FACILE GENERATION OF ALKYL RADICALS BY THE PALLADIUM
ON CARBON CATALYZED THERMOLYSIS OF ALKYLMERCURIALS[1]

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Dibenzylmercury was completely decomposed within 20 min in re-
fluxing xylene in the presence of a catalytic amount of 5%
palladium on carbon, giving mercury and dibenzyl. The generation
of benzyl radicals was confirmed by the formation of 1,3-adduct
to α-phenyl-N-benzylnitrone and 9,10-adduct to anthracene. Other
alkylmercurials showed a similar but less satisfactory result.

Dibenzylmercury (DBM) and other organomercurials have been known to generate
free radicals either by photolysis or thermolysis.[2] The thermolysis reaction
conditions are, however, too severe to be used as a source of free radicals and
only a few examples of their free radical addition reactions are known to date.
Bass, for example, reported that benzyl radicals generated from DBM at 190 °C
reacted with anthracene to give 9,10-dibenzyl-9,10-dihydroanthracene and other
adducts in low yield.[3a] Pyrolysis of DBM in phenetole led to the 52% decompo-
sition of DBM in 2 h at 141 °C.[3b] We have found that, in the presence of a
catalytic amount of 5% palladium on carbon, DBM is decomposed much faster under
milder reaction conditions, and wish to report here this decomposition of organo-
mercurials as a convenient method for generation of free radicals.[4]

When a xylene solution of DBM (100 mg, 0.23 mmol) was heated at 140 °C with
4 mg of 5% palladium on carbon, DBM was completely decomposed in 20 min to give
debenzyl and metallic mercury as the only reaction products. In the absence of
the Pd-C catalyst, DBM was recovered unchanged (100%) under these reaction condi-
tions. When 0.4 mg of palladium acetate was added in place of the Pd-C, 50-
60% of DBM was decomposed. The effects of 5% platinum, rhodium and ruthenium
supported on carbon were examined. Neither rhodium nor ruthenium on carbon showed
any noticeable catalytic effect on the decomposition of DBM. Platinum on carbon
decomposed DBM to the same extent as Pd-C, but a certain amount of reduction
of the benzene ring took place at the same time. So far, the decomposition by
Pd-C catalyst gave the most satisfactory and reproducible results, and the amount
of Pd-C could be reduced down to 1,5 mg to effect 100% decomposition. At the
temperature lower than 140 °C, the rate of decomposition was considerably retarded,
although, even in refluxing benzene, 22% of DBM was decomposed in 5h. The results
are summarized in Table 1.

The generation of benzyl free radicals was confirmed by the formation of 1,3-

Table 1. Thermal Decomposition of Dibenzylmercury
in the Presence of Catalysts[a]

Catalyst[b]	Conditions	% Decomposition	
		From Hg[c]	From NMR[d]
Pd-C	Xylene/ 140 °C/ 20 min	91	100
Pd(OAc)$_2$		52	62
Pt-C		83	100
Rh-C		+[e]	5
Ru-C		+[e]	10
None		0	0
Pd-C	Xylene/ 110 °C/ 1 h	20	29
Pd(OAc)$_2$		11	13
Pt-C		8	9
Pd-C	Benzene/ 80 °C/ 5 h	15	22
Pd(OAc)$_2$		0	10
Pt-C		+[e]	0[f]

a) In a typical experiment, a mixture of DBM (100 mg, 0.26 mmol)
   and the catalyst in 10 ml of the solvent was heated. The amounts
   of the catalysts were; 4-5 mg each of Pd-C, Pt-C, Rh-C, and Ru-C,
   and 0.3-0.4 mg of Pd(OAc)$_2$.
b) 5% Pd-C, Pt-C, Rh-C and Ru-C, supplied by Nippon Engelhard Co.,
   were used.
c) Because of the deposit of mercury on the upper part of the
   reaction flask and it's dispersion in carbon, it was always
   weighed lower.
d) Calculated from the ^{1}H NMR of dibenzyl and DBM.
e) Could not be determined.
f) A certain amount of the reduction of benzene ring took place.

