BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (3), 953—954 (1979)

The Modified Wurtz Reaction Using Tetrakis(*p*-dimethylaminophenyl)ethylene

Yuji MIYAHARA,* Takanari SHIRAISHI, Takahiko INAZU,
and Tamotsu YOSHINO
Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashi-ku, Fukuoka 812

(Received September 4, 1978)

Synopsis. The Wurtz reaction has been found to be catalyzed by easily removable tetrakis(*p*-dimethylaminophenyl)ethylene. This modification facilitated the separation of products in the syntheses of [2.1.2.1.]-, [2.2.2.2]-, and [3.2.3.2]paracyclophanes, the isolated yields of which were better than in the case of tetraphenylethylene.

The Müller-Röscheisen modification of the Wurtz reaction using tetraphenylethylene(TPE)[1] has been used extensively, especially in the synthesis of cyclophanes.[2] Although the reaction has been claimed to be catalytic, TPE is gradually consumed and 1,1,2,2-tetraphenylethane **1** is formed as a reduction product. Separation of the desired cyclophanes from TPE and **1** is often troublesome owing to a similarity in properties. For the practical synthesis of cyclophanes an easily removable substitute for TPE is desirable[3] and the acid-soluble tetrakis(*p*-dimethylaminophenyl)ethylene (TDAPE) has been found suitable for the purpose.

TDAPE was readily prepared by the reductive dimerization of 4,4′-bis(dimethylamino)benzophenone with tin powder in concentrated hydrochloric acid.[4] In spite of the electron-rich nature as evidenced by the fact that in chloroform it is easily oxidized to a violet pigment, it is known to react with sodium in ether yielding a bluish green powder of the disodium adduct.[5] In tetrahydrofuran (THF) TDAPE and sodium reacted smoothly to afford a wine-colored solution which was similar in reactivity to a solution of the TPE-disodium adduct. Thus, the Wurtz reaction was catalyzed effectively by TDAPE (0.05 mol per mol of benzyl halide was sufficient) as shown in Table 1.

TABLE 1. THE WURTZ REACTION OF BENZYL HALIDES

Reactant	Yields of 1,2-diphenylethane (%)		
	TDAPE		TPE
	ca. −40 °C	Room temp	Room temp
$PhCH_2Cl$, Na-K	87	46	78[80(Na)][1]
$PhCH_2Br$, Na	77	66	(78)[1]

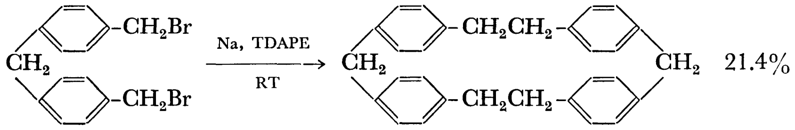
$$2\,PhCH_2X \xrightarrow[\text{TDAPE, THF}]{\text{Na or Na-K}} PhCH_2CH_2Ph$$

Although the reactions at room temperature were less fruitful compared with the corresponding TPE-catalyzed reactions, especially in the case of the chloride (see Experimental), the yields were improved by lowering the reaction temperature. The use of a liquid sodium–potassium alloy (Na–K) enabled a large metallic surface to be established and, thus, facilitated adduct formation especially at low temperatures.

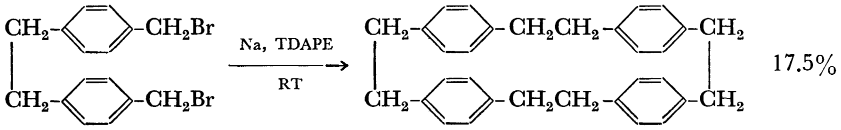
To demonstrate the applicability of the modified Wurtz reaction to cyclophane synthesis several paracyclophanes have been synthesized. The cyclization was conducted by the addition over 24 h of a dihalide to a solution of the TDAPE–Na (or K) adduct at *ca.* −40 °C for the chloride **6** or, for convenience, at room temperature for the bromides **2** and **4**. Separation of the products from TDAPE was readily effected by acid-washing. The yields of **3** and **5** were satisfactory compared with those reported using TPE. The simplicity of separation without loss of yield in the Wurtz reaction will also be valuable in the synthesis of other systems.

