Table II
Properties of *N*-Methylbenzanilides

Substituents	Mp or bp, °C (mm)	Lit. mp, °C	Formula[g]
4′-NO_2	109	111–112[a]	
4′-NO_2	147.5–148.5		$C_{14}H_{11}ClN_2O_3$
4′-NO_2-4-MeO	74–75		$C_{15}H_{14}N_2O_4$
3,4′-di-NO_2	140–141		$C_{14}H_{11}N_3O_5$
4′-NO_2-4-Cl	90–92		$C_{14}H_{11}ClN_2O_3$
4′-NO_2-4-Me	89–91		$C_{15}H_{14}N_2O_3$
3′-NO_2	102–103		$C_{14}H_{12}N_2O_3$
3′-Br	214–218 (15)		$C_{14}H_{12}BrNO$
4′-Br	72–73	77[b]	
H	55–57	63[a]	
4′-MeO	76–78	79–80[c]	
4′-CO_2Me	63		$C_{16}H_{15}NO_3$
4-NO_2	109–110	110–111[d]	
3-NO_2	107–109	109[e]	
3-Cl	33–35	40[f]	
4-MeO	Oil, tlc pure		$C_{15}H_{15}NO_2$

[a] See ref 14. [b] F. B. Dains and F. Eberly, *J. Amer. Chem. Soc.*, **55,** 3859 (1933). [c] F. W. Bentley and R. A. W. Johnstone, *J. Chem. Soc. B*, 1804 (1971). [d] R. N. Ring, J. G. Sharefkin, and D. Davidson, *J. Org. Chem.*, **27,** 2428 (1962). [e] D. H. Hey and R. A. J. Long, *J. Chem. Soc.*, 4110 (1959). [f] P. Grammaticakis, *Bull. Soc. Chim. Fr.*, 862 (1963). [g] Satisfactory analytical data were obtained for all new compounds listed.

mostatted cuvettes in the spectrophotometer, while sealed ampoules were required for the higher temperature reactions in series 5. First-order rate constants were calculated graphically from plots of log ($D_\infty - D_t$) *vs.* time. All rate constants listed in Table I are averages of two or more runs, with agreement between runs being within 4%.

Acknowledgment. The authors thank Mr. C. Carolane for synthesizing the three *N*-arylazetidinones.

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Synthetic Reactions by Complex Catalysts. XXXII. Reaction of *o*-Xylylene Halides with Copper–Isonitrile Complex. *o*-Xylylene Intermediates

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The system of *o*-xylylene halide with Cu(0)–*tert*-butyl isocyanide was subjected to the reaction with an electron-deficient olefin such as acrylate, fumarate, and maleate. In the case of *o*-xylylene dibromide, tetrahydronaphthalene derivative **3** was produced in a moderate yield. As one of possible mechanisms, an unstable intermediate of *o*-xylylene (**6**) was proposed. The system of $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene with Cu(0)–*tert*-butyl isocyanide reacted with an electron-deficient olefin to produce naphthalene derivatives (**4**). Similarly, the intermediacy of α,α'-dibromo-*o*-xylylene (**7**) was proposed for the production of 1,4-dibromotetrahydronaphthalene followed by dehydrobromination to the final naphthalene derivative. In the case of *o*-xylylene dichloride, tetrahydronaphthalene derivative (**3**) as well as the dihydronaphthalene derivative (**5**) were produced, for which two *o*-xylylene intermediates (**6** and **8**) were presented, respectively. Concerning the formation of **6** and **8**, the effect of substituents in the aromatic ring on the product ratio of **5** to **3** was examined. The ratio of **5** to **3** increases with the increase of σ^+ of the substituent.

Intramolecular dehalogenation of *o*-xylylene dihalide by means of a transition metal has provided a convenient route[1] leading to the transient formation of a reactive intermediate of *o*-xylylene. Metallic iron has often been used for this purpose.[2] Roth and Meier[3] succeeded in the isolation of unstable *o*-xylylene in the form of a stable π complex with iron tricarbonyl in the reaction of *o*-xylylene dibromide with diiron nonacarbonyl.

