distilled, bp 142° (21 mm), assay 98.7%. **Neododecyl alcohol** from Eastman was used as received.

Procedure.—The fast reactions (50% completion in less than 30 min) were run in 250-ml iodine flasks in 25-ml portions containing all ingredients except isocyanate. The reaction was begun by the addition with an automatic pipet of 2 ml of the isocyanate and stopped after a measured time by the addition of 5 ml of dibutylamine. Vigorous stirring kept the maximum temperature rise below 0.5°. Each flask yielded one point of the concentration–time curve. For these reactions, the error was generally less than ±2%.

Slower reactions (50% reaction in more than 30 min) were run in a 1-l. flask with 275 ml of reaction mixture. After certain time intervals, 25-ml aliquots were transferred to erlenmeyer flasks containing a measured amount of dibutylamine in dioxane.

The unreacted isocyanate was determined by back titration of the excess dibutylamine[11] with 1 N HCl using a mixed indicator (0.075% bromocresol green and 0.025% methyl red in methanol) showing a sharp color change at pH 5.1. To maintain a homogeneous solution, 50 to 100 ml of methanol was added to the reactant mixture prior to titration. All reactions were run in a thermostat at 25.5° controlled by a TECAM TEMPUNIT (La Pine Scientific Co.) to ±0.05°C.

The reaction of hexamethylene diisocyanate with neododecyl alcohol was followed in a water-cooled Abbe-3L refractometer (precision ±0.0001) (Bausch and Lomb) at 25°. The linear dependence of refractive index on the concentration of reactants and formed urethan was experimentally extablished. The difference of the refractive index between the initial reaction mixture ($n^{25}\text{D}$ 1.4445) and the diurethan ($n^{25}\text{D}$ 1.4613) allowed an exact determination of the course of the reaction. The use of neododecyl alcohol permitted following the reaction to completion, since the diurethan did not crystallize at room temperature. The use of the refractometer had the advantage of positive temperature control which prevented exotherm of the urethan reaction.

The conversion of the experimental points to pseudo-second-order rate constants was achieved by drawing concentration *vs.* time curves. The tangents to the curves at these points were established with a mirror device. The rate constant for any point on the curve is then given by

$$k_{\text{bi}} = \frac{\tan \alpha}{[\text{RNCO}][\text{ROH}]}$$

where $\tan \alpha = d[\text{RNCO}]/dt$. This procedure was adopted to obtain a more accurate "rate constant" than is possible by a $1/C$ *vs.* time plot or, in the case of unequal concentration of the two reactants, a plot of $1/(b - a) \ln [(a - x)/(b - x)]$ *vs.* time. The reason for this is that the rate constant of the urethan reaction is not a constant and varies with the extent of reaction and initial concentration of reactants and solvent. For example, Ephraim and co-workers[12] point out that, besides strongly affecting the absolute value of the "rate constant," both positive and negative deviations from the second-order plot occur if the solvent is changed; *i.e.*, the "rate constant" changes during the course of the reaction.

Similar observations are made on Fe(AA)_3-catalyzed reactions provided they are run in dilute solution in a solvent. When the solvent was excess BuOH, the k_{bi} value remained practically constant throughout the reaction (pseudo first order). In all solvents tested (benzene, toluene, heptane, dioxane, diethylene glycol dimethyl ether, methyl ethyl ketone, and acetonitrile), the rate constant increased with the extent of reaction. An example of this is given in Table V for reaction between BuOH (0.6 M) and BuNCO (0.6 M) catalyzed by Fe(AA)_3 (2.62×10^{-3} M) in benzene at 25.5°.

TABLE V

Extent of reaction, %	k_{bi}, l. mole^{-1} min^{-1}
10	0.368
20	0.391
30	0.386
40	0.412
50	0.453
60	0.497
70	0.528
80	0.522

For these reasons, the "rate constants" of the individual kinetic runs are compared at the same extent of reaction.

The over-all accuracy of the rate constants, as judged from repeat experiments, should be at least ±10%.

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[11] H. E. Stagg, *Analyst*, **71**, 557 (1946).

[12] S. Ephraim, A. E. Woodward, and R. B. Mesrobian, *J. Am. Chem. Soc.*, **80**, 1326 (1958).

Thermal Decomposition of Copper and Silver Aryls in Aprotic Media[1]

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The thermal decomposition of phenyl- and *p*-tolylcopper in ether suspension and of phenyl- and *p*-tolylsilver in ether suspension and in pyridine solution has been studied. Addition of *p*-benzoquinone suppressed the yield of hydrocarbons remarkably. A cross product was formed in a statistical ratio on the competitive decompositions in homogeneous media. Probable mechanisms are discussed.

