Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

A convenient organomercury CH_2 transfer system

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(Received April 24th, 1972)

In a recent communication[1], Scheffold and Michel have reported that benzyl(iodomethyl)mercury, $PhCH_2HgCH_2I$, transfers CH_2 to olefins, producing cyclopropanes, at a substantially faster rate than do the previously reported[2] mercury-based CH_2 transfer systems, the reagent pairs $Hg(CH_2Br)_2 + Ph_2Hg$ and $ICH_2HgI + Ph_2Hg$. This variation of our basic CH_2 transfer process was recommended as an improved procedure for the preparation of cyclopropanes by the organomercury route. However, the $PhCH_2HgCH_2I$ used by these authors was prepared by the reaction of diazomethane with benzylmercuric iodide. Diazomethane is both toxic and potentially explosive[3], and one is perforce restricted to small-scale preparation of the required mercurial reagent (a 10 mmol preparation is described[1]). It is the purpose of the present communication to point out that by making use of some new and some long-known organomercury chemistry, one may derive the rate-accelerating benefits of the benzyl substituent and at the same time avoid the use of the potentially hazardous diazomethane and its irritating (and possibly carcinogenic[4]) precursors.

Bis(iodomethyl)mercury now can be prepared easily and in good yield by the reaction of iodomethylzinc iodide with a mercuric halide in THF[5,6]. (The method of choice is described in ref. 6). The well-known facility with which substituent redistribution occurs in mercury systems[7] provides the basis for its effective utilization in cyclopropane synthesis. By itself, bis(iodomethyl)mercury reacts as rapidly with olefins as does $PhCH_2HgCH_2I$. Thus when $Hg(CH_2I)_2$ (8.3 mmol) was heated at 85° in cyclooctene (20 ml) under nitrogen, the yield of the expected bicyclo[6.1.0]nonane was 43% after 1 h, 78% after 2 h and 98% after 6 h. These yields, however, are based on the utilization of only one of the two CH_2 groups of $Hg(CH_2I)_2$. Transfer of the second CH_2 was much slower (25% after 20 h further reaction time), possibly because of the insolubility of ICH_2HgI.

As we have shown[2], ICH_2HgI can be caused to transfer its CH_2 to olefins by the addition of one molar equivalent of diphenylmercury to the reaction mixture by virtue of the reaction sequence shown in eqns. 1 and 2. However, the CH_2 transfer reaction is

$$ICH_2HgI + Ph_2Hg \longrightarrow PhHgI + PhHgCH_2I \qquad (1)$$

$$PhHgCH_2I \longrightarrow \frac{1}{2} Ph_2Hg + \frac{1}{2} Hg(CH_2I)_2 \qquad (2)$$

relatively slow. When 10 mmol each of ICH_2HgI and Ph_2Hg in 20 ml of cyclooctene were heated at 85°, the bicyclo[6.1.0] nonane yield was 28% after 3 h, 42% after 6 h, 59% after 12 h and 76% after 23 h. In marked contrast, in a similar reaction in which dibenzylmercury was used in place of diphenylmercury, the rate of bicyclo[6.1.0] nonane formation was considerably faster: 30% yield after 1 h, 60% after 2 h, 69% after 4 h and 75% after 6 h. In this reaction, benzylmercuric iodide was isolated in good purity in 80% yield. The iodomethylmercuric iodide used in such reactions may be prepared by melting and heating on the steam bath an equimolar mixture of bis(iodomethyl)mercury and mercuric iodide until the red color of the latter is discharged. Alternatively, a reaction of equimolar quantities of bis(iodomethyl)mercury and dibenzylmercury with an excess of cyclooctene also served well in the preparation of bicyclo[6.1.0] nonane. Although the initial rate was somewhat slower than that observed with the $ICH_2HgI/(PhCH_2)_2Hg$ reagent pair, a 75% yield of bicyclo[6.1.0] nonane was obtained within 7 h. A further possibility to be tested is the synthesis of $PhCH_2HgCH_2I$ by the reaction of ICH_2ZnI with benzylmercuric halide, although we see no special advantage in this.

Our previous study[2] made it quite clear that the reactions between monohalomethylmercury compounds and olefins do not proceed by way of a free CH_2 intermediate and that the rate of reaction depends upon the nucleophilicity of the olefin used. The results of Scheffold and Michel[1] confirm the latter point.

Monohalomethylmercury compounds have and will continue to have only limited utility in the synthesis of cyclopropanes from olefins, especially in view of the recent improvements relating to the generation of iodomethylzinc iodide[8-10] which is the more generally applicable reagent. In those cases where the zinc reagent cannot be used, the reagent systems based on $Hg(CH_2I)_2/(PhCH_2)_2Hg$ or $ICH_2HgI/(PhCH_2)_2Hg$ which we describe here may serve with advantage. Our studies in this area are continuing.

ACKNOWLEDGMENTS

The authors are grateful to the U.S. Air Force Office of Scientific Research (NC)-OAR (Grant AF-AFOSR-72-2204) for generous support of this research and to the National Science Foundation for a fellowship to C.K.H.

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