to a large excess of powdered, solid carbon dioxide in a 2-liter flask. The carbonation required fifteen minutes.

The reaction mixture was resolved by appropriate and standard procedures, and the following products were isolated and identified. (1) Ethyl iodide; characterized by conversion to ethylmercuric iodide[9] by the Grignard reagent prepared from the ethyl iodide. (2) *n*-Butyl iodide (30% yield); characterized both by conversion to *n*-butylmercuric iodide and to *n*-valero-α-naphthylamide (*via* RMgI and α-naphthyl isocyanate[10]). (3) Propionic acid (43.4% yield); characterized by *p*-phenylphenacyl derivative.[11] (4) *n*-Valeric acid (34.8% yield);[12] characterized by *p*-phenylphenacyl derivative.

A similar reaction was carried out by adding 100 cc. of 0.87 molar *n*-butyllithium solution to 13.6 g. (0.087 mole) of ethyl iodide in 50 cc. of ether cooled to −70°. After fifteen minutes the mixture was carbonated. The respective yields of *n*-valeric and propionic acids were 38.4 and 42.2%. Identification of *n*-butyl iodide obtained from the reaction was made by converting it to *n*-butylmercuric iodide.

Ethyllithium–*n*-Butyl Iodide.—A 100-cc. portion of 1.03 molar ethyllithium solution (0.10 mole) was placed in a 250-cc. three-necked flask and cooled to −70° in a bath of acetone and carbon dioxide. To this rapidly stirred solution was added 18.4 g. (0.10 mole) of *n*-butyl iodide in 50 cc. of ether. The mixture was stirred for fifteen minutes at −70° and then carbonated.

The following products were isolated and identified: (1) ethyl iodide; (2) *n*-butyl iodide; (3) propionic acid, 48.0% yield; (4) *n*-valeric acid, 36.4% yield. Each of these products was characterized by the derivatives mentioned in the preceding section.

Summary

The reversibility of the following halogen–metal interconversion reactions has been established

$$C_6H_5Li + p\text{-}CH_3C_6H_4I \rightleftarrows p\text{-}CH_3C_6H_4Li + C_6H_5I$$
$$C_2H_5I + n\text{-}C_4H_9Li \rightleftarrows C_2H_5Li + n\text{-}C_4H_9I$$

Some possible applications of the X–M interconversion reactions have been considered.

AMES, IOWA

RECEIVED JANUARY 27, 1941

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(9) Marvel, Gauerke and Hill, THIS JOURNAL, **47**, 3009 (1925).

(10) Gilman and Furry, *ibid.*, **50**, 1214 (1928).

(11) Drake and Bronitsky, *ibid.*, **52**, 3715 (1930).

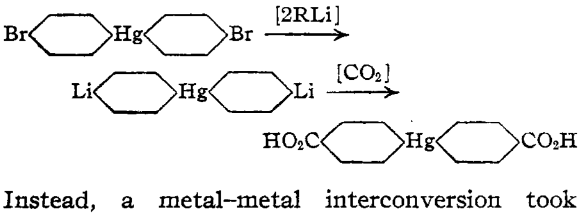
(12) The method for quantitatively estimating propionic and *n*-valeric acids in mixtures of the two was patterned after the procedure of Crowell, *ibid.*, **40**, 453 (1918).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

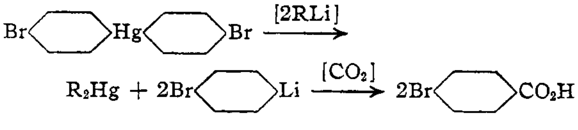
The Catalytic Effect of Organolithium Compounds in Some Interconversion Reactions[1]

BY HENRY GILMAN AND R. G. JONES

The two preceding papers on reversible metal–metal[2a] and reversible halogen–metal[2b] interconversions provide an explanation for an unusual reaction which is catalyzed by organolithium compounds. This reaction was discovered incidental to a broader study concerned with the introduction of water-solubilizing groups in organometallic compounds. It was hoped that the following typical sequence of reactions might occur.



