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

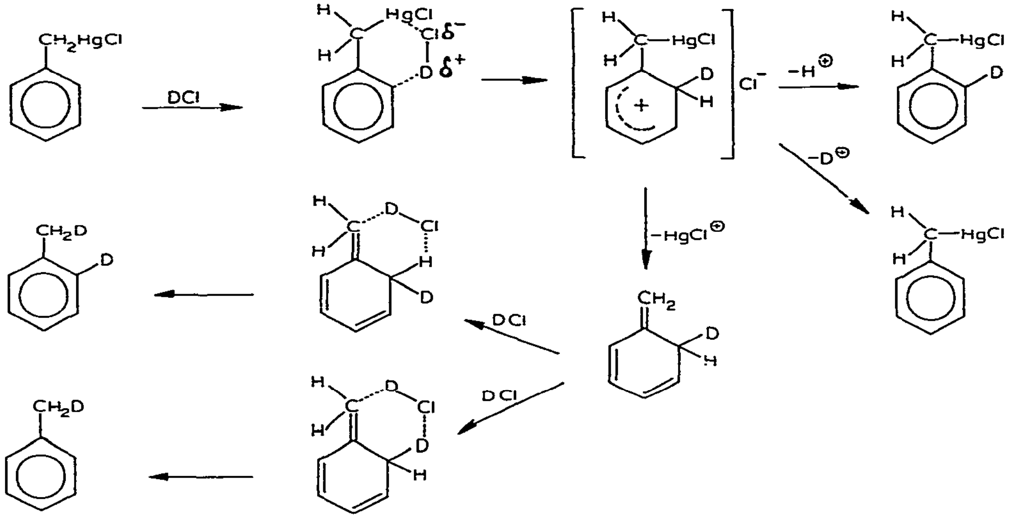
NOTE

ABNORMAL ACETYLDEMERCURATION OF BENZYLMERCURY CHLORIDE

YU. G. BUNDEL, V. I. ROZENBERG, A. L. KURTS, N. D. ANTONOVA AND O. A. REUTOV
Moscow State University, Department of Chemistry, Moscow, (U.S.S.R.)

(Received April 10th, 1969)

Acidic cleavage of benzylmercury chloride by deuterium chloride has been shown to involve two competitive reactions: deuterodemercuration with transfer of the reaction center, resulting in a mixture of deuterotoluenes (α-*d*-mono- and α-*d*,*o*-*d*-dideuterotoluenes), and a hydrogen isotope exchange reaction in the organomercury compound giving rise to $PhCH_2HgCl$ with deuterium exclusively in the *ortho*-position of the benzene nucleus[1]. The presence of deuterium in the *ortho*-position in the products of both reactions enables demercuration and isotope exchange to be discussed in terms of the combined mechanisms:



A detailed analysis of the reaction products demonstrated the almost complete absence of "normal" attack at the α-carbon.

In the protodemercuration of $PhCH_2HgCl$ labelled with deuterium in the *ortho*-position, no intramolecular deuterium migration from the *ortho*- to the α-position in the methylenecyclohexadiene structure suggested was observed during its stabilization. Hanstain and Traylor adopted a similar scheme for their protolysis of benzylboric acids[2].

The electrophilic and steric properties of the reagent define whether the attack is directed at the *ortho*- or the *para*-position in the benzene ring, or at the exocyclic carbon. For elucidation of common dependencies characterizing the reaction center transfer in benzylmercury derivatives, investigation of another model reaction—acylation of benzylmercury chloride by acetyl chloride in the presence of aluminium bromide—has been initiated by the present authors. Recently, Kurts *et al.*[3] showed that aromatic and aliphatic mercury derivatives can be smoothly acylated by acid chlorides, in the presence of aluminium bromide, into unsymmetrical ketones.

Acetyldemercuration of benzylmercury chloride was carried out in methylene chloride under a dry argon atmosphere at different reagent ratios, and at a temperature between −20 and −40° (Table 1). Chromatographic analysis of the DNPH* derivatives of ketones resulting from this reaction shows two carbonyl compounds containing no mercury: *p*-tolylmethyl-ketone (I) and -diketone (II) containing (according to elementary analysis of its DNPH) two acetyl groups.