The preparations and some reactions of copper aryls and silver aryls have been reported, for instance, by Gilman and Straley[2] and Starkey, *et al.*,[3] but the thermal decomposition mechanism of these compounds does not seem to have been well characterized. Gardner and co-workers[4] studied the action of silver bromide on a mixture of phenylmagnesium bromide and *p*-anisylmagnesium bromide and on mixtures of phenylmagnesium bromide and various alkylmagnesium bromides. They also studied the thermal decomposition of a mixture of *p*-tolylsilver and *p*-anisylsilver. In all cases, all possible coupling products were formed and no evidence of reaction with solvent was found. They proposed that the decomposition of organosilver compounds is a bimolecular reaction of them rather than an interaction of free radicals formed initially.

As for alkylcopper and alkylsilver series, considerable work on their decomposition reactions has been performed by Semerano,[5] Gilman,[6] Bawn,[7] and Costa,[8]

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[1] Presented at the 18th Meeting of the Chemical Society of Japan, Tokyo, April 1965; Abstract, p 450.

[2] H. Gilman and J. M. Straley, *Rec. Trav. Chim.*, **55**, 821 (1936).

[3] F. A. Bolth, W. M. Whaley, and E. B. Starkey, *J. Am. Chem. Soc.*, **65**, 1456 (1943).

[4] (a) J. H. Gardner, L. Joseph, and F. Gollub, *ibid.*, **59**, 2583 (1937); (b) L. Joseph and J. H. Gardner, *J. Org. Chem.*, **5**, 61 (1940); (c) E. A. Bickley and J. H. Gardner, *ibid.*, **5**, 126 (1940).

[5] G. Semerano, L. Riccoboni, and F. Callegari, *Ber.*, **74**, 1297 (1941).

[6] H. Gilman, R. G. Jones, and L. A. Woods, *J. Org. Chem.*, **17**, 1630 (1952).

[7] (a) C. E. H. Bawn and F. J. Whitby, *Discussions Faraday Soc.*, **1**, 228 (1947); (b) C. E. H. Bawn and R. Johnson, *J. Chem. Soc.*, 3923 (1960); (c) C. E. H. Bawn and F. J. Whitby, *ibid.*, 3926 (1960); (d) C. E. H. Bawn and R. Johnson, *ibid.*, 4162 (1960).

[8] (a) G. Costa and A. Camus, *Gazz. Chim. Ital.*, **86**, 77 (1956); (b) G. Costa, A. M. Camus, and E. Pauluzzi, *ibid.*, **86**, 997 (1956); (c) G. Costa, G. De Alti, and S. Lin, *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis. Mat. Nat.*, **31**, 265 (1961); (d) G. Costa, G. De Alti, L. Stefani, and G. Boscarato, *Ann. Chim.* (Rome), **52**, 289 (1962).

and their co-workers. Bawn and co-workers[7] investigated the decomposition of copper and silver alkyls in alcoholic media. Methylsilver decomposed quantitatively to give ethane, while methylcopper gave methane mainly. From the above and other results, it was suggested that silver alkyls decompose to give free alkyl radicals, while copper alkyls do not decompose to give free radicals but react directly with the solvent. Costa and co-workers[8] isolated methylsilver, having a composition of $2CH_3Ag \cdot AgNO_3$, and methylcopper, having that of CH_3Cu, and studied their decomposition reactions. They found the evidence of formation of free radicals in the decomposition of methylcopper. On the other hand, they concluded that the decomposition of methylsilver proceeds by an intramolecular mechanism where methyl radicals are not formed during the reaction. The different mechanisms as described above are proposed even for the decompositions of silver or copper alkyls which have been comparatively well investigated.

Therefore, the present investigation was undertaken to determine the mechanism of the thermal decomposition of silver aryls and copper aryls, which may have some connection with the mechanisms of Ullmann and Sandmeyer reactions. The decomposition reactions of phenyl- and *p*-tolylcopper in ether and of phenyl- and *p*-tolylsilver in ether and in pyridine were studied. The copper aryls used were synthesized from arylmagnesium bromide and cuprous iodide, and the silver aryls from arylmagnesium bromide and silver bromide.