Instead, a metal–metal interconversion took place and *p*-bromobenzoic and terephthalic acids, but no mercury containing carboxylic acids were formed.



The terephthalic acid owed its formation to a secondary halogen–metal interconversion reaction when excess RLi compound converted the *p*-bromophenyllithium to *p*-dilithiobenzene.

These abortive experiments suggested an examination of a more reactive halogen compound like *o*-bromoanisole which is known to undergo prompt Br–M interconversion.[3] In a competitive reaction, a mixture of one equivalent of each of the following compounds—*o*-bromoanisole, diphenylmercury, and *n*-butyllithium—was allowed to react for varying intervals of time prior to carbonation. Reaction was apparently complete in one-half minute or less, and the sequence of transformations follows:

$$(C_6H_5)_2Hg + 2n\text{-}C_4H_9Li \longrightarrow (n\text{-}C_4H_9)_2Hg + 2C_6H_5Li \qquad [1]$$

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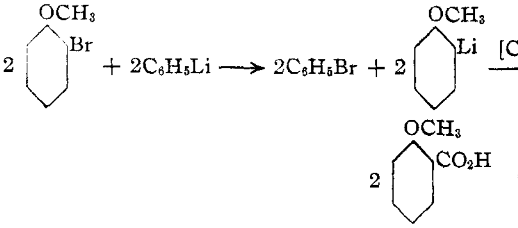
(1) Paper XXXVIII in the series: "Relative reactivities of organometallic compounds." The preceding paper is, Gilman and Jones, THIS JOURNAL, **63**, 1441 (1941).

(2) (a) Gilman and Jones, *ibid.*, **63**, 1439 (1941); (b) Gilman and Jones, *ibid.*, **63**, 1441 (1941).

(3) Leading references to earlier work on halogen–metal interconversion reactions are contained in a paper by Gilman, Langham and Moore, THIS JOURNAL, **62**, 2327 (1940).



[II]

The practically complete conversion of diphenylmercury to di-*n*-butylmercury [I] shows that the M–M interconversion, which used up the *n*-butyllithium, took place much more rapidly than the X–M interconversion. The high yield of *o*-methoxybenzoic acid [II] and the absence of any benzoic acid or *n*-valeric acid are best explained by assuming that the phenyllithium (formed in reaction [I]) acted in a known[3] manner on the *o*-bromoanisole to effect an X–M interconversion [II].

Next, one of the most reactive compounds in an X–M interconversion, *o*-iodoanisole, was used in a corresponding competitive reaction with diphenylmercury and *n*-butyllithium. When the mixture was carbonated after a reaction time of one-half minute, only an insignificant quantity of diphenylmercury was obtained and the reaction products were again *o*-methoxybenzoic acid and di-*n*-butylmercury. Thus even in the presence of *o*-iodoanisole the M–M reaction took place more rapidly than the X–M reaction in the system examined.

If, however, the reaction was allowed to proceed for more than one minute at room temperature before carbonation the chief products were *diphenylmercury* and *o*-methoxybenzoic acid. This reappearance of diphenylmercury can be accounted for satisfactorily by an iodine–mercury interconversion which is catalyzed by RLi compound. That is, the iodobenzene formed in a reaction analogous with [II] reacted with the di-*n*-butylmercury formed in reaction [I] to give diphenylmercury.

$$2C_6H_5I + (n\text{-}C_4H_9)_2Hg \xrightarrow{[RLi]} 2n\text{-}C_4H_9I + (C_6H_5)_2Hg \quad [III]$$

Reaction [III] does not take place in the absence of an RLi compound, not a trace of diphenylmercury being formed when a mixture of iodobenzene and di-*n*-butylmercury in ether was allowed to stand for several days. However, when to such a mixture there was added 2.5 parts of an RLi compound per 1000 parts of iodobenzene a reaction took place immediately, and was complete in several minutes to give a 91% yield of diphenylmercury. Similarly, diethylmercury in the presence of a catalytic quantity of ethyllithium reacted with iodobenzene and with *p*-iodotoluene to give the corresponding diarylmercury compounds in yields of 91 and 94.5%, respectively. In neither case could any diethylmercury be isolated from the reaction mixture.