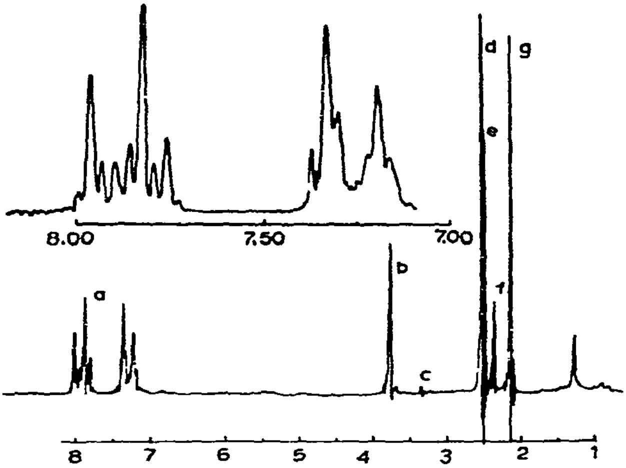


Fig. 1. PMR spectrum of the reaction products of benzylmercury chloride with acetyl chloride in the presence of $AlBr_3$ (ratio 1/2.5/2.5) (Jeol C-60-HL).

The structure of diketone (II) and the quantitative ratio of mono- and diketones and unreacted $PhCH_2HgCl$ were determined by means of proton magnetic resonance. A typical spectrum of the reaction products is shown in Fig. 1. The spectrum contains: signal (a) within 7.10–8.10 ppm, its multiple structure being characteristic of the *para*-substituted benzene ring where the substituents differ sharply in their electronegativities; signal (b) with chemical shift of the methylene protons in CH_2COCH_3 (I) of diketone (II) 3.75 ppm; and also four singlet signals: (d) (δ 2.52 ppm), (e) (δ 2.50 ppm), (f) (δ 2.37 ppm) and (g) (δ 2.13 ppm) within the absorption range of the methyl groups, which may be assigned, respectively, to the $COCH_3$ protons in diketone (II) and ketone (I), to the CH_3 protons in ketone (I),

---

* DNPH = dinitrophenylhydrazine.

and to the methyl protons of CH_2COCH_3. Signal (c) (δ 2.97 ppm) coinciding with that of the methylene protons in benzylmercury chloride was also found*.

Relative signal intensities obtained by the electronic integration method support the validity of the signal assignment and establishes that at 5% accuracy the reaction products contain exclusively *p*-tolylmethylketone (I) and *p*-acetylbenzylmethylketone (II).

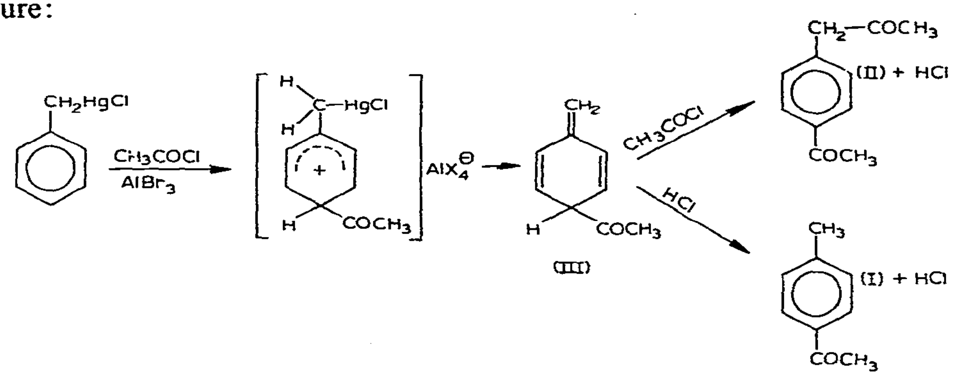
Signal interpretation in the absorption range of the aromatic protons shows that it is a superimposition of two AA'BB' spectra which may be referred, respectively to the proton systems in both diketone (II) and ketone (I). Analysis within A_2X_2 approximation leads to the following chemical shifts and spin–spin coupling constants: diketone (II) $\delta_A = 7.89$ ppm, $\delta_B = 7.26$ ppm, $J_{AB} = 8.5 \pm 0.1$ Hz; ketone (I), $\delta_A = 7.81$ ppm, $J_{AB} = 8.2 \pm 0.1$ Hz**.