The present paper deals with systems in which *o*-xylylene halides are treated with Cu(0)–*tert*-butyl isocyanide in the presence of an electron-deficient olefin. In the course of our investigations of copper–isonitrile complexes,[4] we found that metallic copper was dissolved in liquid isonitrile under nitrogen to form a soluble complex. The complex exhibited a broad, unresolved esr signal (*g* value = 2.0041), which was taken to suggest a Cu(0)–isonitrile species. Interestingly, the Cu(0)–isonitrile complex[4] was found to react with the carbon–halogen bond and sometimes the carbon–hydrogen bond to form the organocopper–isonitrile complexes. In these reactions, the oxidative additions of the carbon–halogen bond and of the carbon–hydrogen bond, respectively, onto the Cu(0)–isonitrile complex may probably be assumed. For example, the Cu(0)–isonitrile complex reacts with benzyl halide to give a benzylcopper–

isonitrile complex (**1**). The formation of **1** was demonstrated by a trapping experiment with allyl bromide to produce 4-phenyl-1-butene (eq 1). On the other hand, the

$$\mathrm{C_6H_5CH_2Cl} + \mathrm{Cu^0(RNC)}_l \longrightarrow$$

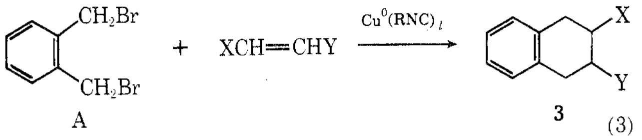
$$\underset{\mathbf{1}}{\mathrm{C_6H_5CH_2CuCl(RNC)}_m} \xrightarrow{\mathrm{CH{=}CHCH_2Br}} \mathrm{C_6H_5CH_2CH_2CH{=}CH_2} \quad (1)$$

reaction of 1,4-dichloro-2-butene with the Cu(0)–isonitrile complex selectively produced butadiene, in which all attempts to trap an organocopper intermediate (**2**), however, failed. It implies that **2** rapidly undergoes the 1,4-elimination of copper chloride–isonitrile complex to give butadiene.

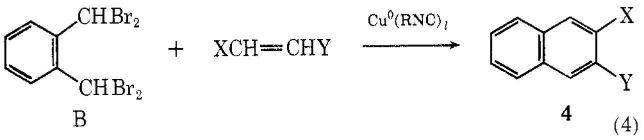
$$\mathrm{ClCH_2CH{=}CHCH_2Cl} + \mathrm{Cu^0(RNC)}_l \longrightarrow$$

$$\underset{\mathbf{2}}{\mathrm{ClCH_2CH{=}CHCH_2CuCl(RNC)}_m} \xrightarrow{-\mathrm{CuCl_2(RNC)}_n} \mathrm{CH_2{=}CHCH{=}CH_2} \quad (2)$$

These findings prompted us to investigate the reactions of *o*-xylylene halides with the Cu(0)–isonitrile complex which might lead to the formation of *o*-xylylene intermediate. Now we wish to report that derivatives of tetrahydronaphthalene (**3**), naphthalene (**4**), and dihydronaphthalene (**5**) are produced when *o*-xylylene dibromide (A), $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene (B) and *o*-xylylene dichloride (C) are treated with Cu(0)-*tert*-butyl isocyanide in the presence of an electron-deficient olefin, as shown in eq 3–5. It is noteworthy that in the reaction with *o*-xylylene dichloride, the product ratio of **3** to **5** varied by substituents on the aromatic ring, *i.e.*, an electron-withdrawing substituent favors the formation of **5**. All these products, **3–5**, may be explained in terms of the following *o*-xylylene intermediates **6–8**, respectively.