When phenylcopper in boiling ether and then in ether–xylene medium at 80° and phenylsilver in boiling ether were decomposed, both in suspension, the main reaction products were biphenyl together with some benzene. On the similar decomposition of *p*-tolylcopper or *p*-tolylsilver, 4,4′-bitolyl was likewise obtained as the main product (see Table I). The yield of biaryls reached about 65–80%, based on arylmagnesium bromide used. In the above reactions, addition of *p*-benzoquinone, a radical acceptor, decreased significantly the yield of the corresponding biaryls and benzene or toluene.

TABLE I

THERMAL DECOMPOSITION OF COPPER AND SILVER ARYLS IN SUSPENSION

Run	Method[a]	Reactant (mole × 10^3)[b]	Added *p*-benzoquinone, mole × 10^3	—Product yield, %— Ph–Ph[c] or Ar–Ar[d]	PhH or ArH
1	A	PhCu (40)	. .	66	20
2	A	PhCu (40)	. .	73	13
3	B	PhCu (30)	. .	67	5
4	B	PhCu (40)	. .	65	8
5	A	PhCu (41)	83	35	15
6	A	PhCu (41)	74	40	12
7	A	PhCu (40)	20	31	7
8	B	PhCu (30)	15	33	1
9	A	ArCu (39)	. .	62	24
10	A	PhAg (42)	. .	67	15
11	A	PhAg (40)	. .	79	14
12	A	PhAg (40)	20	9	6
13	A	PhAg (30)	15	11	4
14	A	ArAg (40)	. .	70	13

[a] See Experimental Section. [b] As 100% yield from arylmagnesium bromide used. [c] Ph, phenyl group. [d] Ar, *p*-tolyl group.

Phenylmagnesium bromide (1 mole equiv) and *p*-tolylmagnesium bromide (1 mole equiv) prepared separately were added to cuprous iodide (2.4 mole equiv) in ether and reacted below −20° to give a mixture of phenylcopper and *p*-tolylcopper. When the above mixture was competitively decomposed in boiling ether and then in ether–xylene at 80°, a considerable amount of a cross product, 4-methylbiphenyl, was produced, together with biphenyl, 4,4′-bitolyl, benzene, and toluene. Similar results were obtained when a mixture of phenylsilver and *p*-tolylsilver prepared by a similar method was decomposed in boiling ether (see Table II, runs 15 and 16). In these cases, "product distribution ratio" has a value close to 2, in which the product distribution ratio (r) is defined by eq 1,

$$r = \frac{[\text{Ph–Ar}]}{[\text{Ph–Ph}]^{1/2}[\text{Ar–Ar}]^{1/2}} \qquad (1)$$

where Ph is a phenyl group and Ar is a *p*-tolyl group. Moreover, even when phenyl- and *p*-tolylsilver solids synthesized separately were mixed in fresh ether and decomposed, the cross product was remarkably formed. With a mixture of phenyl- and *p*-tolylcopper solids, the similar results were obtained.

As it had been found that silver aryls have some solubility in pyridine, pyridine solutions of phenylsilver and *p*-tolylsilver were prepared separately by adding the solid silver aryl to pyridine below −25° and filtering at the same temperature to remove the undissolved substances. When the pyridine solutions were mixed together and decomposed at 50°, 4-methylbiphenyl, in addition to biphenyl and 4,4′-bitolyl, was produced and the product distribution ratio was 1.8:1.85. The value was not decreased by addition of *p*-benzoquinone to the decomposition mixture. In these cases, arylation products of pyridine were not detected.

For the thermal decomposition of copper and silver aryls in aprotic media, there are two mechanistic possibilities, that is, a free-radical mechanism and a bimolecular interaction without direct intervention of free radicals. It appears that copper and silver aryls decompose by a similar mechanism in aprotic media, for there were not remarkable differences in the experimental results of their decompositions. The fact that remarkable amounts of a cross product was formed on the decomposition in suspension of a mixture of solid copper aryls or silver aryls is difficult to be interpreted by a direct interaction mechanism of two molecules. The reason is that an exchange process such as eq 2 cannot greatly occur because of the insolubility of copper or silver aryls in the ether medium.

$$(\text{PhAg})_2 + (\text{ArAg})_2 \longrightarrow 2(\text{PhAg}\cdot\text{ArAg}) \qquad (2)$$