It was then shown that a catalyzed reaction like [III] is reversible. When *p*-iodotoluene and diphenylmercury were allowed to react in the presence of a trace of phenyllithium, both di-*p*-tolylmercury and diphenylmercury were obtained. From a corresponding experiment using iodobenzene and di-*p*-tolylmercury, there was isolated both diphenylmercury and di-*p*-tolylmercury.

A catalytic quantity of RLi compound is necessary for reaction [III], and organolithium compound is present at the end of the reaction as evidenced by a positive color test.[4] The mechanism of these catalyzed reactions finds an adequate explanation on the basis of the reversible M–M interconversion [IV] and reversible X–M interconversion [V] reactions described previously.[2]

$$\begin{array}{ll} R_2Hg + 2R'Li \rightleftarrows R'_2Hg + 2RLi & [IV] \\ 2R'I + 2RLi \rightleftarrows 2RI + 2R'Li & [V] \\ \hline R_2Hg + 2R'I \rightleftarrows R'_2Hg + 2RI & [VI] \end{array}$$

Addition of equations [IV] and [V] gives reaction [VI] or the previously mentioned reaction [III].

Scope of Reaction.—Inasmuch as Grignard reagents do not, under the experimental conditions, undergo an X–M interconversion reaction like that of [V], one would not expect the RMgX compounds to catalyze a reaction like [VI]. This finds support in some experiments.

The reaction is either limited to aryl iodides or goes much more slowly with aryl bromides. This may be due to the known slower Br–M interconversion or to a possible irreversibility of the bromine–lithium interconversion.

From a synthetic viewpoint, any aryl iodide *not containing a functional group which could* destroy the catalyst can be converted to the corresponding R_2Hg compound. For example, an 87% yield of di-*p*-chlorophenylmercury was obtained from *p*-chloroiodobenzene, diphenyl-

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[4] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925). See also, Gilman and Yablunky, *ibid.*, **63**, 839 (1941), for other color tests for RLi compounds.

TABLE I

REACTION BETWEEN 4,4'-DIBROMODIPHENYLMERCURY AND RLi COMPOUNDS

RLi	Mole	$(BrC_6H_4)_2$-Hg, mole	Reaction medium	Reaction time	Temp., °C.	Yields of acids, %	
						Terephthalic	*p*-Bromobenzoic
n-C_4H_9Li	0.04	0.015	50/50$(C_2H_5)_2O$-Bz	20 min.	50	20	36[a]
n-C_4H_9Li	.04	.015	$(C_2H_5)_2O$	3 min.	25	8.8	66
n-C_4H_9Li	.027	.010[b]	$(C_2H_5)_2O$	3 min.	−62	8.5	48[c]
CH_3Li	.03	.0075	$(C_2H_5)_2O$	3 min.	25	4.7	79
n-C_4H_9Li	.04	.015[d]	Pet. ether (b. p., 28–38°)	20 hr.	30	76	12.9

[a] A reaction comparable with this using 0.05 mole of *n*-C_4H_9Li and 0.02 mole of *p*-dibromobenzene in 50–50 ether-benzene at 50° for twenty minutes gave, subsequent to carbonation, terephthalic acid (26.5%), *p*-bromobenzoic acid (41%), and 4,4'-dibromobenzophenone (10%). [b] Sixty-five % of unchanged 4,4'-dibromodiphenylmercury was recovered from this reaction. [c] The low yield of acids in this case is probably due to carbonating by adding solid carbon dioxide to the reaction mixture rather than pouring the mixture jetwise upon a large excess of powdered solid carbon dioxide. Yields are based upon the quantity of 4,4'-dibromodiphenylmercury not recovered. [d] Unreacted 4,4'-dibromodiphenylmercury (29.4%) was recovered.

mercury and phenyllithium. Unfortunately, the accessible tetraethyllead has not so far been used successfully for the formation of aryllead compounds. In this case, absence of reaction may be due to a slow or non-reversible lead–lithium interconversion, and if this proves to be the explanation then RNa or RK compounds may be more effective catalysts than RLi compounds.