Experimental

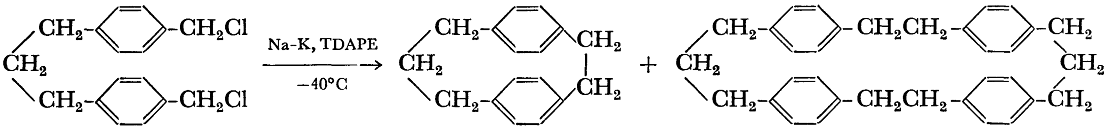
All the melting points are uncorrected. The PMR spectra were recorded at 60 MHz with a Hitachi R-20B spectrometer. The ^{13}C-NMR spectra were obtained at 22.6 MHz using a Hitachi R-22 spectrometer equipped with FT accessories. The mass spectra were obtained on a JEOL 01 SG mass



2 **3**



4 **5**



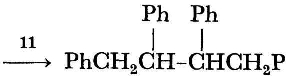
6 **7** 13.8% **8** 8.5%

spectrometer.

Tetrakis(p-dimethylaminophenyl)ethylene, TDAPE.[4] To a stirred solution of 4,4′-bis(dimethylamino)benzophenone (50 g) in concd HCl (750 ml) was added tin powder (90 g) in small portions over a 3 h period at 90—100 °C. After stirring for 6 h the solution was allowed to cool and the precipitate formed was collected by filtration and treated with excess aq NaOH. The precipitate was extracted with warm benzene, washed with water, dried over Na_2SO_4, and concentrated. TDAPE was obtained as a 1/2 benzene solvate (35.5 g, 70%). Rapid crystallization of TDAPE from benzene–hexane gave yellow needles free from benzene but on standing in the solution the crystals turned gradually into prisms. The PMR spectrum(C_6D_6) and analyses indicate that the prisms are a 1/2 benzene solvate. TDAPE: yellow needles, mp 321—323 °C (sealed tube, lit,[6] mp 310—314 °C) Found: C, 80.83; H, 8.09; N, 11.17%. Calcd for $C_{34}H_{40}N_4$: C, 80.91; H, 7.99; N, 11.10%. TDAPE.1/2 benzene: greenish yellow prisms, mp 318—323 °C. Found: C, 81.67; H, 8.05; N, 10.40%. Calcd for $C_{37}H_{43}N_4$: C, 81.73; H, 7.97; N, 10.30%. A solution of TDAPE in $CDCl_3$, yellow at first, turned rapidly to violet with precipitation exibiting broad PMR peaks and a strong ESR signal, indicating the presence of radical cationic species formed by air oxidation. Therefore chloroform which was originally used for extraction is not suitable as the solvent.

The Wurtz Reaction of Benzyl Halide. To a solution of TDAPE (2.5 g, 0.005 mol) in THF (freshly distilled from sodium-benzophenone, 400 ml) was added a Na–K alloy (1 : 2 by weight, 6 ml) or sliced sodium (6 g) with stirring under nitrogen. After stirring for 30 min, to the deep wine-colored solution was added a solution of benzyl halide (0.1 mol) in THF (200 ml) at room temperature of at *ca.* −40 °C. Care was taken to prevent complete disappearance of the color of the adduct. After the addition the solution was filtered and evaporated. The residue was taken up in benzene and washed with dil HCl and water and the solution dried ($MgSO_4$), concentrated and distilled under reduced pressure yielding 1,2-diphenylethane. In the reaction of benzyl chloride at room temperature a considerable amount of residue remained after distillation, which gave, after purification through a silica gel column(chloroform), colorless prisms of high melting point and low solubility in common solvents in 8% yield. This product shows complex PMR signals at δ 6.6—7.5 and 2.3—3.3 ppm ($CDCl_3$), but MS (M^+ 362) and ^{13}C-NMR data [δ_{TMS} ($CDCl_3$) 41.0, 54.3, 125.4, 126.3, 127.7, 128.2, 128.6, 128.8, 130.7, and 133.3 ppm] indicate that it is 1,2,3,4-tetraphenylbutane **9**. The structure was confirmed by comparison with a sample of meso-**9** prepared by the reduction of tetraphenylthiophene.[7] Mp 182—183 °C (lit,[7a] 181—182 °C). Found: C, 92.65; H, 7.24%. Calcd for $C_{28}H_{26}$: C, 92.77; H, 7.23%. The formation of this product may be explained in terms of the incipient proton abstraction from benzyl chloride as follows:[8]

$$\underset{\mathbf{10}}{\mathrm{PhCH_2Cl}} \longrightarrow \mathrm{PhCH^{-}Cl} \xrightarrow{\mathbf{10}} \underset{\mathbf{11}}{\mathrm{PhCHClCH_2Ph}}$$



$$\xrightarrow{\mathbf{11}} \mathrm{PhCH_2\overset{\overset{\displaystyle Ph}{|}}{C}H\text{-}\overset{\overset{\displaystyle Ph}{|}}{C}HCH_2Ph}$$

