Notes

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Convenient Preparation of Tetraarylbutatrienes[1]

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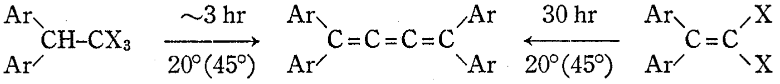
One-step efficient route to tetraarylbutatrienes was provided by the reaction of 1,1,1-trihalo-2,2-diarylethanes or 1,1-dibromo-2,2-diphenylethylene with metallic copper (or cuprous chloride) in dimethylformamide at 20—45°.

Keywords——tetraarylbutatriene; copper-induced coupling; 1,1,1-trihalide; vinylidene bromide; copper; cuprous chloride

In the course of our study on synthetic utilities of vinylene carbonate telomers[3] possessing polyhalomethyl groups at the terminal position, we found the facile and one-step conversion of diaryltrihaloethanes (**1**) and -dihaloethylenes (**2**) with copper powder or cuprous chloride into the title compounds (**3**). There have appeared many papers on copper-induced couplings of organic halides[4] including activated olefinic halides which give 1,3-dienes[5] and conjugated diallenes.[6] Methods reported so far for synthesizing farely stable butatrienes from the readily accessible compounds involve several steps and are much less numerous than those for allenes, the simplest cumulenes and naturally occurring skeleton.[7]



$$\mathrm{Ar_2CH{-}CX_3} \xrightarrow[20^\circ(45^\circ)]{\sim 3\,\mathrm{hr}} \mathrm{Ar_2C{=}C{=}C{=}CAr_2} \xleftarrow[20^\circ(45^\circ)]{30\,\mathrm{hr}} \mathrm{Ar_2C{=}CX_2}$$

1 **3** **2**

($Ar=C_6H_5$, p-Cl-C_6H_4, X=Cl, Br)

Treatment of trichloromethyl compounds (**1**) with copper powder at 45° in dimethylformamide under nitrogen atmosphere[8] resulted in the smooth formation of dehalogenated coupling cumulenes (**3**) as a major product (Table) in addition to the minor compounds including olefinic compounds (**2**) and (4,4′-dichloro-)benzophenones. The bromo compound (**1**) was reactive sufficiently to give the cumulene under the milder conditions (at room temperature for 1.5 hr), as might be expected.

Cuprous chloride in dimethylformamide was comparably (or slightly less) effective for the conversion of **1**. Utilizing freshly precipitated copper[9] under the similar conditions, compound (**2**) (X=Br) gave the identical butatriene in satisfactory yield, although the reaction proceeded much more sluggish and the chloro derivative was practically

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[1] Presented in part at the 93rd Annual Meeting of the Pharmaceutical Society of Japan, Tokyo, April 1973. Abstract II, p. 74.

[2] Location: *Hongo, Bunkyo-ku, Tokyo, 113, Japan.*

[3] T. Tamura, T. Kunieda, and T. Takizawa, *J. Org. Chem.*, **39**, 38 (1974); T. Matsuura, T. Kunieda, and T. Takizawa, *Chem. Pharm. Bull.* (Tokyo), **25**, 1225 (1977) and the preceding papers in this series.

[4] P.E. Fanta, *Synthesis*, **1974**, 9.

[5] T. Cohen and T. Poeth, *J. Am. Chem. Soc.*, **94**, 4363 (1972).

[6] F. Toda and Y. Takehira, *J. C. S. Chem. Commun.*, **1975**, 174.

[7] H. Fischer "The Chemistry of Alkenes," S. Patai Ed. Interscience Publisher, New York, 1964, p. 1025.

[8] The reaction in the air gave somewhat lower yield (35% of **3** from 1,1-bis(p-Chlorophenyl)-2,2,2-trichloroethane.

[9] P.H. Gore and G.K. Hughes, *J. Chem. Soc.*, **1959**, 1615.