adduct $\underset{\sim}{2}$ from the reaction with α-phenyl-N-benzylnitrone $\underset{\sim}{1}$ (Scheme 1).[5] Nitrones
are known to react with free radicals to give 1,3-adduct via nitroxides.[6] In the
presence of $\underset{\sim}{1}$, DBM gave $\underset{\sim}{2}$ (R=CH$_2$Ph) in 62% yield. Other dialkylmercurials such as
di-n-propyl, diisopropyl, diisobutyl and di-sec-butylmercury were decomposed in
the presence of $\underset{\sim}{1}$ and their degree of decomposition was determined by the reaction
products and the amount of the deposited mercury. In some cases, new nitrone $\underset{\sim}{3}$
and/or hydroxylamine $\underset{\sim}{4}$ were obtained. They are considered to be formed by the
known disporportionation reaction of the intermediate nitroxides. The results
are given in Table 2. The lower yield of the adduct $\underset{\sim}{2}$ from the dialkylmercurials
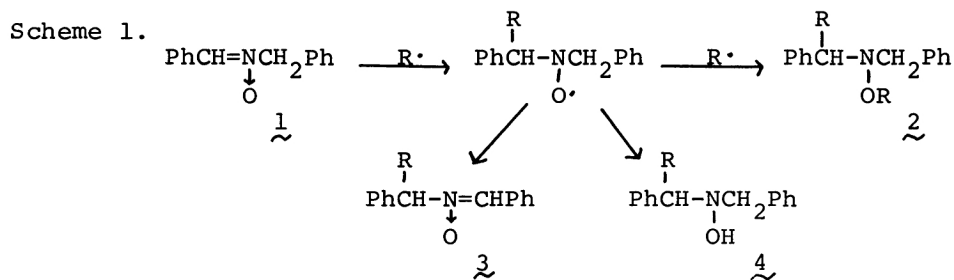compared to DBM could be explained by the lower stability of the free radicals

Scheme 1.

PhCH=NCH$_2$Ph $\xrightarrow{\text{R·}}$ PhCH-NCH$_2$Ph $\xrightarrow{\text{R·}}$ PhCH-NCH$_2$Ph
                                  | |
                                  O·   OR

with R above both middle and right structures; arrows branch from O· to:

PhCH-N=CHPh   PhCH-NCH$_2$Ph
     ↓ |
     O   OH

$\underset{\sim}{1}$ $\underset{\sim}{3}$ $\underset{\sim}{4}$ $\underset{\sim}{2}$

Table 2.   Products of Reactions of R_2Hg with $\underset{\sim}{1}$[a]

R	1,3-Adduct $\underset{\sim}{2}$ (%)	Nitrone $\underset{\sim}{3}$ (%)	Hydroxylamine $\underset{\sim}{4}$ (%)	Hg (%)
PhCH$_2$	62	—	—	92
s-C$_4$H$_9$	21	16	—	95
i-C$_4$H$_9$	—	1	—	60
n-C$_3$H$_7$	—	3	—	72
i-C$_3$H$_7$[b]	18	15	6	97

a)   In a typical run, nitrone 1 (0.01 mol), R_2Hg (0.01 mol) and 5%
      Pd-C (50 mg) in xylene (30 ml) at 140 °C for 3 h.
b)   At 80 °C in benzene.

generated from them.   In the presence of $\underset{\sim}{1}$ and absence of palladium catalyst,
the decomposition of all the dialkylmercurials required much longer reaction time
than the decomposition of the dialkylmercurials alone.   The nitrone seems to have
a stabilizing effect on these dialkylmercurials.   No direct interaction between
the dialkylmercurials and $\underset{\sim}{1}$ was suggested by the NMR and IR spectra.   When DBM
was allowed to react with an equimolar amount of anthracene in the presence of
Pd-C catalyst at 140 °C in xylene, 9,10-dibenzyl-9,10-dihydroanthracene was
obtained in 33% yield together with small amounts of 9,10-dibenzylanthracene and
10,10'-dibenzyl-9,9',10,10'-terahydro-9,9'-bianthryl.   This result also confirmed
the free radical generation from the thermolysis of DBM catalyzed by palladium
on carbon.

