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A NOVEL CLEAVAGE OF CARBODIIMIDES BY PHENYL(BROMODICHLOROMETHYL)MERCURY

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We have studied the reaction of phenyl(bromodichloromethyl)mercury with olefins, which gives gem-dichlorocyclopropanes, in some detail.[1] In an extension of these studies to the reactions of this organomercury reagent with other unsaturated compounds we have investigated its action on carbodiimides. Imines have been shown to react with dichlorocarbene as generated by the Doering-Hoffmann procedure[2,3], but thus far no study of the reactions of carbenes or carbenoid reagents with carbodiimides has been reported.

The results of the present study may be summarized by equation 1.

$$C_6H_5HgCCl_2Br + RN{=}C{=}NR \longrightarrow C_6H_5HgBr + RN{=}CCl_2 + RN{\equiv}C \qquad (1)$$

Thus the reaction of diisopropylcarbodiimide (1 molar equivalent) with phenyl(bromodichloromethyl)mercury (1 molar equivalent) in chlorobenzene solution was carried out at about 80° until phenylmercuric bromide precipitation began to occur. At this point external heating was discontinued. The deep yellow-brown reaction mixture was filtered to remove phenylmercuric bromide (isolated in 95% yield) and the filtrate was distilled in

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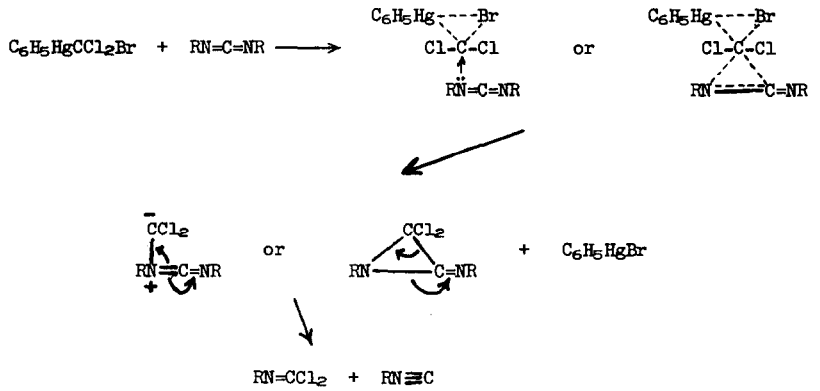
vacuum into a receiver at -78°. G.l.c. analysis (25% General Electric Co. SE-30 Silicone Gum on Chromosorb W at 62°) showed the presence of N-isopropyldichloroazomethine[4], $(CH_3)_2CHN{=}CCl_2$, (63% yield) as well as of five minor products. One of these was identified as isopropylisonitrile by comparison of its infrared spectrum with that of an authentic sample prepared by the procedure of Ugi and Meyr.[5,6] The other products were shown to derive from the reaction of isopropylisonitrile with phenyl(bromodichloromethyl)mercury in a separate experiment, but they were not identified.[7] Increasing the mercurial/carbodiimide ratio to 2 increased the yield of N-isopropyldichloroazomethine to 92%, a result which is in agreement with the diversion of mercurial in the 1:1 experiment to reaction with the isonitrile formed in the primary reaction. An increase in the yield of isopropylisonitrile could not be achieved by decreasing the mercurial/carbodiimide ratio to 0.1; apparently the isonitrile is much more reactive than is the carbodiimide.

Very similar results have been encountered in our study of the reaction of phenyl(bromodichloromethyl)mercury with dicyclohexylcarbodiimide: N-cyclohexyldichloroazomethine[8] was formed in yields comparable to those obtained in the isopropyl case and cyclohexylisonitrile was identified in the product mixture.

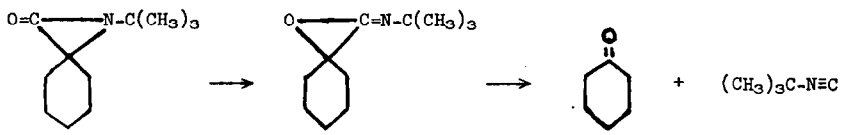
This novel cleavage of carbodiimides has no preparative applications, both isonitriles and N-organodichloroazomethines being more easily accessible by other routes. The mechanism of this new reaction remains unknown. Some qualitative aspects, however, are worth commenting on. The mercurial-carbodiimide reaction appears to occur much more rapidly than does the cyclopropanation of olefins by phenyl(trihalomethyl)mercury compounds. Qualitatively the mercurial-carbodiimide reaction resembles the reaction occurring between these organomercury reagents and triphenylphosphine[9], which also

proceeds very rapidly. The reaction of phenyl(bromodichloromethyl)mercury with cyclooctene does not involve a bimolecular reaction between mercurial and olefin[10]. However, we suggest that stronger nucleophiles than simple olefins may react directly with the mercurial in a bimolecular reaction with a transition state resembling that suggested for the iodomethylzinc iodide-olefin reaction by Simmons et al.[11]. In the case of the very rapid mercurial-carbodiimide reaction a course as outlined below could be followed.



A similar course appears to be followed in the reaction of azobenzene with phenyl(bromodichloromethyl)mercury, since N-phenyldichloroazomethine was the principal product isolated.[12]

The cleavage reaction observed in the present study bears a striking resemblance to the decomposition of 1-t-butyl-3,3-pentamethyleneaziridinone[13] which is believed to proceed via an intermediate oxirane.



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(4) Anal. [found(calcd.)]: C 34.15(34.32); H 5.14(5.04); N 10.09(10.00); Cl 50.53(50.64). NMR (CCl_4): doublet (6H) at 1.2 p.p.m. and multiplet (1H) at 3.8 p.p.m. downfield from TMS. IR (CCl_4): 2985(s), 2940(w), 2915(w), 2870(w), 1770(m), 1660(s), 1650(sh), 1475(w), 1465(w), 1395(m), 1380(m), 1355(m), 1130(m), 882(s), 680(m), 615(m) cm^{-1}. These spectra were identical with those of an authentic sample prepared by chlorination of isopropyl isothiocyanate using the procedure of R.S. Bly, G.A. Perkins and W.L. Lewis, J. Amer. Chem. Soc. 44, 2896 (1922).

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(6) Anal. [found(calcd.)]: C 69.54(69.51); H 11.00(10.21). IR (CCl_4): 2955(s) 2920(s), 2845(m), 2310(w), 2130(s), 1485(s), 1470(sh), 1410(s), 1385(s), 1355(s), 1160(s), 1120(s), 910(s) cm^{-1}.

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