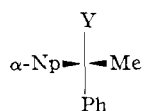


there is complete correspondence with respect to configuration between germanium and silicon enantiomers with the same sign of rotation. In addition, Brewster's rules of atomic asymmetry, which in the case of methyl α -naphthylphenylsilyl compounds correctly predict the configurations of the H, Cl, Br, OH, OMe, and other derivatives,⁶ predict the same configuration, *viz.*



for $(-)\text{GeH}$, $(+)\text{GeCOOH}$, $(-)\text{GeOMe}$, $(+)\text{GeCl}$, and their silicon analogs. Hence, it follows that retention of configuration is involved in each of the reactions so specified in Scheme I, and that in all similar cases studied to date (except bromination²), the stereochemistry of displacements at asymmetric germanium is the same as that of displacements at silicon.

The stereochemistry described above is in accord with other known reactions. Studies on vinyl metal-lics,⁷ and other organometallic systems⁸ indicate that metalation, or halogen-metal exchange, carbonation, and addition to a carbonyl group each occur with retention of configuration. Thermal rearrangements of silane- and germanocarboxylates to ethers have been shown to be intramolecular processes,⁹ and would be expected to involve "flank" attack, leading to retention of configuration. Similar results were found in the intramolecular rearrangements of α -hydroxysilanes to silyl ethers.^{5,6}

The most significant result of this study is the remarkable optical stability of methyl- α -naphthylphenylgermyllithium, which through the carbonation cycle, is shown to have essentially complete optical stability in ether at room temperature over 30 min. While organometallics such as *sec*-butyllithium¹⁰ have considerable optical stabilities in hexane at low temperatures, the presence of diethyl ether leads to rapid racemization. Further studies are in progress.

Configurational relationships were established by weighing known quantities of silicon and germanium enantiomers, dissolving them in ether or pentane and immediately pumping off the solvent. Compounds of like configuration had narrow mixed melting point ranges, whereas compounds of unlike configuration had melting point ranges of from 10 to 25°. Analyses and infrared spectra were in accord with the assigned structures of all compounds.

Acknowledgment.—This research was sponsored in part by the National Research Council of Canada.

(6) A. G. Brook and W. M. Limburg, *J. Am. Chem. Soc.*, **85**, 832 (1963).

(7) D. Y. Curtin and J. W. Crump, *ibid.*, **80**, 1922 (1958).

(8) H. M. Walborsky and F. J. Impastato, *ibid.*, **81**, 5835 (1959); H. M. Walborsky and A. E. Young, *ibid.*, **83**, 2595 (1961).

(9) A. G. Brook, *ibid.*, **77**, 4827 (1955); A. G. Brook and R. J. Mauris, *ibid.*, **79**, 971 (1957).

(10) D. Y. Curtin and W. J. Koehl, *ibid.*, **84**, 1967 (1962).

(11) Cities Service Corporation Fellow, 1962-1963.

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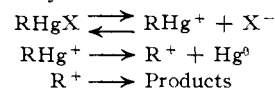
Generation of Phenyl Radical *via* Reduction of Phenylmercuric Cation

Sir:

The solvolysis of alkylmercuric salts such as acetate (or more effectively perchlorate) has been well established to be a general route to afford carbonium ions.¹ Among the many possible mechanisms proposed for this

(1) F. R. Jensen and R. J. Ouellette, *J. Am. Chem. Soc.*, **83**, 4477, 4478 (1961); **85**, 363 (1963).

reaction,²⁻⁴ the most probable and simplest one as outlined by Jensen and Ouellette¹ involves the ionization of alkylmercuric salt followed by dissociation of carbon mercury linkage to yield carbonium ion and mercury.



Robson and Wright⁴ pointed out that phenylmercuric acetate does not undergo heterolysis in methanol with boron trifluoride. Jensen and Ouellette in their elegant work also emphasized that the reaction has been found to be general for all alkyl groups, and the ionic mechanism is beyond doubt; however, the fate of solvolysis of phenylmercuric salts was not mentioned.