(3)



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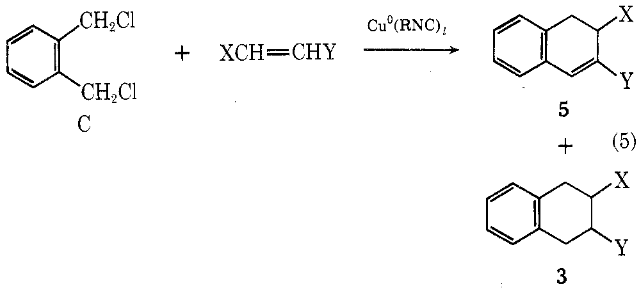
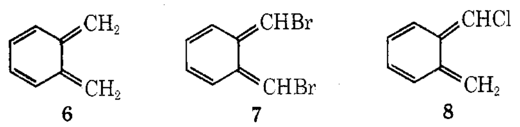


(5)

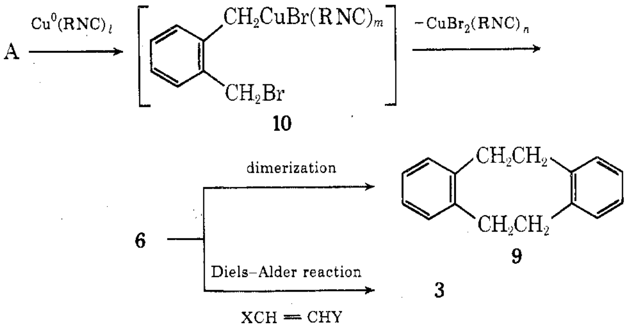
X = H, $\mathrm{CH_3}$, $\mathrm{CO_2R'}$; Y = $\mathrm{CO_2R'}$, CN



Results and Discussion

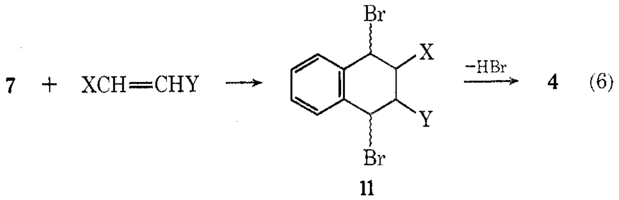
On treating *o*-xylylene dibromide with Cu(0)-*tert*-butyl isocyanide complex, dibenzocyclooctadiene (**9**) was produced along with a few minor products. However, when this reaction was carried out in the presence of an electron-deficient olefin such as acrylate and fumarate, tetrahydronaphthalene derivatives (**3**) were selectively produced without being accompanied by **9** (Table I, runs 1–4). The finding may be explained by the formation of a reactive intermediate of *o*-xylylene **6** in the reaction of *o*-xylylene dibromide with Cu(0)-*tert*-butyl isocyanide as shown in Scheme I. The *o*-xylylene intermediate then reacts with an olefin to produce the final product of tetrahydronaphthalene (**3**). As to the reactions of *o*-xylylene **6**, the dimerization and the Diels–Alder reaction with an electron-deficient olefin have been known.[1,2,5] As a mechanistic alternative to *o*-xylylene intermediate, a stepwise mechanism involving an addition of organocopper (**10**) to olefin and the subsequent ring closure may also be conceivable. No experimental observation is at hand to exclude this possibility. However, the observation aforementioned that 1,4-dichloro-2-butene undergoes the 1,4-dechlorination by the Cu(0)–isonitrile complex to produce butadiene may be taken to support the *o*-xylylene mechanism.

Scheme I

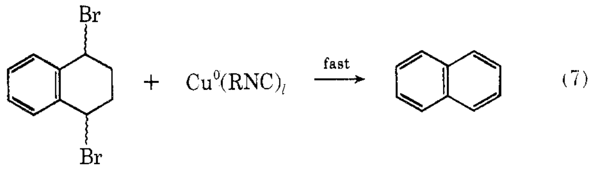


X = H, $\mathrm{CH_3}$, $\mathrm{CO_2R}$; Y = $\mathrm{CO_2R}$, CN

Next, the reaction of $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene with Cu(0)-*tert*-butyl isocyanide complex in the presence of olefin afforded naphthalene derivatives (**4**) (Table I, runs 5 and 6). Dibromotetrahydronaphthalene derivative (**11**) was not isolated among the products. By analogy with the case of *o*-xylylene dibromide, an intermediate of α,α'-dibromo-*o*-xylylene (**7**) may be assumed for this reaction. The subsequent elimination of two molecules of hydrogen bromide from the Diels–Alder adduct (**11**) leads to the formation of **4**. The rapid dehydrobromination of **11** in the present reaction conditions was verified by a reference experiment, in which naphthalene was produced almost exclusively in the reaction of 1,4-dibromotetrahydronaphthalene with Cu(0)–isonitrile complex even in the presence of acrylate (eq 7).