The mobile equilibrium between lithium and magnesium warrants the prediction that organo-

$$2RLi + R'_2Mg \rightleftarrows 2R'Li + R_2Mg$$

magnesium compounds will readily interconvert with R'I types when RLi is used as a catalyst. Other moderately reactive organometallic compounds like R_2Zn, R_2Cd, R_3Al, R_3Ga, R_3In, R_3Tl may likewise be expected to show a reaction like [VI]. In particularly slow reactions, some of the RLi catalyst may be used up in secondary reactions like coupling with RI. On the other hand in rapid reactions with more reactive RM types, it is quite probable that alkyl iodides as well as aryl iodides can be used effectively to broaden the reaction and yield alkylmetallic combinations.

Relative Rates of Interconversion Reactions.—The three interconversion reactions which have been examined extensively in recent years are the M–M, X–M and H–M (metalation) types. Although no rigorous comparisons can be made of such different reactions, it is clear from the results here reported that M–M exchanges take place generally more rapidly than X–M interconversions. On the basis of other experiments,[3] X–M reactions proceed more rapidly generally than H–M reactions. The order M–M > X–M > H–M can be altered by the selection of special cases. For example, an alkylithium compound will probably react more rapidly with the lateral hydrogen in phenylacetylene than with the platinum in tetramethylplatinum. Also, an aryl iodide will probably undergo an X–M reaction more rapidly than aryllead or aryltin compounds will undergo an M–M reaction.

Experimental Part

4,4'-Dibromodiphenylmercury and *n*-Butyllithium.—4,4'-Dibromodiphenylmercury was prepared according to the method of Nesmejanow.[5] The product was contaminated with *p*-bromophenylmercuric chloride. It was, therefore, refluxed in alcohol with hydrazine[6] (to convert RHgX to R_2Hg), and again extracted in a Soxhlet apparatus with chloroform to give a 51% yield of 4,4'-dibromodiphenylmercury which melted at 243°.

The reactions of 4,4'-dibromodiphenylmercury with RLi compounds were carried out in the usual way. Mixtures of *p*-bromobenzoic and terephthalic acids were obtained and these were separated by taking advantage of the greater solubility of the *p*-bromobenzoic acid in ether. The acids were identified through their methyl esters, and the yields of each acid were estimated from the neutral equivalents of the original mixtures of the acids. The results of these experiments are given in Table I.

Competitive Reactions.—The general results of competitive reactions of (1) *o*-bromoanisole, diphenylmercury and *n*-butyllithium; and of (2) *o*-iodoanisole, diphenylmercury and *n*-butyllithium are included in Table II.

The following typical procedure was used in the several reactions, the results of which are given in Table II.

To a solution of 5.9 g. (0.0165 mole) of diphenylmercury and 6.17 g. (0.033 mole) of *o*-bromoanisole in 150 cc. of ether was added, over a period of twenty seconds with good stirring, 50 cc. of ether solution containing 0.033 mole of *n*-butyllithium. One-half minute after the addition of all of the *n*-butyllithium solution, 100 cc. of the reaction solution was removed with a pipet and carbonated. The remaining solution was carbonated after a longer period. The only acid obtained was *o*-methoxybenzoic acid. The ether solution from the carbonation

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(5) Nesmejanow and Kahn, *Ber.*, **62**, 1018 (1929).

(6) Gilman and Barnett, *Rec. trav. chim.*, **55**, 563 (1936).