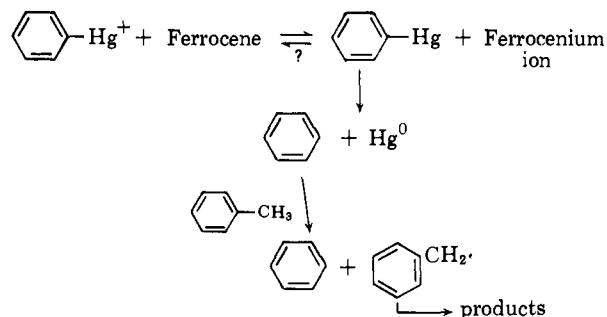
In our Laboratories we have found that phenylmercuric acetate, preferably perchlorate or tosylate, undergoes solvolysis in acetic acid or even toluene in the presence of a reducing agent. For example, with ferrocene, the reaction furnishes the phenyl radical with concomitant oxidation of ferrocene to ferrocenium ion.

Phenylmercuric acetate (Eastman Kodak White Label, m.p. 148-150°) in acetic acid reacts with ferrocene very slowly, as indicated by the gradual appearance of the characteristic blue color of ferrocenium ion. Addition of a catalytic amount of perchloric acid to the mixture led to almost instantaneous formation of the characteristic ferrocenium ion color. Using acrylonitrile as solvent, phenylmercuric acetate and ferrocene initiated polymerization of the monomer and the polymerization process was inhibited by both free radical scavengers such as *p*-hydroquinone and ions such as NaCl, NaNO₂, etc. When the reaction was carried out in toluene with an equimolar (0.1 mmole) amount of phenylmercuric acetate, perchloric acid, and ferrocene, the appearance of ferrocenium ion color was instantaneous and the yield of benzene was practically quantitative. With toluenesulfonic acid, the yield of benzene was 25%.

The previous failure to observe the cleavage of phenyl-mercury bond⁴ is perhaps indicative of the unfavorable energetics for such heterolysis and may be attributed at least partially to the stabilization of phenylmercuric cation by dissipating the positive charge to the aromatic ring.



Since the solvolytic step is reversible, no appreciable demercuration of this cation is anticipated. In the presence of a reducing agent such as ferrocene, the intermediate cation from solvolysis is reduced to phenylmercury (I), followed by demercuration and formation of phenyl radical. When the reaction is carried out in toluene, the phenyl radical abstracts hydrogen from toluene to form benzene and the more stable benzyl radical.⁵



(2) K. Ichikawa and H. Ouchi, *ibid.*, **82**, 3876 (1960).

(3) S. Winstein, *et al.*, *ibid.*, **77**, 3741 (1955); *Chem. Ind. (London)*, 251 (1962).

(4) J. H. Robson and G. F. Wright, *Can. J. Chem.*, **38**, 21 (1960).

(5) S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **77**, 3628 (1955).

It is quite clear that the reduction process has to involve phenylmercuric cation and not the phenyl cation, and therefore a hydride abstraction by phenyl carbonium ion from toluene to yield benzene and benzyl carbonium ion is ruled out. As regards the difference in the yield of benzene between toluenesulfonate and perchlorate, it perhaps reflects the extent of ionization of the salts.

Acknowledgment.—We wish to thank Dr. P. L. Levins for helpful discussion and technical assistance and the Research Committee of Arthur D. Little, Inc., for financial support.