(6)



(7)

The behavior of *o*-xylylene dichloride toward Cu(0)-*tert*-butyl isocyanide is complicated a little. The reaction of *o*-xylylene dichloride with the Cu(0)–isonitrile in the presence of an olefin produced tetrahydronaphthalene derivative (**3**) as well as dihydronaphthalene derivative (**5**). For this reaction two *o*-xylylene intermediates of **6** and **8** may

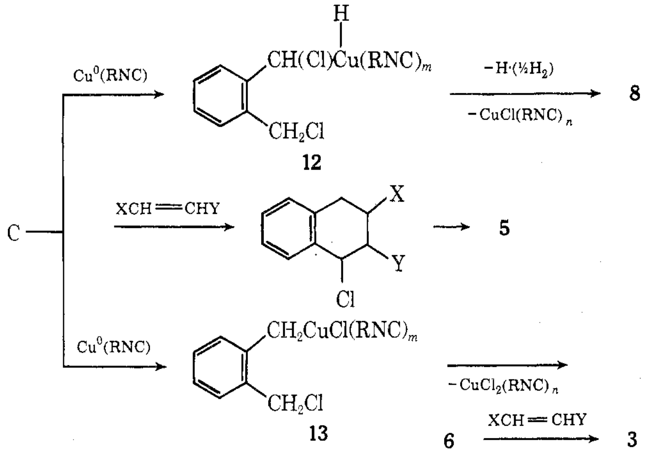
Table I
Reaction of *o*-Xylylene Halides with Cu(0)-*tert*-Butyl Isocyanide in the Presence of Olefin

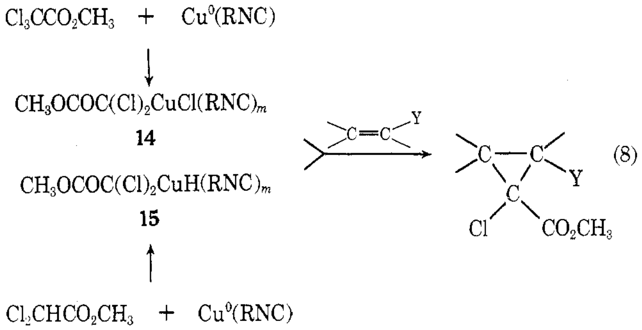
No.	*o*-Xylylene halide[a] (registry no.)	Olefin (registry no.)	Product[b] (%)
1	A (91-13-4)	$CH_2{=}CHCO_2CH_3$ (96-33-3)	**3i**, X = H; Y = CO_2CH_3 (33)[c]
2	A	$CH_2{=}CHCN$ (107-13-1)	**3ii**, X = H; Y = CN (25)[c]
3	A	*trans*-$C_2H_5O_2CCH{=}CHCO_2C_2H_5$ (623-91-6)	**3iii**, X = Y = $CO_2C_2H_5$ (53)
4	A	$CH_3CH{=}CHCO_2C_2H_5$ (10544-63-5)	**3iv**, X = CH_3; Y = $CO_2C_2H_5$ (14)
5	B (13209-15-9)	$CH_2{=}CHCO_2CH_3$	**4i**, X = H; Y = CO_2CH_3 (60)[d]
6	B	*trans*-$C_2H_5O_2CCH{=}CHCO_2C_2H_5$	**4ii**, X = Y = $CO_2C_2H_5$ (55)[e]
7	C (612-12-4)	$CH_2{=}CHCO_2CH_3$ (554-12-1)	**3i**, X = H; Y = CO_2CH_3 (36) **5i**, X = H; Y = CO_2CH_3 (35)
8	C	$CH_2{=}CHCN$	**3ii**, X = H; Y = CN (15) **5ii**, X = H; Y = CN (14)
9	C	*cis*-$C_2H_5O_2CCH{=}CHCO_2C_2H_5$	**3iii**, X = Y = $CO_2C_2H_5$ (26) **5iii**, X = Y = $CO_2C_2H_5$ (18)
10	C	*trans*-$C_2H_5O_2CCH{=}CHCO_2C_2H_5$	**3iii**, X = Y = $CO_2C_2H_5$ (39) **5iii**, X = Y = $CO_2C_2H_5$ (18)
11	C	$CH_3CH{=}CHCO_2C_2H_5$	**3iv**, X = CH_3; Y = $CO_2C_2H_5$ (21) **5iv**, X = CH_3; Y = $CO_2C_2H_5$ (5)