TABLE II

COMPETITIVE REACTIONS OF ARYL HALIDES AND DIPHENYLMERCURY FOR n-C_4H_9Li

Aryl halide	Reaction time	o-CH_3O-$C_6H_4CO_2H$, yield, %	$(C_6H_5)_2Hg$ yield, %
o-$BrC_6H_4OCH_3$	30 sec.	86	
	30 sec.	88	1.0
	12 hr.	79	
	45 hr.	59	1.0
o-$IC_6H_4OCH_3$	30 sec.	86	Trace
	30 sec.	87.5	
	1 min.	87	23.6
	3 min.	87.5	
	40 min.	78	
	15 hr.	56	60
	45 hr.	29	65

mixture, after extraction of the acid, was dried, the ether removed and the residue distilled under reduced pressure to yield di-*n*-butylmercury (b. p. 115° (18 mm.)). Identification was completed by converting the di-*n*-butylmercury to *n*-butylmercuric chloride (mixed m. p.). The recovered diphenylmercury which remained in the distilling flask was washed with petroleum ether and identified by comparison with an authentic specimen.

Diphenylmercury from Iodobenzene and Di-*n*-butylmercury.—To a solution of 0.050 mole of di-*n*-butylmercury in 150 cc. of ether containing a small quantity of *n*-butyllithium, was added 20.4 g. (0.10 mole) of iodobenzene. An exothermic reaction took place immediately. After one hour diphenylmercury began to separate from the solution which still gave a positive color test for RLi. The reaction mixture was hydrolyzed and worked up to yield 16.2 g. (91%) of diphenylmercury, and from the ether solution there was obtained 6.2 g. (68%) of pure *n*-butyl iodide identified by boiling point and refractive index. Bromobenzene gave negative results; and in the absence of RLi compounds, iodobenzene did not react with di-*n*-butylmercury.

Reactions of Aryl Iodides with Diethylmercury.—To 100 cc. of an ether solution containing 0.050 mole of diethylmercury was added 20.4 g. (0.10 mole) of iodobenzene. No reaction took place. After seven hours a 5-cc. sample of the mixture was removed and examined for diphenylmercury. None could be found. To the mixture was then added 3 cc. of an 0.82 molar ethyllithium solution, and an exothermic reaction occurred immediately. After ten minutes the solution was hydrolyzed and worked up to yield 16.0 g. (90.5%) of pure diphenylmercury.

A solution of 0.025 mole of diethylmercury in 50 cc. of ether was treated with 2 cc. of 0.82 molar ethyllithium followed by 10.9 g. (0.050 mole) of *p*-iodotoluene in 10 cc. of ether. Heat was evolved immediately, and within one-half minute a white crystalline precipitate of di-*p*-tolylmercury began to separate. The mixture was worked up after one hour to yield 9.03 g. (94.5%) of pure di-*p*-tolylmercury.

A solution of 0.05 mole of *o*-bromoanisole, 0.025 mole of diethylmercury and 0.003 mole of ethyllithium in 50 cc. of ether underwent no change after standing for four days at room temperature. The diethylmercury (97%) was recovered as ethylmercuric chloride.

Diphenylmercury and *p*-Iodotoluene.—One-half cc. of a 1.12 molar phenyllithium solution was added to 75 cc. of an ether solution containing 3.54 g. (0.010 mole) of diphenylmercury and 4.36 g. (0.020 mole) of *p*-iodotoluene. Crystals of di-*p*-tolylmercury began to separate immediately. After two hours, the mixture was hydrolyzed and 2.85 g. (74%) of di-*p*-tolylmercury was obtained. This experiment was repeated, allowing twelve hours before hydrolysis, and the same results were obtained.

No reaction occurred between diphenylmercury and *p*-iodotoluene in ether solution in the presence of ethylmagnesium bromide or *p*-chlorophenylmagnesium bromide.

Di-*p*-tolylmercury and Iodobenzene.—A mixture of 7.64 g. (0.020 mole) of di-*p*-tolylmercury, 8.16 g. (0.080 mole) of iodobenzene and 100 cc. of ether was treated with 2 cc. of 1.12 molar phenyllithium solution to give a faint positive color test. After five hours, the color test was still faintly positive. The mixture was hydrolyzed and the unreacted di-*p*-tolylmercury, 5.54 g. (71%), was filtered off. The ether layer was separated, the ether removed and the residue subjected to steam distillation to remove the aryl iodides. Diphenylmercury was obtained in a yield of 1.32 g. (9.4%) based upon the iodobenzene taken.