     For the generation of alkyl radicals, it would be more convenient if this
method could be applied to alkylmercuric halides which are mostly solid, stable
and easier to handle.   With 30 mg of Pd-C, benzylmercuric chloride (1.0 g, 3.1 mmol)
in 10 ml of xylene was heated at 140 °C for 1 h to give the metallic mercury in
ca. 90% yield.   As the reaction products, benzyl chloride and dibenzyl were obtained
by the ratio of 4:1.   In the presence of an equimolar amount of $\underset{\sim}{1}$, benzyl chloride
(34%) and 1,3-adduct $\underset{\sim}{2}$ (38%) were obtained.   No dibenzyl was found in the reaction
mixture.   When 4 mmol of isopropylmercuric bromide or sec-butylmercuric chloride
was heated with an equimolar amount of $\underset{\sim}{1}$ and 50 mg of Pd-C in xylene at 140 °C,
60-80% of these mercurials were decomposed after 3 h giving the small amount of
1,3-adduct and the metallic mercury.   Organomercury(II) halides are usually said
to provide mercury(I) halide and radical-derived products on photolysis and thermo-
lysis.[7]   On the other hand, Inamoto and Yoshifuji have reported that the thermolysis
of alkylmercuric chlorides at 230-265 °C under reduced pressure gave alkyl chloride
and mercury in good yields.[8]   Although there is a difference in the reaction
conditions, our results were in an agreement with Inamoto's findings.   The improve-
ment of the reaction conditions is now attempted.

     The palladium on carbon catalyzed reactions described above are presumed to
proceed through the electron transfer from the dialkylmercurials to Pd(II) followed
by cleavage to R· and RHg^+.   Reduced reactivity of alkylmercuric halides would be

ascribed to the higher electronegativity of the halogen atoms. A detailed mechanistic study is in progress.

References
1) Presented at the annual meeting of Chemical Society of Japan, April, 1983
    in Kyoto.
2) J. L. Wardell, "Comprehensive Organometallic Chemistry", ed by G. Wilkinson,
    F. G. A. Stone and E. W. Abel, Pergamon Press, New York, Vol. 2, Chap. 17, (1982).
3) a) K. C. Bass and P. Nababsing, J. Chem. Soc., 1965, 4396;
    b) K. C. Bass and G. M. Taylor, ibid.(B),   1970, 1615.
4) Transition metal-catalyzed decomposition of organomercurials is not without
    precedents. Finely divided nickel, palladium, platinum, copper, gold and
    silver metals have proven useful for effecting the thermal decomposition to
    give the dimerization products due to a number of organomercurials. However,
    these reactions require more drastic conditions than ours and no external
    trapping of the free radicals has been made. (G. A. Razuvaev and M. M. Koton,
    Zh. Obshch. Khim., 4, 647 (1934)).
5) CIDNP experiments were carried out without success. Spinning of the NMR
    sample tube was not able to prevent the catalyst from precipitating out of the
    solution.
6) M. Iwamura and N. Inamoto, Bull. Chem. Soc. Jpn., 43, 856 and 860 (1970).
7) M. M. Koton and F. S. Florinskii, Zh. Obshch. Khim., 9, 2196 (1939); V. Weinmayr,
    J. Am. Chem. Soc., 81, 3590 (1959).
8) N. Inamoto and M. Yoshifuji, Bull. Chem. Soc. Jpn., 43, 2574 (1970).