[a] A = *o*-xylylene dibromide, B = *o*-xylylene tetrabromide, C = *o*-xylylene dichloride. [b] Satisfactory analytical data were reported for all new compounds listed in the table. [c] Reference 1. [d] M. S. Newman and H. V. Zahn, *J. Amer. Chem. Soc.*, **65**, 1097 (1943). [e] K. Auwers and A. Fruhling, *Justus Liebigs Ann. Chem.*, **422**, 196 (1900).

be assumed. Monochloro-*o*-xylylene intermediate (**8**) would arise *via* the organocopper–isonitrile complex (**12**) formed by an oxidative addition of the benzylic carbon–hydrogen bond onto the Cu(0)–isonitrile complex, which in turn undergoes the elimination of copper chloride–isonitrile complex (Scheme II). The evolution of hydrogen gas in the reaction of *o*-xylylene dichloride with the Cu(0)–isonitrile complex was really observed, which is taken as a support to the intermediacy of copper hydride species (**12**). Concerning Scheme II, we may refer to our previous findings of the reactions of Cu(0)–isonitrile with trichloroacetate and with dichloroacetate in the presence of olefin, both of which produce the same cyclopropane derivative.[4] The transient formations of organocopper–isonitrile complexes, **14** and **15**, both of which contain the Cu–C(Cl)$_2$CO$_2$CH$_3$ moiety, have been presented for the reactions. Both the α-carbon–chlorine bond of trichloroacetate and the α-carbon–hydrogen bond of dichloroacetate would be assumed to react with the Cu(0)–isonitrile complex through the fashion of oxidative addition.

Scheme II

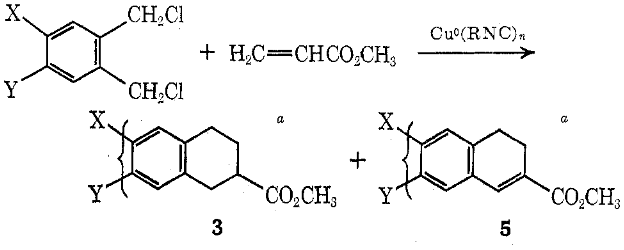




(8)

The stereochemistry of tetrahydronaphthalene derivative (**3**) obtained in the reaction of *o*-xylylene dichloride or dibromide with 1,2-dicarbethoxyethylene (fumarate and maleate) is worthy of notice. A single product of *trans*-2,3-dicarbethoxytetrahydronaphthalene, irrespective of the starting isomers of 1,2-dicarbethoxyethylene, was detected. In a separate experiment, however, *cis*-2,3-dicarbethoxytetrahydronaphthalene was found to be isomerized rapidly into the trans isomer by Cu(0)–isonitrile complex. Therefore, the product stereochemistry could not be taken as a criterion to determine the reaction mechanism, *i.e.*, the

Table II



X	Y	$\sigma_p{}^+$ of substituent X	Product ratio[b] 3:5
CH_3	CH_3[c]	−0.31	1:0
F	H	−0.07	1:trace
H	H	0	1:1
Cl	H	+0.11	1:1.8

[a] The position of the substituents X, Y in the products was not determined. [b] Yields (**3** + **5**) were 60–70% in all runs. [c] 4,5-Dimethyl-*o*-xylylene dichloride was used.