Since copper and silver aryls are mostly inert to simple ketones,[2] it seems that in the decompositions *p*-benzoquinone functioned mainly as a radical scavenger and decreased the yield of hydrocarbons. However, since *p*-benzoquinone is a conjugated ketone, the direct reaction of it with copper or silver aryls may be possible to some extent. If a radical mechanism is involved, there will be present the processes represented by the following equations, where M represents Cu

$$\text{PhM} \longrightarrow \text{Ph}\cdot + \text{M}$$

$$\text{ArM} \longrightarrow \text{Ar}\cdot + \text{M}$$

TABLE II

COMPETITIVE DECOMPOSITIONS OF COPPER OR SILVER ARYLS

Run	Reactant (mole × 10^3)[a]	Medium condition	Product yield, mole × 10^3 (mole ratio) Ph–Ph[b]	Ph–Ar[c]	Ar–Ar	PhH	ArH	r[d]
15	PhCu (40.0)	Homogeneous suspension in ether	5.80	10.5	5.13	8.70	11.3	1.92
	ArCu (40.0)		(1.00)	(1.82)	(0.89)			
16	PhAg (37.0)	Homogeneous suspension in ether	6.63	12.8	7.42	5.68	6.97	1.83
	ArAg (39.0)		(1.00)	(1.93)	(1.12)			
17	PhCu (<20)	Heterogeneous suspension in ether	2.27	2.36	1.20			1.42
	ArCu (<20)		(1.00)	(1.04)	(0.53)			
18	PhAg (<20)	Heterogeneous suspension in ether	2.42	3.45	1.93			1.59
	ArAg (<20)		(1.00)	(1.43)	(0.80)			
19	PhAg	Pyridine solution	0.230	0.953	1.22			1.80
	ArAg		(1.00)	(4.15)	(5.30)			
20	PhAg	Pyridine solution	0.126	0.679	1.08			1.85
	ArAg		(1.00)	(5.39)	(8.57)			
21	PhAg	Pyridine solution + p-benzoquinone	0.193	0.465	0.309			1.90
	ArAg		(1.00)	(2.41)	(1.60)			

[a] As 100% yield from arylmagnesium bromide used. [b] Ph, phenyl group. [c] Ar, p-tolyl group. [d] Product distribution ratio.

$$\mathrm{Ph}\cdot + \mathrm{Ph}\cdot \xrightarrow{k_1} \mathrm{Ph\text{-}Ph} \qquad (3)$$

$$\mathrm{Ar}\cdot + \mathrm{Ar}\cdot \xrightarrow{k_2} \mathrm{Ar\text{-}Ar} \qquad (4)$$

$$\mathrm{Ph}\cdot + \mathrm{Ar}\cdot \xrightarrow{k_3} \mathrm{Ph\text{-}Ar} \qquad (5)$$

$$\mathrm{Ph}\cdot \text{ or } \mathrm{Ar}\cdot + \mathrm{HS} \longrightarrow \mathrm{PhH} \text{ or } \mathrm{ArH} + \mathrm{S}\cdot$$

or Ag and HS is solvent etc. It can be safely presumed that phenyl and p-tolyl radicals have the same reactivities for radical recombination; so the following relation (6) is obtained, where $^1/_2$ is a statistical correction coefficient.

$$k_1 = k_2 = {}^1/_2 k_3 \qquad (6)$$

Consider a homogeneous system. From the differential rate expressions of the elemental processes (eq 3–5) and the relation of eq 6, the relation of $r = 2$ is derived. In fact, the competitive decompositions in homogeneous systems always gave a product distribution ratio close to 2. At the present time, since the direct detection of aryl radicals has not been performed on decomposition of copper or silver aryls, a mechanism such as a direct bimolecular interaction cannot always be ruled out. It seems, however, more probable from the experimental results, that both copper aryls and silver aryls decompose by a free-radical mechanism in aprotic media.

Experimental Section

Reagents.—Phenylmagnesium bromide and p-tolylmagnesium bromide solutions were prepared by the usual method by treating pure bromobenzene and p-bromotoluene (0.1 mole), trespetively, with magnesium turnings[9] (0.11 g-atom) in purified ether (60 ml) and filtering under a nitrogen atmosphere to remove the remaining solid materials. The concentrations of the above Grignard reagents were determined by the acid titration method.[10]

Cuprous iodide was prepared by the method given in the literature[11] from cupric sulfate, potassium iodide, and sodium thiosulfate. After being washed successively with distilled water, methanol, and ether, it was dried on silica gel under vacuum to give a white powder product. Silver bromide was prepared from silver nitrate and potassium bromide. By after-treatment similar to that of cuprous iodide except with exclusion of light as much as possible, silver bromide was obtained as yellow powder. It was stored on silica gel under vacuum in the dark till it was used.