Table I. Conversion of Compounds (**1** and **2**) into Butatrienes (**3**)

Compound	Ar	X	Conditions (°C)	Conditions (hr)	Isolated yield (%)
1	C_6H_5	Br	20	1.5	64
1	C_6H_5	Cl	45	3	48
1	p-Cl-C_6H_4	Cl	45	3	51[a] (41)[b]
2	C_6H_5	Br	20	30	53[c]
2	p-Cl-C_6H_4	Cl	45	30	Trace (trace)[b]

a) In addition, 4,4′-dichlorobenzophenone (20%) was obtained.
b) With cuprous chloride.
c) Unchanged **2** (34%) was recovered.

unreactive.[10]

Simple procedure as well as the availability of starting materials would make the present route attractive for the preparation of such cumulenes, though yields are not so high. Reactions described here appear to involve initial oxidative addition to give organocopper intermediates,[4,5] and extremely low reactivity of the olefinic halides (**2**) (Table I) would preclude their possibility as intermediates in the conversion of **1** to cumulenes (**3**), but mechanistic details including primary coupling products are uncertain at present.

Experimental

Tetraarylbutatrienes (3)——a) A mixture of 2,2-diaryl-1,1,1-trihaloethanes (**1**) (1 g) and commercially available (or freshly precipitated) copper powder (1 g) or cuprous chloride (1.5 g) in dimethylformamide (10 ml) was stirred at room temperature (or 45°) under nitrogen atmosphere. Yellow precipitates started to deposit shortly and after a few hours, insoluble materials were collected by filtration and washed with chilled benzene. Inorganic substances were removed by extraction with warm methylene chloride and the extracts were evaporated *in vacuo* to give tetraphenyl- and tetrakis(p-chlorophenyl)-butatrienes as golden yellow crystals which were further purified by recrystallization from benzene–n-hexane and methylene chloride, respectively.

3 (Ar=C_6H_5): mp 236—238° (lit.,[12] 236°, 237°), UV $\lambda_{\text{max}}^{\text{benzene}}$ 420 nm, IR (Nujol) 1695, 775 and 700 cm^{-1}, NMR ($CDCl_3$) δ 7.25—7.70 (m). *Anal.* Calcd. for $C_{28}H_{20}$: C, 94.38; H, 5.62. Found: C, 94.62; H, 5.58.

3 (Ar=p-Cl–C_6H_4): mp 294—298° (dec.) (lit.,[13] 286°), UV $\lambda_{\text{max}}^{\text{benzene}}$ 438 nm, IR (Nujol) 1585, 1485, 1095, 1015, 917 and 830 cm^{-1}. *Anal.* Calcd. for $C_{28}H_{16}Cl_4$: C, 68.02; H, 3.24. Found: C, 68.30; H, 3.31.

Water was added to the combined filtrate and washings, and it was extracted with methylene chloride. The extracts were evaporated to leave an oil which was chromatographed on silica gel using n-hexane as an eluting solvent to afford another amounts of **3** (30—80 mg) in addition to small amounts of **2** and (4,4′-dichloro)benzophenones.

b) The mixture of 1,1-dibromo-2,2-diphenylethylene (**2**) (0.5 g) and freshly precipitated copper[9] (0.5 g) in dimethylformamide (3 ml) was stirred at room temperature for 30 hr. In the working-up as above, the identical cumulene was obtained in addition to the unchanged **2** (0.17 g).

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10) Bis(cyclooctadiene)nickel (O) which was successfully employed for the coupling of alkenyl halides,[11] was unsatisfactory for the present purpose.
11) M.F. Semmelhack, P.M. Helquist, and J.D. Gorzynski, *J. Am. Chem. Soc.*, **94**, 9234 (1972).
12) R. Kuhn and H. Krauch, *Chem. Ber.*, **88**, 309 (1955); J. Godineau, P. Cadiot, and A. Willemart, *Compt. Rend.*, **246**, 2499 (1958) *etc.*
13) E.E. Fleck, *J. Am. Chem. Soc.*, **71**, 1034 (1949).