). No methane was evolved in a Zerewitinoff determination nor did the compound react with sodium, phenyl isocyanate or diluted acetyl chloride. The halogen atom was inert toward alcoholic silver nitrate, zinc dust in ammoniacal alcohol and sodium amalgam in ethanol–ether. The pure compound is stable if kept dry and free from acidic media.

It was sensitive toward acids and, indeed, seemed to be reversibly formed in such media from the parent alcohol. Thus when a comparable preparation was made in di-*n*-butyl ether and the solution after hydrolysis with cold aqueous ammonium chloride, was dried with anhydrous sodium sulfate and sodium carbonate, the active hydrogen evolved with methylmagnesium iodide from an aliquot was 72% of that expected for (5-chloro-2-furyl)-phenylcarbinol. When the oil remaining after evaporation of the ether was heated with a drop of dilute acetic acid it lost water and solidified. The solid, m. p. 114° (cor.) after crystallization from petroleum ether, was identical with the ether described above.

**α-(5-Bromo-2-furyl)-benzyl Ether**, (III: R$^1$, R$^2$, R$^3$ = H; X = Br).—This compound was obtained in 23% yield (m. p. 127–128° (cor.) after crystallization from petroleum ether, b. p. 50–70°) when it was prepared like the chloro analog and hydrolysis was effected with aqueous ammonium chloride. The compound was less soluble in ethanol than the chloro analog but, similarly, it gave no active hydrogen in the Zerewitinoff analysis. Its molecular weight (cryoscopic, in benzene) was found to be 460 (calcd. 448). It was much less stable than the chloro analog.

*Anal.* Calcd. for $C_{22}H_{16}O_3Br_2$: C, 54.1; H, 3.3. Found: C, 53.6; H, 3.5.

When the reaction mixture after Grignard reagent treatment is hydrolyzed with acid rather than with ammonium chloride solution, the product is usually γ-benzalcrotonolactone rather than the ether.

**γ-Benzalcrotonolactone, (V: R$^1$, R$^2$, R$^3$ = H).**—To 10 cc. of concd. sulfuric acid was added 4.5 g. (0.0225 mole) of bis-5-chlorofuryl-2-methylphenyl ether at such a rate that evolution of hydrogen chloride was not too violent. After two hours the mixture was diluted to 75 cc. volume with cracked ice. The precipitate was filtered, after trituration, washed with water and dissolved in 30 cc. of hot 95% ethanol. Dilution with hot water to turbidity caused crystallization of 3.14 g. (81%) of γ-benzalcrotonolactone. Repurification by crystallization from water–ethanol, from 8% hydrochloric acid, or by distillation (b. p. 171° (10 mm.)) raised the melting point to 86°.

*Anal.* Calcd. for $C_{11}H_8O_2$: C, 76.7; H, 4.7. Found: C, 76.7; H, 5.0.

An equally good yield is obtained when the sulfuric acid is replaced by acetyl chloride, and the compound is likewise produced when the ether is boiled an hour in ethanol. Similar treatment in benzene does not affect the ether.

A solution of γ-benzalcrotonolactone in concd. sulfuric acid is orange-red in color. The compound is recovered unchanged by dilution of this solution, just as it is unaffected by ethanolic hydrogen chloride. It dissolves in boiling 5% aqueous sodium hydroxide and decomposes, but acidification after a short time yields an acid, m. p. 154°, which is difficult to purify owing to insolubility. Its analysis (C, 69.5; H, 5.3) approximates to that of β-(phenylacetyl)-acrylic acid.

**Reduction of Benzalcrotonolactone.**—A sealed tube containing 1 g. (0.006 mole) of benzalcrotonolactone with 20 cc. each of 40% hydriodic acid and glacial acetic acid was heated six hours at 160°, then diluted with water and reduced with sulfur dioxide until iodine was absent. The exhaustive ether extract was washed with sodium carbonate and the alkaline solution acidified and ether-extracted. This exhaustive ether extract was distilled, finally at 15 mm. pressure, to leave 1.02 g. (92% yield) of δ-phenyllevulinic acid, m. p. 54°, neut. equiv., 199 (calcd. 192). This acid was identified as its semicarbazone, m. p. 182–183° dec.[9]

**Oxidation of Benzalcrotonolactone.**—A suspension of 0.5 g. (0.003 mole) of benzalcrotonolactone and 2 g. of chromic anhydride in 20 cc. of glacial acetic acid was stirred one day at 25° and then filtered. After evaporation of the filtrate under 15 mm. pressure the residue was twice extracted with 25 cc. of dry ether. To this solution was added 5 drops of aniline. The precipitate, filtered and washed with dilute acid and water, weighed 0.09 g., m. p. 195°. This yield (16%) was identified by mixed melting point as the monoanilide of maleic acid after it was crystallized (m. p. 197°) from hot 1:9 ethanol–water.

The ether and hydrochloric acid filtrates were evaporated to leave a residue from which 0.07 g. of benzoic acid, m. p. 118° (yield 20%), could be obtained by sublimation. It was identified by mixed melting point.