Ether was dried with calcium chloride and with metallic sodium and then distilled in the presence of sodium. Xylene, bp 137–140°, was obtained from commercial grade mixed xylene by the usual procedures for purification. Pyridine was purified and dried as follows. It was allowed to stand with barium oxide for about 2 weeks. After being filtered rapidly, it was treated with an excess of ethylmagnesium bromide–ether solution and was filtered. The filtrate was distilled and the fraction boiling from 114 to 116° was collected.

p-Benzoquinone was purified by sublimation, mp 114.6–115.4°.

Standard Samples Used in Gas Chromatography and in Identification.—Benzene (bp 80.1°), toluene (bp 110.6°), o-nitrotoluene (bp 222°), biphenyl (mp 69.5–70°), 4-methylbiphenyl (prepared from diazotized p-toluidine and benzene,[12] mp 47.5–48.3°), and 4,4′-bitolyl (prepared by the reaction between p-tolylmagnesium bromide and p-bromotoluene in the presence of anhydrous ferric chloride,[13] mp 120.5–121.6°) were purified by the appropriate methods such as washing, drying, distillation, recrystallization, and column chromatography. Each of them showed only one peak in the gas chromatogram.

Syntheses of Copper Aryls and Silver Aryls.—The general procedures for preparation of copper aryls are similar to the following specific procedure for phenylcopper. To a 200-ml four-necked reaction flask provided with a stirrer, a thermometer, a dropping funnel, and a nitrogen inlet tube were added 9.15 g (0.048 mole) of cuprous iodide powder and 80 ml of ether. An amount of phenylmagnesium bromide–ether solution corresponding to 0.04 mole of C_6H_5MgBr was added dropwise under a nitrogen atmosphere to the suspension of cuprous iodide in ether cooled by a Dry Ice–methanol bath with vigorous stirring, while the reaction mixture was maintained below −20° by controlling the dropping rate. As the phenylmagnesium bromide solution was added, the cuprous iodide dissolved and yellowish phenylcopper was precipitated. After completing the addition of phenylmagnesium bromide, the reaction mixture was stirred about 1 hr below −20°. At that time, it was confirmed by the color test using Michler's ketone[14] that unreacted phenylmagnesium bromide did not remain.

For silver aryls, the same procedure was repeated except that 9.05 g (0.048 mole) of silver bromide powder was substituted in place of cuprous iodide and the reaction temperature was maintained below −25°. As phenylmagnesium bromide was added, the silver bromide dissolved and the reaction solution colored notably reddish purple and then pale white-purple phenylsilver was precipitated. When being stirred for about 2 hr below −25° after complete addition of phenylmagnesium bromide, no unreacted phenylmagnesium bromide remained as shown by the above color test.

Thermal Decompositions of Copper Aryls and Silver Aryls in Suspension.—The standard methods are as follows.

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[9] Purity 99.96%. The same lot of magnesium was used in all experiments.

[10] H. Gilman, E. A. Zoellner, and J. B. Dickey, *J. Am. Chem. Soc.*, **51**, 1576 (1929); H. Gilman, P. D. Wilkinson, W. P. Fishel, and C. H. Meyers, *ibid.*, **45**, 150 (1923).

[11] G. B. Kauffman and R. P. Pinnell, *Inorg. Syn.*, **6**, 3 (1960).

[12] M. Gomberg and J. C. Pernert, *J. Am. Chem. Soc.*, **48**, 1372 (1926).

[13] M. S. Kharasch and W. H. Urry, *J. Org. Chem.*, **13**, 101 (1948); M. S. Kharasch and E. K. Fields, *J. Am. Chem. Soc.*, **63**, 2316 (1941).

[14] H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

Method A.—The suspension of phenylcopper in ether in the reaction flask prepared as described above, as it was, was refluxed with stirring under a nitrogen atmosphere at 35° for about 2 hr by substituting a Dimroth reflux condenser for the dropping funnel. Then, after substituting a Widmer fractionating column for the reflux condenser, 50 ml of xylene was added and most of ether was distilled off. Again, substituting the reflux condenser for the fractionating column, the reaction mixture was heated at 80° for 2 hr to complete the decomposition. The resulting products[15] in the solution were determined by gas chromatographic analysis as described below.

