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ON THE FORMATION OF DICHLOROMETHYLENE CARBENE BY THE PHOTOCHEMICAL REACTION OF PERCHLOROVINYL PHENYL MERCURY

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It is well known that common alkylidene carbenes have been usually generated by treatment of appropriate vinyl halides with potassium tert-butoxide (1, 2) or alkyllithium (3, 4).

However, it may be impossible to apply the above method to the generation of dichloromethylene carbene, being a new carbene, since perchlorovinyl lithium converts preferentially to dichloroacetylene by the trans-β-elimination as indicated by G. Köbrich (5).

In an attempt to find a new route for the generation of dichloromethylene carbene, the photochemical reaction of phenyl perchlorovinyl mercury (I)* has been investigated.

Irradiations of I (2.2 g) were carried out in various solvents (60-70 ml) with a 120 W low-pressure mercury arc lamp at room temperature for 10 hr. In these cases, it was clearly observed that the solvent had a very marked effect on the photolytic behavior of I, and the two different types of photolytic products were formed according to the solvent used. The results on the formation of mercurials in a variety of solvents are given in Table I.

TABLE I

Yields of Mercurials from Photolysis of I

Solvent	Yield, %	
	PhHgCl	Metallic Hg
Dioxane	-	95
Tetrahydrofuran	-	95
Diethyl ether	20	70
Tetrahydrofuran[a] and Cyclohexane	-	90
Methyl alcohol	95	5
tert-Butyl alcohol	95	-
Cyclohexane	100	-

[a] Mixed solvent with 1 : 1 molar ratio

Furthermore, besides the constituents listed in Table I, several liquid products were always produced in every case. The photoproduct analysis in methanol or cyclohexane is presented in Table II.

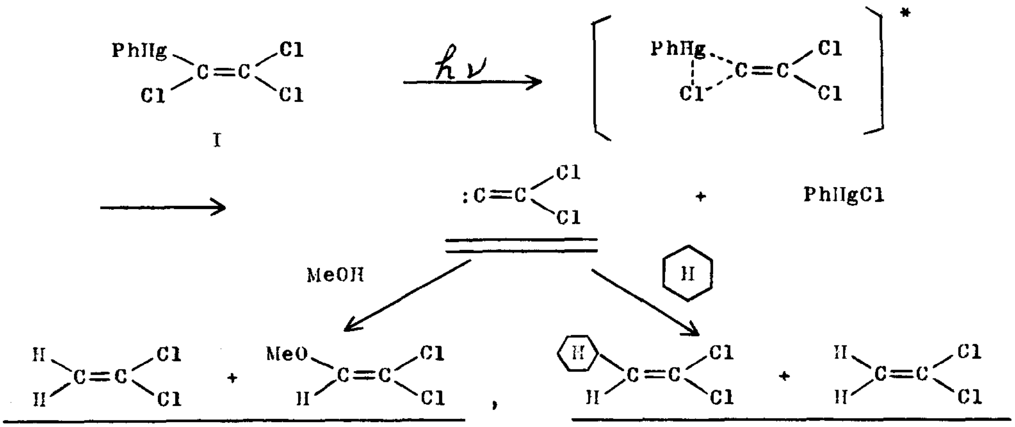
TABLE II

The photoproducts from I in Some Solvents

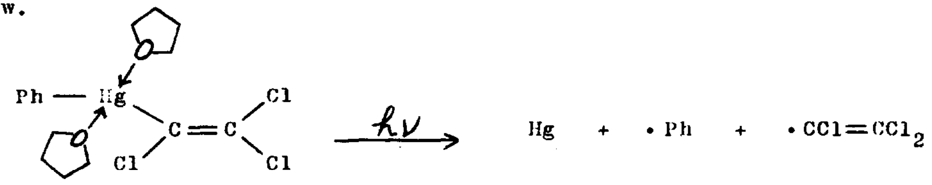
R-H	Reaction Time (hr)	Yield, %				
		PhHgCl	Hg	$\mathrm{H_2C{=}CCl_2}$[a]	$\mathrm{RHC{=}CCl_2}$[a]	$\mathrm{ClC{\equiv}CCl}$
CH_3OH	10	51	Trace	28	2	Trace
	16	80	None	Trace	25	None

[a] Based on PhHgCl formed.

From these results, it seems to be reasonable to conclude that, in either methanol or cyclohexane, the expected carbene may be successfully generated, accompanied by the elimination of phenyl mercuric chloride from I.