**γ-(Diphenylmethylene)-crotonolactone** (V: R$^1$, R$^2$ = H; R$^3$ = phenyl).—A solution of 43.6 g. (0.25 mole) of ethyl 5-chloro-2-furoate in 200 cc. of ether was added to an ether solution of 0.52 mole of phenylmagnesium bromide. Hydrolysis was effected with cold aqueous ammonium chloride and the ether layer, dried with sodium sulfate and carbonate, was treated with the decomposed oil resulting by evaporation of a small amount of this solution. This insured smooth liberation of hydrogen chloride during evaporation of the main bulk of ether,

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[8] W. J. Chute and G. F Wright, *J. Org. Chem.*, **10**, 541 (1945).

[9] K. Russwurm and J. Schulz, *Ann.*, **308**, 67 (1899).

since otherwise the residual oil decomposed violently after about one minute. The dark purple residue was crystallized from 95% ethanol (with Norit A decolorizer) to yield 30 g. (48%) of (diphenylmethylene)-crotonolactone, m. p. 111°.

*Anal.* Calcd. for $C_{17}H_{12}O_2$: C, 82.2; H, 4.8. Found: C, 81.8; H, 5.3.

A slightly higher yield (56%) was obtained from either 5-bromo-2-furyl phenyl ketone or ethyl 5-bromo-2-furoate under the same conditions, but none was obtained from ethyl 5-iodo-2-furoate.

**$\delta,\delta$-Diphenyllevulinic acid** (VIII: $R^3$ = phenyl).—A solution of (diphenylmethylene)-crotonolactone (1 g.) was boiled in 5 cc. of 47% hydriodic acid for five hours, then made basic, extracted with ether, acidified and again extracted with ether. Evaporation of this latter extract yielded an oil which was crystallized from petroleum ether (b. p. 70°) to yield 0.5 g. of $\delta,\delta$-diphenyllevulinic acid, m. p. 107°. This acid was identical, according to mixed melting point, with that prepared by the method of Tchichibabin[4] from diphenylfurylcarbinol. A solution of 22.8 g. (0.09 mole) of this compound in 45 g. of *abs.* ethanol was treated with hydrogen chloride until it became warm and then was boiled under reflux for four hours. Subsequent dilution with 250 cc. of 5% aqueous sodium carbonate yielded an oil which was distilled at 226–227° (7 mm.) to yield 12.9 g. (48 mole %) of the ethyl diphenyllevulinate, $n^{25}$D 1.552, $d^{25}_4$ 1.159. This ester was hydrolyzed in 72% yield by reflux in 10 parts of 5% hydrochloric acid. The hydrolyzate was extracted with ether and the extract then washed with 5% aqueous sodium hydroxide. The basic solution was acidified and extracted with ether. Evaporation left an oil which was crystallized from a mixture of ethyl and petroleum ether (b. p. 70°), to give a solid, m. p. 107–108°; mol. wt. (Rast), 270 (calcd. 268); active hydrogen (Zerewitinoff), 1.1 (calcd. 1).

Diphenyllevulinic acid was also prepared in 55% yield by a similar reduction of $\alpha$-bromo-$\gamma$-(diphenylmethylene)-crotonolactone.

*Anal.* Calcd. for $C_{17}H_{16}O_3$: C, 76.2; H, 6.0. Found: C, 76.0; H, 6.6.

Oxidation of this compound with alkaline potassium permanganate gave a 74% yield of benzophenone and a 10% yield of succinic acid. The compound was cleaved by reflux with methanolic potassium hydroxide to give a 70% yield of diphenylmethane (identified as its dinitro derivative, m. p. 182–183°) and a 91% yield of succinic acid (identified as the *p*-toluidide, m. p. 263°).

**Alkaline Cleavage of $\gamma$-(Diphenylmethylene)-crotonolactone.**—Steam distillation of 1 g. of the lactone in 100 cc. of 5% aqueous sodium hydroxide gave an oily distillate from which, by ether extraction, a 77% yield of *asym*-diphenylacetone was obtained after evaporation and crystallization from petroleum ether (b. p. 70°). Both forms (m. p. 46° and 61°) were obtained but they gave the same oxime, m. p. 163°, authenticated by mixed melting point.

When 1 g. of the lactone was boiled for six hours with 10 g. of potassium hydroxide in 25 cc. of methanol a solid potassium salt precipitated upon cooling. This was converted to a 46% yield of fumaric acid by acidification. The methanolic filtrate on dilution yielded an oil which was treated with 3 cc. of fuming nitric acid to give dinitrodiphenylmethane, m. p. 183°, in 67% yield.