ARTHUR D. LITTLE, INC.
CAMBRIDGE 40, MASSACHUSETTS

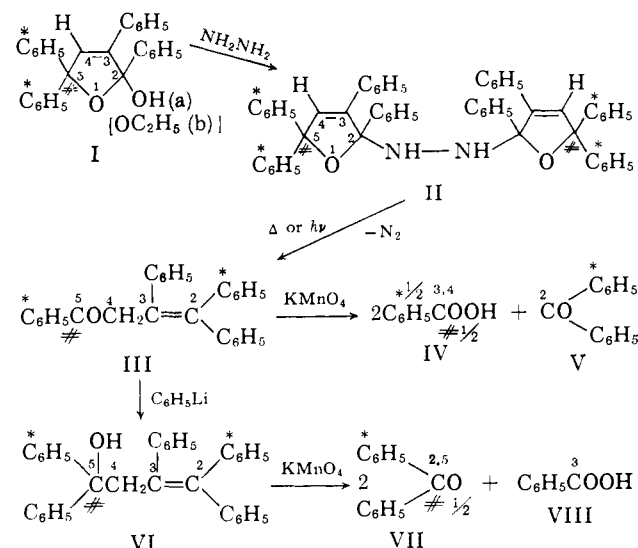
CHI-HUA WANG

RECEIVED MAY 8, 1963

A Novel Phenyl Group Migration during Pyrolysis and Photolysis of Bis-(2,3,5-tetraphenyl-2-dihydrofuranyl)-hydrazine

Sir:

This rearrangement was discovered during reinvestigation of the cyclic hemiketal, 2,3,5-tetraphenyldihydrofuranol-2 (Ia)¹ and its conversion supposedly through the *acyclic cis* hydroxy ketone form into a "hydrazone" for which the *sym,bis cyclic* hydrazine structure II is now suggested on the basis of the following data. The compound gave the correct C, H, and N analyses and molecular weight; it was converted under acid catalysis into the cyclic ketal Ib and dehydratively rearranged to tetraphenylfuran^{1b}; it showed λ_{\max} 253.5 μ , (ϵ 28,400) corresponding to two styryl groups, two infrared NH peaks,² a narrow one at 3560 cm^{-1} , and a broad one at 3440 cm^{-1} persisting on dilution and suggestive of intramolecular hydrogen bonding, and no absorption in the 1600 cm^{-1} range corresponding to NH_2 or $\text{C}=\text{N}$ groups of *gem,bis* hydrazine or *acyclic* azine structures.²



The symbols * and # indicate the respective locations of the C^{14} label in the two tracer experiments. The 2-5 numbering is used throughout to trace the four ring carbons of I and II.

Pyrolysis of II at its melting point (220°), in refluxing decalin (190°), and in dimethylformamide (153°), and photolysis in benzene,³ caused evolution of nitrogen (identified in one case, v.p.c.) and formation of the β , γ -unsaturated ketone III⁴ (50-60%). The *gem*-di-

(1) (a) S. Salkind and V. Teterin, *J. prakt. Chem.*, **133**, 195 (1932); (b) R. E. Lutz, C. L. Dickerson, and W. J. Welstead, Jr., *J. Org. Chem.*, **27**, 3062 (1962); (c) further studies in these areas are in progress.

(2) Determined in CCl_4 (Perkin-Elmer 421 grating spectrophotometer) and interpreted by W. L. Truett, duPont Co., Waynesboro, Va.

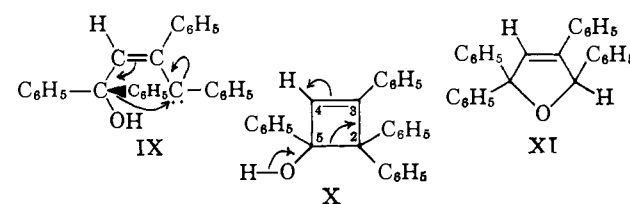
(3) Hanovia 450-watt high pressure mercury arc lamp. Pyrex filter.

(4) Erroneously formulated (a) as a butenol^{1a} and (b) as a cyclic enol ether

phenyl group in each moiety of II at position-5 of the numbered four-carbon system is located in the resulting ketone III at carbon-2, the other end of this same four-carbon system. Empirically, therefore, a phenyl group migration has occurred.

