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The Reductive Coupling of Organic Halide Using Hydrazine and a Palladium Catalyst. II.[1] Homocoupling of 1-Iodoalkanes

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Synopsis. The hydrogenolysis and dimerization of iodoalkanes were catalyzed by Pd in the presence of an appropriate reducing agent. Hydrazine was found to be effective for the coupling of 1-iodoeicosane to give tetracontane, $C_{40}H_{82}$, in a 74% yield. The yield of the coupling product decreased with the decrease of the number of the carbon atoms in the 1-iodoalkanes. Both alkylhydrazines and alkenes were shown not to take part in the reaction as a reaction intermediate.

We reported[1,2] that iodoarenes were converted to the corresponding biaryls in high yields by the use of a catalytic amount of palladium amalgam. No report has been published on the coupling of haloalkanes by the use of a catalytic amount of metal. Stille and Lau[3] reported that the reactive haloalkanes such as 9-bromofluorene were coupled with a stoichiometric amount of a palladium(0) complex. The present study has, therefore, been carried out in order to examine the homocoupling of the inert haloalkanes by the use of a catalytic amount of palladium metal or its salts. The higher iodoalkanes gave the corresponding bialkyls in high yield.

Results and Discussion

As shown in Table 1, 1-iodoalkanes reacted with hydrazine in the presence of catalytic amounts of palladium salt to produce coupling products. The highest yield was obtained in the case of 1-iodoeicosane. Palladium chloride was reduced in the initial stage of the reaction to give the metal, and the palladium metal formed was quantitatively recovered after the reaction. The coupling of iodoalkanes was examined with a catalytic amount of palladium metal in place of its salt to give the corresponding dimers in low yield (Eqs. 1 and 2).

$$2RI + Pd \longrightarrow RR + PdI_2 \tag{1}$$

$$PdI_2 + NH_2NH_2 \longrightarrow Pd + 2HI + N_2 + H_2 \tag{2}$$

Table 1. Reductive homocoupling of 1-iodoalkanes using hydrazine and palladium catalyst[a)]

Iodoalkane	Coupling product	Yield/%[b)]
1-Iodohexane	Dodecane	0.7
1-Iodooctane	Hexadecane	5.4
1-Iododecane	Eicosane	7.9
1-Iodododecane	Tetracosane	14.8
1-Iodotetradecane	Octacosane	33.9
1-Iodotetradecane	Octacosane	44.5[c)]
1-Iodohexadecane	Dotriacontane	40.3[d)]
1-Iodooctadecane	Hexatriacontane	47.2[d)]
1-Iodoeicosane	Tetracontane	55.3[d)]
1-Iodoeicosane	Tetracontane	74.2[c,d)]

a) A reaction mixture of iodoalkane(25.0 mmol), NaOH (125 mmol), and $PdCl_2$(2.5 mmol) in 16 ml of MeOH containing of 85% $NH_2NH_2 \cdot H_2O$(15 mmol) was refluxed for 6 h. b) Yield determined by GLPC. c) The 1.5-fold amounts of NaOH and 85% $NH_2NH_2 \cdot H_2O$ were used. d) Yield of the crude product.

To determine the products and the effect of hydrazine on the present reaction, the reaction involving 1-iodotetradecane(**1**) was examined, as shown in Table 2. The reaction products consisted of 1-methoxytetradecane(**2**), 1-tetradecene(**3**), tetradecane(**4**), and octacosane(**5**). The distribution of these products was strongly affected by the presence or absence of palladium and/or hydrazine. The highest yield of the dimer was obtained in the reaction with 85% hydrazine hydrate. In the absence of the catalyst, the methanolysis of iodoalkane occurred, and the hydrogenolysis and dimerization did not. No hydrazine was necessary for the coupling of iodoalkanes, in contrast with that of iodoarenes.[1]

The facts that an alkylhydrazine($RNHNH_2$) was prepared with anhydrous hydrazine and haloalkane[4] and that its decomposition produced the corresponding alkanes (RH and RR)[5] indicate that the reaction *via* alkylhydrazine derivative might be involved in the present system. Several results which exclude this are as follows: (1) The yield of **5** with tetradecylhydrazine (Run 4) was lower than that with hydrazine hydrate (Run 2)[6] and (2) No reaction of hydrazine hydrate with **1** occurred.

Since the reaction with methylhydrazine (Run 3) gave **3** in 46.4% yield, the dimerization of **3** was examined. Its intermediate may be denied from the following results: (1) No octacosene was detected (Run 2), and (2) No reductive coupling of **3** occurred under the experimental conditions in Run 2 except **1**, because **3** was quantitatively recovered.

It is consequently concluded that the coupling of

Table 2. Effect of reducing agent on the reductive homocoupling of 1-iodotetradecane by the use of palladium chloride as catalyst[a)]

Run	Reducing agent	Products/%[b)]			
		2	**3**	**4**	**5**
1	None	11.0	15.1	59.8	13.3
2	85% $NH_2NH_2 \cdot H_2O$	12.2	19.5	36.4	33.9
3	CH_3NHNH_2	0.0	46.4	48.9	3.3
4	n-$C_{14}H_{29}NHNH_2$	5.1	44.1	99.5	8.0
5	$C_6H_5NHNH_2$	36.3	13.4	50.8	Trace

a) A mixture of **1**(25.0 mmol), $PdCl_2$(2.5 mmol), and NaOH(125 mmol) in 16 ml of MeOH containing the reducing agent(15 mmol) was refluxed for 6 h with stirring. b) Based on the iodoalkane.