In another experiment 0.117 mole of iodobenzene and 0.013 mole of di-*p*-tolylmercury in 100 cc. of ether was used with a trace of phenyllithium and the mixture was allowed to stand eighteen hours before it was worked up. A yield of 12.5% of diphenylmercury resulted.

Diphenylmercury and *p*-Chloroiodobenzene.—To a solution of 3.54 g. (0.010 mole) of diphenylmercury and 4.76 g. (0.020 mole) of *p*-chloroiodobenzene in 100 cc. of ether was added 1 cc. of 1.12 molar phenyllithium. Within one-half minute crystals of di-*p*-chlorophenylmercury began to separate. The mixture was hydrolyzed after two and one-half hours and worked up to give 3.68 g. (87%) of di-*p*-chlorophenylmercury (mixed m. p.).

Tetraethyllead and Aryl Iodides.—Ethyllithium solution was added to a solution of 0.027 mole of tetraethyllead and 0.06 mole of iodobenzene in 60 cc. of ether to give a good positive color test. After twenty-four hours the mixture was hydrolyzed. No tetraphenyllead could be found. By saturating the dry ether solution with hydrogen chloride, 92.5% of the starting material was recovered as triethyllead chloride. This experiment was repeated with negative results even when the mixture was allowed to stand several days before hydrolyzing. Likewise, there was no reaction in an experiment using tetraethyllead, *p*-iodotoluene and a little ethyllithium in ether.

Summary

A study of some competitive reactions shows that metal–metal interconversions generally take place more rapidly than halogen–metal interconversions.

Reaction [C], which may be of synthetic value, takes place with catalytic quantities of RLi compound

$$\begin{array}{rcll} R_2Hg + 2R'Li & \rightleftharpoons & R'_2Hg + 2RLi & [A] \\ 2R'I + 2RLi & \rightleftharpoons & 2RI + 2R'Li & [B] \\ \hline R_2Hg + 2R'I & \rightleftharpoons & R'_2Hg + 2RI & [C] \end{array}$$

The mechanism of this catalyzed reaction follows from the addition of the reversible M–M reaction [A] and the reversible X–M reaction [B].

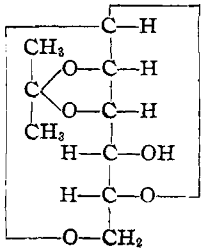
Ames, Iowa Received February 6, 1941

[Contribution from the National Institute of Health, U. S. Public Health Service]

D-Mannosan<1,5>β<1,6> or Levomannosan[1]

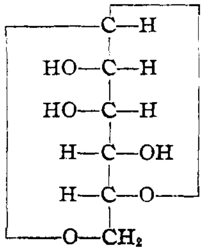
By A. E. Knauf, Raymond M. Hann and C. S. Hudson

The polysaccharide (a D-mannan) which constitutes the greater part of the endosperm of palm seeds, seems to play a biological role which is similar to that of starch in many other seeds. Since the procedure using the pyrolysis of starch[1a] is the most convenient method of preparing D-glucosan<1,5>β<1,6> (levoglucosan) it seemed of interest to learn whether the pyrolysis of the so-called vegetable ivory, which is readily available as waste turnings, etc., in the manufacture of buttons from the large seeds of the ivory-nut palm (*Phytelephas macrocarpa*, Ruiz and Pav.), would yield some analogous simple anhydride of the D-mannose series. The first experiment verified this surmise. The pyrolysis under reduced pressure yielded a dark red-colored water-soluble sirup and some tar; treatment of this aqueous solution with decolorizing carbon, followed by removal of most of the water, left a light colored heavy sirup, which was then thinned somewhat with acetone. Overnight there crystallized in abundance a beautiful substance which was found to be a condensation product (I) of acetone with a non-reducing D-mannosan; since it seemed improbable that the required amount of acetone could have been produced in the pyrolysis it was