**$\alpha$-Bromo-$\gamma$-(diphenylmethylene)-crotonolactone** (V: $R^1$ = H; $R^2$ = Br; $R^3$ = phenyl).—Treatment of 0.023 mole of ethyl 4,5-dibromo-2-furoate,[10,4] (m. p. 57–58°) with 0.056 mole of phenylmagnesium bromide in the manner described for the 5-bromofuroic ester yielded a dark purple residue which was washed with ether and then with petroleum ether and then crystallized from carbon tetrachloride with Norit A decolorizer. The lactone, m. p. 158° was obtained in 53% yield; mol. wt., Rast, 332 (calcd., 327). It also was produced in 13% yield by bromination of diphenylfurylcarbinol in carbon tetrachloride.

*Anal.* Calcd. for $C_{17}H_{11}O_2Br$: C, 62.3; H, 3.4. Found: C, 62.3; H, 3.7.

When 2 g. of this lactone was steam distilled with 28 cc. of 5% aqueous sodium hydroxide a 34% yield of *asym*-diphenylacetone was isolated and identified as described previously. The alkaline residue after acidification gave a 62% yield of diphenylacetic acid, m. p. 143–144° (identified as diphenylacetamide, m. p. 167°) as well as an 8% yield of oxalic acid (identified as the *p*-toluidide, m. p. 268°).

**$\alpha$-Chloro-$\gamma$-(diphenylmethylene)-crotonolactone** (V: $R^1$ = H; $R^2$ = Cl; $R^3$ = phenyl).—Treatment of ethyl 4,5-dichloro-2-furoate,[7] (m. p. 116–118°) as described above, gave an 81% yield of lactone, m. p. 127° after crystallization from 95% ethanol with Norit A decolorizer.

*Anal.* Calcd. for $C_{17}H_{11}O_2Cl$: Cl, 12.6. Found: Cl, 12.6. Alkaline cleavage as described above gave 20, 53 and 5% yields of *asym*-diphenylacetone, and diphenylacetic and oxalic acids respectively.

**$\beta$-Chloro-$\gamma$-(diphenylmethylene)-crotonolactone** (V: $R^1$ = Cl; $R^2$ = H; $R^3$ = phenyl).—This lactone, m. p. 128.5° after crystallization from ethanol, was prepared from ethyl 3,5-dichloro-2-furoate[7] (m. p. 72–73°, $\chi$ ester). A mixed melting point with $\alpha$-chloro-$\gamma$-(diphenylmethylene)-crotonolactone was lowered to 98°. The compound did not yield *asym*-diphenylacetone when boiled with alkali.

*Anal.* Calcd. for $C_{17}H_{11}O_2Cl$: Cl, 12.6. Found: Cl, 12.6.

**$\alpha,\beta$-Dichloro-$\gamma$-(diphenylmethylene)-crotonolactone** (V: $R^1$, $R^2$ = Cl; $R^3$ = phenyl).—This lactone, m. p. 178° after crystallization from ether–ethanol, was obtained either from ethyl 3,4,5-trichloro-2-furoate (yield 55%) or from ethyl 5-bromo-3,4-dichloro-2-furoate (yield 41%). It would not yield *asym*-diphenylacetone when boiled with alkali.

*Anal.* Calcd. for $C_{17}H_{10}O_2Cl_2$: Cl, 22.4. Found: Cl, 22.7.

The same compound was obtained in 42% yield from ethyl 5-bromo-3,4-dichloro-2-furoate, m. p. 99–100°, and phenylmagnesium bromide.

**$\alpha,\beta$-Dibromo-$\gamma$-(diphenylmethylene)-crotonolactone** (V: $R^1$, $R^2$ = Br; $R^3$ = phenyl).—The yield of lactone from ethyl 3,4,5-tribromo-2-furoate was 27%, m. p. 211° after crystallization from carbon tetrachloride. Steam distillation from alkaline solution did not yield *asym*-diphenylacetone. A small amount of this lactone was produced by bromination of diphenylfurylcarbinol in carbon tetrachloride.

*Anal.* Calcd. for $C_{17}H_{10}O_2Br_2$: Br, 39.4. Found: Br, 39.6.

**bis-Diphenylfurylmethyl Ether.**—A mixture of 87 g. (0.347 mole) of diphenylfurylcarbinol and 150 cc. of 10% aqueous acetic acid was boiled for seventeen hours. The solid, weighing 61 g. (73 mole %), was ground and washed with acetone, m. p. 215°. Crystallization from benzene plus ethyl acetate raised this melting point to 216° dec. A higher melting point (225°) may have been due to faster heating. The molecular weight (cryoscopic in benzene) was 485 (calcd. 482).

*Anal.* Calcd. for $C_{34}H_{26}O_3$: C, 84.8; H, 5.38. Found: C, 85.2; H, 5.38.

## Summary

1. Reaction between 5-halogenofurfurals and phenylmagnesium bromide leads to the formation in fair yield of the *sym*-ethers corresponding to the expected carbinols.

2. Evidence has been obtained by Zerewiti-

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[10] H. B. Hill and C. R. Sanger, *Proc. Am. Acad. Arts Sci.*, **12**, 164 (1885-6).

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

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[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-

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[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).

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[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).