Pyrolysis and photolysis of samples of II C^{14} -labeled, respectively, in the *gem*-diphenyl groups (*) and at the 5-carbon atom (#) traced the migration and limited mechanistic possibilities.⁵ In the first case (*) the resulting sample of unsaturated ketone III* upon permanganate oxidation gave benzophenone V* and benzoic acid IV* each containing half of the C^{14} activity. Except for the possibility of total scrambling of the locations of the four phenyl groups which would have led to the same result, this showed that carbon-5 of II* had lost one of its two labeled phenyl groups, that carbon-2 had gained one, and that the migration must have been transannular or *cis*-1,4. The mechanistically improbable migration of a 5-phenyl group of II* in successive steps around the ring to the 2-position is excluded because it would have led to a 2-*gem*-diphenyl group in the unsaturated ketone III with one-third or less of the C^{14} activity,^{5b} depending on the order and reversibility of the steps. That total scrambling of the locations of the C^{14} -labeled phenyl groups had not occurred was rigorously proved in the case of dimethylformamide pyrolysis by addition of phenyllithium to the unsaturated ketone III* and oxidation of the resulting pentaphenylbutenol VI* to benzophenone VII* containing all of the C^{14} and benzoic acid VIII containing none (scrambling would have led to C^{14} contents of 75 and 25%, respectively^{5b}).

The pyrolysis and photolysis reactions can be expressed stoichiometrically as intramolecular oxidation of the hydrazo group to molecular nitrogen and reduction of the two ring moieties by hydrogen transfer from the hydrazo group.^{5b} The drive for furanization existing before this reaction is absent afterward because of the lower oxidation stage of the nitrogen-free products (e.g., III, IX-XI). Initial formation of a carbene-like transition is suggested, e.g., IX, followed by 5-2 migration of a phenyl group⁶ and formation of the unsaturated ketone III, either through its diene-ol or through the cyclobutenol X.^{5b,7}



Preliminary study of the dihydrofuran, presumably XI, which has been made by lithium aluminum hydride reduction of Ia to a glycol and subsequent cyclo-dehydration [m.p. 94-95°; analyzed; λ_{\max} 254 μ , (ϵ

[K. Scholtis, *Ann.*, **557**, 82 (1945)]. For structure proof see (c) R. E. Lutz and C. L. Dickerson, *J. Org. Chem.*, **27**, 2040 (1962).

(5) (a) Samples of C^{14} -labeled II, * and #, were prepared from samples of Ia made from acetophenone labeled, respectively, in the phenyl group and at the carbonyl carbon. To be certain that there had been no rearrangement in going from Ia to II, C^{14} -labeled II* was converted into Ib, which upon chromic acid oxidation gave benzophenone carrying all of the C^{14} ; (b) details and mechanistic discussion will appear in the forthcoming paper.

(6) Cf. (a) 1,3-Methyl shift [P. Yates and S. Danishefsky, *J. Am. Chem. Soc.*, **84**, 879 (1962)]; 1,3-, 1,4- and 1,5-phenyl shifts [(b) M. Stiles and A. J. Libbey, Jr., *J. Org. Chem.*, **22**, 1243 (1957)]; (c) P. T. Lansbury and R. L. Letsinger, *J. Am. Chem. Soc.*, **81**, 940 (1959)]; (d) *cf. cis*-1,5 phenyl shift in photolysis of *cis*-dibenzoyl ethylene [G. W. Griffin and E. J. O'Connell, *ibid.*, **84**, 4148 (1962)]; *cf. references* cited in a-c.

(7) Cf. (a) P. A. Leermakers and G. F. Vesley, *J. Org. Chem.*, **28**, 1160 (1963); *cf. (b)* R. E. Lutz, L. T. Slade, and P. A. Zoretic, *ibid.*, **28**, 1358 (1963); work in this field is under further investigation, and the reactions are subject to possible reinterpretation in terms of carbene intermediates [*cf. (c)* G. I. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85**, 99, (1963)].