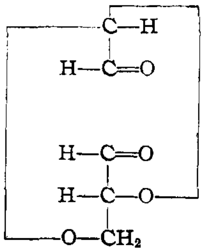
(I)[2]

2,3-Isopropylidene D-mannosan<1,5>β<1,6>



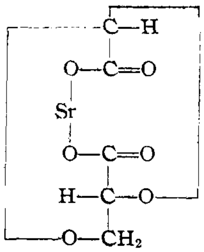
(II)

D-Mannosan<1,5>β<1,6> (levomannosan)



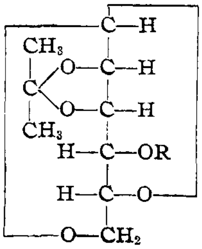
(III)

L′-Oxy-D-methylene diglycolic aldehyde



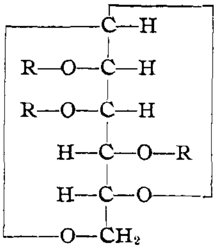
(IV)

Strontium L′-oxy-D-methylene diglycolate



(V)

(a) $R = CH_3CO—$
(b) $R = C_6H_5·CO—$
(c) $R = p\text{-}CH_3·C_6H_4·SO_2—$
(d) $R = CH_3—$



(VI)

(a) $R = CH_3CO—$
(b) $R = C_6H_5·CO—$
(c) $R = p\text{-}CH_3·C_6H_4·SO_2—$

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[1] Publication authorized by the Surgeon General, U. S. Public Health Service. The research was presented by one of us (C. S. H.) in a lecture before the Northeastern Section of the American Chemical Society in Cambridge, Mass., on May 9, 1940; publication at that time was limited to the statement ("The Nucleus," issue of May, 1940) that "the address on mannosan will set forth the properties and proof of structure of this new carbohydrate, as well as the method of obtaining it from vegetable ivory, a product of vegetable origin widely employed in the manufacture of buttons." The idea of seeking for a mannosan in the pyrolysis products from vegetable ivory had occurred independently to Zemplén, Gerecs and Valatin who have published (*Ber.*, **73B**, 575–580 (1940), issued June 4, manuscript received April 12), a description of two crystalline derivatives of the substance (its triacetate and its trimethyl ether). They prepared the mannosan itself in amorphous form by the deacetylation of its pure triacetate; fortunately it has crystallized readily in our studies. We do not find exact proof in their article for the definite structural and stereochemical formula (*i. e.*, the 1,5 and β-1,6 rings) that they ascribe to the mannosan; however our concurrent work proves conclusively through its new data that their formula, which is formula (II) of the present article, is the correct one. Zemplén, Gerecs and Valatin have named the mannosan *levomannosan* in suggestion of its similarity to the long known *levoglucosan* (C. Tanret, 1894); we are inclined to the view that the systematic naming D-mannosan<1,5>-β<1,6> and D-glucosan<1,5>β<1,6> of such anhydrides, which is now possible because of the convenient periodate method of correlating their structure and configurations (Jackson and Hudson, see ref. 5), has advantages which will in time be generally regarded as decisive. These considerations led Richtmyer and Hudson (see ref. 6) to name the corresponding anhydride of the D-altrose series D-altrosan<1,5>β-<1,6> rather than *levoaltrosan*. Since our colleagues have introduced the name *levomannosan* we include it in the title of the present article as synonymous with the systematic name D-mannosan<1,5>β<1,6>. An alternative systematic name would be D-mannopyranosanβ<1,6>.

[1a] Pictet and Sarasin, *Helv. chim. acta*, **1**, 87 (1918).

[2] In drawing these projection formulas we follow the conventions that are discussed with full clearness by K. Freudenberg in his "Stereochemie," edition of 1933, p 664.