1-iodoalkanes with hydrazine may not proceed through the hydrazine derivative and the alkene. Presumably, the hydrogenolysis and dimerization of 1-iodoalkanes proceed *via* an alkylpalladium complex, and the hydrazine used is consumed for reducing the palladium iodide formed.

Experimental

Materials. The reagents used were of commercial grade except of 1-iodooctane,7) 1-iododecane,7) 1-iodododecane,7) 1-iodotetradecane(**1**),7) 1-iodohexadecane,7) 1-iodooctadecane7) (mp 34.2—35.0 °C, lit,8) 33.7—34.1 °C), 1-iodoeicosane7) (mp 39.5—40.0 °C, lit,8) 41.3—41.6 °C). Anhydrous hydrazine9) was prepared by the methods given in the literature. The purity of all iodoalkanes determined by GLPC was over 98%.

Preparation of Tetradecylhydrazine(a New Compound): A mixture of anhydrous hydrazine (13 g, 0.38 mol), 1-bromotetradecane (21 g, 0.072 mol), and ethanol (15 ml) was refluxed with a magnetic stirrer for 35 h in a flask equipped a reflux condenser with a drying tube. The mixture was cooled until room temperature and then poured into water (50 ml) of 7 g of sodium hydroxide. The solid products and the ether-extractable materials were combined, and distilled under reduced pressure in a nitrogen atmosphere, giving 8.65 g (52%) of the hydrazine: bp 185—188 °C/1.5 kPa; white crystals, mp 40.5—42.0 °C. This melting point agreed closely with the value interpolated from the results of Westphal4) for dodecylhydrazine (31 °C) and hexadecylhydrazine (57—58 °C). This new hydrazine was identified with maleic acid derivative. The *cis*-2-butenedioic dihydrazide showed: mp 116.5—117.3 °C; Found: C, 69.87; H, 10.60; N, 9.11%. Calcd for $C_{18}H_{32}N_2O_2$: C, 70.09; H, 10.46; N, 9.08%. Since the free hydrazine slowly decomposed in air, it was prepared before every use.

Reductive Coupling of 1-Iodoalkane Using Hydrazine and Palladium Catalyst. A mixture of 1-iodoalkane (25.0 mmol), NaOH (125 or 188 mmol), and $PdCl_2$ (2.5 mmol) in 16 ml of MeOH containing 85% $NH_2NH_2 \cdot H_2O$ (15 or 22.5 mmol) was refluxed for 6 h with stirring. The resulting mixture was filtered, and the residual metal was washed with hexane, and subsequently water. The organic layer was separated from the aqueous layer and evaporated. The yield of dimer was determined by GLPC. The dimers having more than twenty-eight carbon atoms were separated as a residue in the vacuum distillation using the Büchi Kugelrohrofen GRK-50, weighed, and recrystallized from hexane–methanol. Dotriacontane: mp 66.7—67.5 °C (lit,10) 69.5—70.6 °C); Found: C, 85.38; H, 14.81%. Calcd for $C_{32}H_{66}$: C, 85.24; H, 14.76%. Hexatriacontane: mp 72.5—73.3 °C (lit,10) 75.2—76.1 °C); Found: C, 85.20; H, 14.91%. Calcd. for $C_{36}H_{74}$: C, 85.29; H, 14.71%. Tetracontane: mp 78.8—79.5 °C (lit,8) 81.2—81.4 °C); Found: C, 85.20; H, 14.82%. Calcd. for $C_{40}H_{82}$: C, 85.32; H, 14.68%.

Reductive Coupling of 1-Iodotetradecane with Various Reducing Agents. A mixture of **1** (25.0 mmol), $PdCl_2$ (2.5 mmol), and NaOH (125 mmol) in 16 ml of MeOH containing the reducing agent (15 mmol) was stirred for 6 h under reflux. The resulting mixture was filtered, and the residual metal was washed with hexane and then with water. After the organic layer was separated from the aqueous layer, the reaction products were obtained by the evaporation of the solvent, and analyzed by GLPC and GC-MS. Since both **3** and **4** gave an overlapped peak on the column used (SE-30), the peak of **3** was separated from that of **4** by brominating **4** with a bromine–tetrachloromethane solution, followed by the estimation of **4**. Octadecane and eicosane were used as the internal standards.

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References

1) Part I: R. Nakajima, Y. Shintani, and T. Hara, *Nippon Kagaku Kaishi*, **1981**, 249.

2) R. Nakajima, Y. Shintani, and T. Hara, *Bull. Chem. Soc. Jpn.*, **53**, 1767 (1980).

3) J. K. Stille and K. S. Y. Lau, *J. Am. Chem. Soc.*, **98**, 5841 (1976).

4) O. Westphal, *Ber.*, **74**, 759 (1941).

5) L. P. Kuhn, *J. Am. Chem. Soc.*, **73**, 1510 (1951).

6) In order to correct the amounts of the decomposition products of tetradecylhydrazine, an experiment was done under the same conditions as in Run 4 (Table 2) except for the absence of **1**; the decomposition products were different from those in Run 4: **3**(12.6%), **4**(62.4%), **5**(3.5%), and tetradecylamine (19.5%). This means that no correction is possible for the decomposition products of tetradecylhydrazine.

7) H. Stone and H. Shechter, *Org. Synth.*, Coll. Vol. IV, 323 (1963).

8) H. J. Becker and J. Strating, *Rec. Trav. Chem.*, **59**, 933 (1940).

9) L. I. Smith and K. L. Howard, *Org. Synth.*, **24**, 53 (1944).

10) Y. Abe, Y. Nakamura, A. Iwasaki, and N. Ono, *Yukagaku*, **20**, 224 (1971).