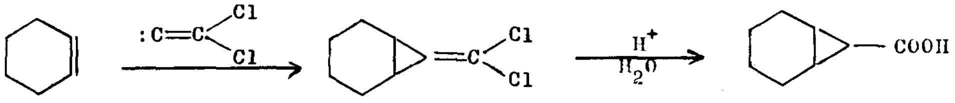
On the other hand, in tetrahydrofuran or dioxane, benzene, trichloroethylene, and hexachlorobutadiene were obtained as the principal liquid products along with metallic mercury. The above abnormality may be explained as due to the stronger coordinating ability of tetrahydrofuran or dioxane to mercury atom in I. Accordingly, the complex formation of solvent with I significantly suppresses the intramolecular interaction between mercury atom and α-chlorine atom as seen in the case of cyclohexane or methanol. As a consequence, the photolysis of complex (II) gives rise to perchlorovinyl and phenyl radicals by the independent cleavage of two carbon-mercury bonds as shown below.



II

Concerning the formation of dichlorocarbene from phenyl trihalomethyl mercury, such intramolecular α-chlorine abstraction has been recently expected by D. Seyferth (6) or J. A. Landgrebe (7). Although it, therefore, was of interest to investigate the thermal reaction of I, I in cyclohexane was considerably stable even in more drastic conditions. This fact probably reveals that the chlorine abstraction of I may be remarkably accelerated in photochemically excited state.

Moreover, in order to ascertain the feasibility of the addition of dichrolomethylene carbene to olefin, the photochemical reaction of I (4.0 g) in a mixture of cyclohexane (45 ml) and cyclohexene (35 ml) has been carried out. The expected cyclohexene-dichloromethylene carbene adduct (III) was obtained in 20 % yield together with a trace of the unidentified insertion products. III was readily converted to 7-norcarane carboxylic acid (IV) by hydrolysis with concentrated sulfuric acid (cf. ref. 8).



III IV

Further work is in progress on the reaction of this new carbene with olefins.

References and Remarks

1. M. Tanabe and R. A. Walsh, J. Am. Chem. Soc. **85**, 3522 (1963).
2. H. Günther and A. A. Bother-By, Chem. Ber. **96**, 3112 (1963).
3. H. D. Hartzler, J. Am. Chem. Soc. **86**, 526 (1964).
4. G. Köbrich and W. Drischel, Tetrahedron, **22**, 2621 (1966).
5. (a) G. Köbrich and K. Flory, Chem. Ber. **99**, 1773 (1966); Tetrahedron Letters, 1138 (1964). (b) G. Köbrich, Angew. Chem. Internat. Edit. **6**, 41 (1967).

* I was synthesized as follows; a mixture of equimolar biphenyl mercury and perchlorovinyl mercuric bromide in methanol was stirred at 40° for 7 hr. The white precipitate (PhHgBr) formed was filtered off and the filtrate was condensed under the reduced pressure. I was obtained in 85 % yield, mp 66.5-67.0° , from pentane, needles.

6. (a) D. Syferth and J. M. Burlitch, *J. Am. Chem. Soc*. **84**, 1757 (1962);**85** 2667 (1963);**86**, 2730 (1964). (b) D. Seyferth, J. M. Burlitch, and J. K. Heeren, *J. Org. Chem*. **27**, 1491 (1962). (c) D. Seyferth, R. J. Minasz, A. J. -H. Treiber, J. M. Burlitch, and S. R. Dowd, *ibid*. **28**, 1163 (1963). (d) D. Seyferth and M. A. Eisert, *J. Am. Chem. Soc*. **86**, 121 (1964). (e) D. Seyferth, J. Y.-P. Mui, and L. J. Todd, *ibid*. 2961 (1964). (f) D. Seyferth, J. Y.-P. Mui, M. E. Gordon, and J. M. Burlitch, *ibid*. **87**, 682 (1965). (g) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J. H. Treiber, and S. R. Dowd, *ibid*. 4259 (1965). (h) M. E. Gordon, K. V. Darragh and D. Seyderth, *ibid*. **88**, 1831 (1966).

7. J. A. Landgrebe and R. D. Mathis, *ibid*. **86**, 524 (1964);**88**, 3545, 3552 (1966).

8. (a) T.M. Joyce, Jr., U. S. Patent 2, 398, 430; *Chem. Abst*. **40**, 3768 (1946). (b) K. Bott and H. Hellmann, *Angew. Chem.* **78**, 932 (1966).