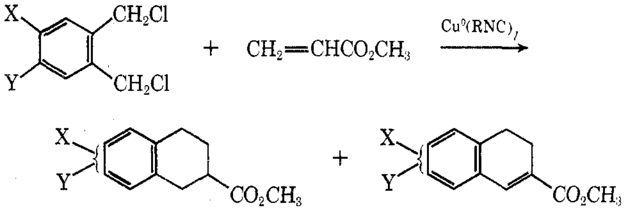
Table III
Characterization of Products[a]

Compd	Ir, cm^{-1}	Nmr, τ[b]	Mass
3i	>3000, 1735, 745	3.02 (4 H, s) 6.36 (3 H, s) 6.88–7.45 (5 H, m) 7.65–8.40 (2 H, m)	
3ii	>3000, 2210, 750	2.98 (4 H, s) 6.90–7.36 (5 H, m) 7.60–8.20 (2 H, m)	
3iii	>3000, 1735, 750	3.01 (4 H, s) 5.87 (4 H, q) 6.75–7.30 (6 H, m) 8.75 (6 H, t)	
3iv	>3000, 1734, 745	3.60 (4 H, s) 5.92 (2 H, q) 6.80–8.10 (6 H, m) 8.76 (3 H, t) 9.00 (3 H, d)	
3v	>3000, 1730, 870	3.14 (2 H, s) 6.30 (3 H, s) 7.00–7.43 (5 H, m) 7.82 (6 H, s) 7.90–8.40 (2 H, m)	218 (M$^+$) 187 (– OCH_3) 159 (– CO_2CH_3)
3vi	>3000, 1736, 862, 808	2.82–3.60 (3 H, m) 6.32 (3 H, s) 6.80–7.50 (5 H, m) 7.70–8.40 (2 H, m)	208 (M$^+$) 177 (– OCH_3) 149 (– CO_2CH_3)
3vii	>3000, 1738, 860, 805	2.64–3.10 (3 H, m) 6.27 (3 H, s) 6.70–7.40 (5 H, m) 7.72–8.40 (2 H, m)	224 (M$^+$) 193 (– OCH_3) 165 (– CO_2CH_3)
4i	>3000, 1710, 785, 770	1.47 (1 H, s) 1.80–2.57 (6 H, m) 6.03 (3 H, s)	
4ii	>3000, 1725, 785, 765	1.30 (2 H, s) 1.50–2.07 (4 H, m) 5.10 (4 H, q) 8.63 (6 H, t)	
5i	>3000, 1710, 1630, 750	2.56 (1 H, s) 2.86 (4 H, s) 6.26 (3 H, s) 6.88–7.66 (4 H, m)	
5iii	>3000, 1740, 1710, 1635, 780	2.52 (1 H, s) 2.87 (4 H, s) 5.77 (2 H, q) 6.02 (2 H, q) 6.68–7.10 (2 H, m) 8.70 (3 H, t) 8.90 (3 H, t)	
5iv	>3000, 1710, 1630, 776	2.60 (1 H, s) 2.60 (4 H, s) 5.75 (2 H, q) 6.75–7.50 (3 H, m) 8.63 (3 H, t) 9.01 (3 H, d)	
5vi	>3000, 1710, 1634, 866, 820		
5vii	>3000, 1710, 1630, 882, 820	2.42–3.00 (4 H, m) 6.20 (3 H, s) 6.95–7.58 (4 H, m)	222 (M$^+$) 191 (– OCH_3) 163 (– CO_2CH_3)

[a] Satisfactory analytical data were reported for all new compounds listed in the table. [b] $CDCl_3$ solution (TMS).

Diels–Alder reaction mechanism or the stepwise reaction mechanism.