TABLE 1

PRODUCT'S RATIO IN ACETYLDEMERCURATION OF BENZYLMERCURY CHLORIDE ($AlBr_3$ AS CATALYST)

$PhCH_2HgCl/CH_3COCl/AlBr_3$			Time (h)	°C	Ketone/Diketone/$PhCH_2HgCl$ (I)	(II)	
1	1	1	1	−30	1	2	0.42
1	2.5	2.5	2	−20	1	3	traces
1	5	1	2	−40	1	5.5	3.3

The ratio of mono- and diketones observed, and, specifically, (II) being the major reaction product even with an equimolar reagent ratio, suggests that (I) is a result of the primary formation of (II) in the stabilization of the methylcyclohexadiene structure:



This scheme assumes that there are two consecutive–parallel reactions where the hydrogen halide required for a synthesis of (I) is generated probably in the reaction of III with acetyl chloride. The mechanism suggested explains the larger quantity of diketone (II) in the reaction products.

Other known examples of abnormal reactions of benzyl derivatives of organo-

---

* The signal at 1.25 ppm belongs to some unidentified impurity.

** For a solution of pure *p*-methylacetophenone these values are: $\delta_A \approx 7.82$ ppm, $\delta_B = 7.20$ ppm, $J_{AB} = 8.4 \pm 0.1$ Hz.

EXPERIMENTAL

metallic compounds leading to a mixture of mono- and di-substituted products are the interactions of aldehydes and chloromethyl ether with benzylmagnesium halides[4-9].

Acetyldemercuration of benzylmercury chloride in the presence of $AlBr_3$

Experiments were carried out in an atmosphere of pure dry argon.

$PhCH_2HgCl$ (0.44 g, 0.0013 mole) and CH_3COCl (0.26 g, 0.0033 mole) were dissolved in 15 ml of CH_2Cl_2 cooled to $-20°$ and $AlBr_3$ (0.89 g, 0.0033 mole) was added. The mixture was stirred at this temperature for 2 h and decomposed with dilute HCl; the organic layer was washed with water, $NaHCO_3$ solution and saturated NaCl solution and dried over $MgSO_4$. After evaporation of CH_2Cl_2, the residue was dissolved in a standard amount of CH_2Cl_2. The quantitative ratios of ketone (I) to diketone (II) to unreacted $PhCH_2HgCl$ were determined from the PMR spectra.

Chromatographic analysis of the DNPH derivatives of the reaction mixture carried out on alumina (second activity grade) in systems of different polarities showed only two carbonyl compounds. In benzene/ethylacetate (19/1), $R_{F1}=0.7$; $R_{F2}=0.33$. This system was used in the preparative separation of the DNPH derivatives of (I) and (II); the DNPH derivative of (I) has m.p. 256°, and shows no depression with the DNPH derivative of *p*-tolylmethylketone; the DNPH derivative of (II) has m.p. 241°. (Found: C, 51.54; H, 3.96; 3.76. $C_{23}H_{20}N_8O_8$ calcd.: C, 51.48; H, 3.74%.)

REFERENCES

1 Yu. G. Bundel, N. D. Antonova and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, 166 (1 66) 1103.
2 W. Hanstein and T. G. Traylor, *Tetrahedron Letters*, 45 (1967) 4451.
3 A. L. Kurts, I. P. Beletskaya, I. A. Savchenko and O. A. Reutov, *J. Organometal. Chem.*, 17 (1969) P21.
4 R. A. Benkeser and T. E. Johnston, *J. Amer. Chem. Soc.*, 88 (1966) 2220
5 R. A. Benkeser and W. De Talvo, *J. Amer. Chem. Soc.*, 89 (1967) 2141.
6 J. Schmidlin and A. Garcia-Banus, *Ber.*, 45 (1912) 3193
7 W. G. Young and S. Siegel, *J. Amer. Chem. Soc.*, 66 (1944) 354.
8 L. Malm and L. Summers, *J. Amer. Chem. Soc.*, 73 (1951) 362.
9 S. Siegel, W. M. Boyer and R. R. Jay, *J. Amer. Chem. Soc.*, 73 (1951) 3237.