9

Synthesis of Paracyclophanes. [2.1.2.1]Paracyclophane **3** was prepared as follows. To a solution of TDAPE (2.5 g, 0.005 mol) in THF (400 ml) was added sliced sodium (11.5 g, 0.5 mol) under argon. After stirring for 30 min, to the deep wine-colored solution was added dropwise a solution of bis(*p*-bromomethylphenyl)methane **2** (17.7 g, 0.05 mol) in THF (500 ml) over a period of 24 h. The reaction mixture was decanted and evaporated and the residue dissolved in benzene, washed with dil HCl and water, dried over $MgSO_4$, and passed through a short column of silica gel to ensure removal of TDAPE. After evaporation of the solvent the residue was sublimed (230—240 °C at 0.03 Torr) and the sublimate recrystallized from benzene–hexane to give **3** as colorless prisms (2.08 g, 21.4%), mp 198—199 °C (lit,[9b] mp 199 °C, 14% yield from the corresponding chloride).

[2.2.2.2]Paracyclophane **5** was prepared analogously from 1,2-bis(*p*-bromomethylphenyl)ethane **4** in 17.5% yield, mp 179—181 °C (lit,[10] mp 185 °C, 7% yield from the corresponding chloride).

The reaction of 1,3-bis(*p*-chloromethylphenyl)propane **6** with Na–K at *ca.* −40 °C over a period of 24 h yielded **7** and **8**, the separation of which was readily effected by fractional sublimation. [3.2]Paracyclophane **7** : sublimed at 200—220 °C at atmospheric pressure, recrystallized from ethanol, colorless needles, mp 146—147 °C (lit,[11] mp 148—149 °C), 1.57 g (13.8%). MS: M^+ 222. PMR($CDCl_3$): δ 6.15, 6.39 (AA′BB′ doublets, J=8 Hz, 8H), 2.95 (s, 4H), 2.9—2.5 (m, 4H), and 2.4—1.8 (m, 2H) ppm. [3.2.3.2]-Paracyclophane **8**: sublimed at 200—220 °C at 0.1 Torr, recrystallized from benzene, colorless prisms, mp 223—224 °C, 967 mg (8.5%). The compound had different properties from those reported (mp 61—62 °C[9a]) but the structure was confirmed by the following data. MS: *m/e* 444(M^+, 64), 222 (67), 131 (56), and 118 (100). PMR($CDCl_3$): δ 6.80, 6.72 (AA′BB′ doublets, J=9 Hz, 16H), 2.86 (s, 8H), 2.6—2.2 (m, 8H), and 2.1—1.5 (m, 4H) ppm. Found: C, 91.64; H, 8.25%. Calcd for $C_{34}H_{36}$: C, 91.84; H, 8.16%.

References

1) E. Müller and G. Röscheisen, *Chem. Ber.*, **90**, 543 (1957).

2) T. Kawato, T. Inazu, and T. Yoshino, *Bull. Chem. Soc. Jpn.*, **44**, 200 (1971).

3) Several catalysts for the Wurtz reaction have been tested to make chromatographic separation efficient: K. Burri and W. Jenny, *Helv. Chim. Acta*, **50**, 1978 (1967).

4) R. Willstätter and M. Goldmann, *Ber.*, **39**, 3765 (1906).

5) W. Schlenk and E. Bergmann, *Justus Liebigs Ann. Chem.*, **493**, 1 (1928).

6) R. Foster and T. J. Thomson, *Trans. Faraday Soc.*, **59**, 1059 (1963).

7) a) E. Bergmann, *J. Chem. Soc.*, **1936**, 505; b) D. P. Wyman, *J. Org. Chem.*, **27**, 3712 (1962).

8) R. Koppang, *Acta Chem. Scand.*, **25**, 3067 (1971).

9) a) H. Steinberg and D. J. Cram, *J. Am. Chem. Soc.*, **74**, 5388 (1952); b) C. Sergheraert, P. Marcincal, and E. Cuingnet, *Tetrahedron Lett.*, 2879 (1977).

10) I. Tabushi, H. Yamada, K. Matsushita, Z. Yoshida, H. Kuroda, and R. Oda, *Tetrahedron*, **28**, 3381 (1972).

11) D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, **73**, 5671 (1951).