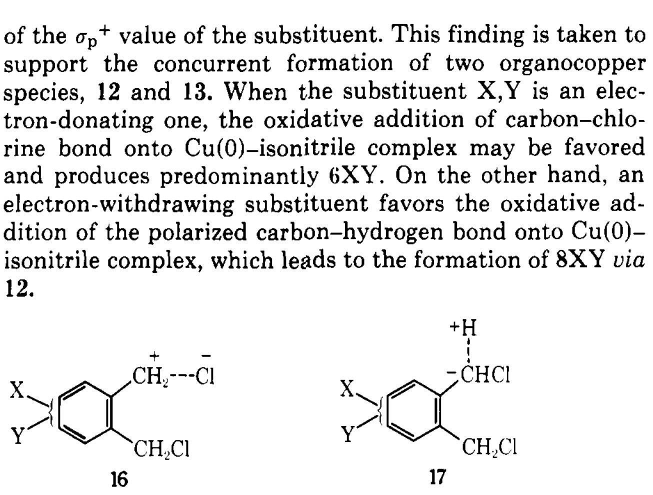
Substitution Effect on the Reaction of *o*-Xylylene Dichloride with Cu(0)–Isonitrile Complex. In the reaction of *o*-xylylene dichloride with Cu(0)–*tert*-butyl isocyanide, two products, **3** and **5**, were obtained, for which the respective *o*-xylylene intermediates **6** and **8** were assumed. Concerning the formation of **6** and **8**, the effect of substituent of the benzene ring upon the ratio of **3** and **5** was examined. Table II shows the ratios of the products **3** and **5**, which have been correlated with the $\sigma_p{}^+$ values of the substituents X. The ratio of **5** to **3** increases with the increase



3 **5**

v, X = Y = CH_3
vi, X = F; Y = H
vii, X = Cl; Y = H

of the $\sigma_p{}^+$ value of the substituent. This finding is taken to support the concurrent formation of two organocopper species, **12** and **13**. When the substituent X,Y is an electron-donating one, the oxidative addition of carbon–chlorine bond onto Cu(0)–isonitrile complex may be favored and produces predominantly 6XY. On the other hand, an electron-withdrawing substituent favors the oxidative addition of the polarized carbon–hydrogen bond onto Cu(0)–isonitrile complex, which leads to the formation of 8XY *via* **12**.



Experimental Section

Reagents. *tert*-Butyl isocyanide was prepared according to Ugi's procedure.[6] *o*-Xylylene dichloride was synthesized from the corresponding *o*-xylene and sulfuryl chloride in the presence of benzoyl peroxide. *o*-Xylylene dibromide and $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene were commercial reagents and were purified by recrystallization before use. 4,5-Dimethyl-*o*-xylylene dichloride was prepared by chloromethylation[7] of *o*-xylene and used after recrystallization. 4-Fluoro-*o*-xylylene dichloride was synthesized from 4-fluoro-*o*-xylene and sulfuryl chloride in the presence of benzoyl peroxide. 4-Fluoro-*o*-xylene was prepared from xylidine and tetrafluoroboric acid according to Starkey's procedure.[8] 1,4-Dibromotetrahydronaphthalene was prepared by the reaction of tetrahydronaphthalene with *N*-bromosuccinimide.[9] The olefins such as acrylate, acrylonitrile, crotonate, fumarate, and maleate were all commercial reagents and purified by distillation under nitrogen.

Reaction of *o*-Xylylene Dibromide with Cu(0)-*tert*-Butyl Isocyanide Complex in the Presence of Olefin. Under nitrogen to a mixture of 0.64 g (10 mg-atoms) of copper powder, 3.3 g (40 mmol) of *tert*-butyl isocyanide, 1.7 g (10 mmol) of diethyl fumarate, and 5 ml of benzene, 1.3 g (5 mmol) of *o*-xylylene dibromide in 5 ml of benzene was added at room temperature. The mixture was heated at 80° with stirring under nitrogen for 10 hr. After the reaction mixture was treated with ether to remove copper bromide–*tert*-butyl isocyanide complex, the extract was concentrated and subjected to glpc analysis. *trans*-2,3-Dicarbethoxytetrahydronaphthalene (**3iii**) was obtained in a yield of 53%. The structure of the products was confirmed by elemental analysis and spectral data. The data are shown in Table III.

Other combinations of *o*-xylylene dibromide and Cu(0)-*tert*-butyl isocyanide complex with methyl acrylate, acrylonitrile, methyl crotonate, and diethyl maleate were carried out according to the procedure mentioned above.

Reaction of *o*-Xylylene Dichloride with Cu(0)-*tert*-Butyl Isocyanide Complex in the Presence of Olefin. Under nitrogen to a mixture of 0.64 g (10 mg-atoms) of copper powder, 3.3 g (40 mmol) of *tert*-butyl isocyanide, 1.7 g (10 mmol) of diethyl fumarate, and 5 ml of benzene, 0.88 g (5 mmol) of *o*-xylylene dichloride in 5 ml of benzene was added at room temperature. After the reaction mixture was heated at 80° with stirring for 10 hr, the mixture was extracted with ether. The extract was concentrated and subjected to glpc analysis. *trans*-2,3-Dicarbethoxytetrahydronaphthalene (**3iii**) and 2,3-dicarbethoxy-3,4-dihydronaphthalene (**5iii**) were isolated in yields of 39 and 18%, respectively.

In the reaction of *o*-xylylene dichloride and Cu(0)-*tert*-butyl isocyanide complex in the presence of acrylonitrile, two products, tetrahydronaphthalene derivative (**3ii**) and dihydronaphthalene derivative (**5ii**) could not be separated by glpc analysis. After the mixture of two products was hydrolyzed with aqueous sodium hydroxide, acidified with sulfuric acid, and then esterified with diazomethane, the mixture was analyzed by glpc. 2-Carbomethoxytetrahydronaphthalene (**3i**) and 2-carbomethoxy-3,4-dihydronaphthalene (**5i**) were isolated.

Other reactions of *o*-xylylene dichloride with Cu(0)-*tert*-butyl isocyanide complex in the presence of olefin were carried out according to the procedure mentioned above.

Reaction of $\alpha,\alpha,\alpha',\alpha'$-Tetrabromo-*o*-xylene with Cu(0)-*tert*-Butyl Isocyanide Complex in the Presence of Olefin. To a mixture of 0.64 g (10 mg-atoms) of copper powder, 3.3 g (40 mmol) of *tert*-butyl isocyanide, 0.86 g (10 mmol) of methyl acrylate, and 5 ml of benzene, 1.2 g (2.5 mmol) of $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene in 5 ml of benzene was added dropwise at room temperature under nitrogen. After the reaction mixture was stirred at 80° for 10 hr, the reaction mixture was treated with ether to remove copper bromide–*tert*-butyl isocyanide complex. The extract was concentrated and subjected to glpc analysis. 2-Carbomethoxynaphthalene (**4i**) was isolated in a yield of 60% by preparative glpc.

The reaction of $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene and Cu(0)-*tert*-butyl isocyanide complex in the presence of diethyl fumarate was carried out according to the procedure mentioned above.

Reaction of *o*-Xylylene Dichloride Bearing a Substituent on the Benzene Ring with Cu(0)-*tert*-Butyl Isocyanide Complex in the Presence of Methyl Acrylate. To a mixture of 0.64 g (10 mg-atoms) of copper powder, 3.3 g (40 mmol) of *tert*-butyl isocyanide, 0.86 g (10 mmol) of methyl acrylate, and 5 ml of benzene, 1.05 g (5 mmol) of 4-chloro-*o*-xylylene dichloride in 5 ml of benzene was added with stirring at room temperature. After the reaction mixture was heated at 80° for 10 hr, the mixture was extracted with ether. The extract was concentrated and subjected to glpc analysis. Dihydronaphthalene derivative (**5vii**) and tetrahydronaphthalene derivative (**3vii**) were isolated in the ratio of 1.8:1 in a total yield of 60%.

The reaction of *o*-xylylene dichloride bearing a substituent on the benzene ring with Cu(0)-*tert*-butyl isocyanide complex was carried out according to the procedure mentioned above.

Registry No.—**3i**, 39246-30-5; **3ii**, 51849-33-3; **3iii**, 51849-34-4; **3iv**, 51849-35-5; **3v**, 51849-36-6; **3vi**, 51849-25-3; **3vii**, 51849-26-4; **4i**, 2459-25-8; **4ii**, 50919-54-5; **5i**, 51849-37-7; **5ii**, 51849-38-8; **5iii**, 28937-23-7; **5iv**, 51849-35-5; **5vi**, 51849-27-5; **5vii**, 51849-28-6; Cu(0)-*tert*-butyl isocyanide, 51898-98-7.

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