The suspension of phenylsilver in ether prepared as described above was refluxed at 35° for 4 hr in a similar manner to that of phenylcopper without addition of xylene. During the reaction a characteristic green color appeared transiently, gray metallic silver was produced in the flask, and a silver mirror appeared on the wall of the flask. The decomposition products in solution were analyzed by gas chromatography.

Method B.—The supernatant ether layer was decanted from the prepared phenylcopper (or phenylsilver) in ether. The remaining phenylcopper (or phenylsilver) precipitates were washed several times with cold ether having a temperature below $-25°$. Then, after adding 80 ml of cold ether, they were decomposed as described above.

In the experiments with *p*-benzoquinone, it was added to the phenylcopper suspension below $-20°$ (or below $-25°$ in the case of phenylsilver) immediately before the decompositions were carried out.

Competitive Decompositions of Copper Aryls and Silver Aryls in Suspension.—Phenylmagnesium bromide (0.040 mole) and *p*-tolylmagnesium bromide (0.040 mole) solutions in ether prepared separately were added dropwise to cuprous iodide (0.088 mole) in 120 ml of ether below $-20°$ with vigorous stirring under a nitrogen atmosphere to obtain a mixture of phenylcopper and *p*-tolylcopper. After completing the reaction and confirming that unreacted Grignard reagents did not remain, the decomposition was carried out and the products were analyzed as described above (run 15). In a similar manner, a mixture of phenylsilver and *p*-tolylsilver was prepared, except that the reaction temperature was kept below $-25°$, and it was decomposed as was described in the case of phenylsilver (run 16).

In run 17, phenylcopper solid[16] (prepared from 0.030 mole of phenylmagnesium bromide and 0.036 mole of cuprous iodide in ether and washed with cold ether) and *p*-tolylcopper solid (prepared from 0.030 mole of *p*-tolylmagnesium bromide and 0.036 mole of cuprous iodide in ether and washed with cold ether) were mixed in 120 ml of ether below $-20°$ in a vessel and were decomposed. In the above mixing, considerable amounts of both solids remained in the reaction flasks and were lost owing to their adherence to the flasks.

Competitive Decompositions of Silver Aryls in Pyridine Solution.—To the phenylsilver solid (prepared from 0.030 mole of phenylmagnesium bromide and 0.036 mole of silver bromide as indicated above) was added 40 ml of pyridine below $-25°$. The resulting mixture was stirred for about 2 hr and then filtered below $-25°$ to obtain a clear, pale brown solution of phenylsilver in pyridine. In a similar manner, a solution of *p*-tolylsilver in pyridine was prepared. About 20 ml of each solution[17] were mixed together below $-25°$ and added to 40 ml of cold pyridine and then decomposed at 50° for 2 hr. In these experiments, it is because of the low solubilities of the silver aryls in pyridine that the product yields were low (runs 19–21).

Quantitative Determination and Identification of the Products.—Quantitative determination of reaction products[18] was performed by gas chromatography (column, Silicone DC 550; carrier gas, H_2). As internal standards, toluene for benzene, benzene for toluene, *o*-nitrotoluene for biphenyl, and biphenyl for 4-methylbiphenyl and 4,4′-bitolyl were used.

Biphenyl, 4-methylbiphenyl, and 4,4′-bitolyl produced in competitive decompositions were identified by melting point measurements, measurements of mixture melting points with authentic samples, and infrared spectra for the samples which had been fraction-collected by gas chromatography.

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[15] In method A, the amount of analyzed biphenyl was corrected by determining previously the biphenyl produced by Wurtz-type reaction during the preparation of phenylcopper.

[16] The compositions could not be determined exactly because the coordinated ether could not be removed completely even under a vacuum at a low temperature. The solid contained a small amount of magnesium salts (mole ratio of Cu to Mg *ca.* 20) as determined by analysis with 8-hydroxyquinoline.

[17] The concentrations of phenylsilver and *p*-tolylsilver were not determined because *r* is independent of them.

[18] It was found by preliminary experiments that the yields and compositions of the decomposition products were unchanged whether the reaction mixture was after-treated by water or not.

Conformational Analysis. XLVI. The Conformational Energies of the Simple Alkyl Groups[1-3]

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A series of 4-alkylcyclohexanecarboxylic acids has been prepared, and the *cis* ⇌ *trans* equilibria between the corresponding esters have been studied. The data allow the conformational free energies of the various groups to be calculated as follows (at 25° in ethanol solution): methyl, 1.8; ethyl, 1.8; isopropyl, 2.1; and carbethoxyl, 1.2 kcal/mole.

The conformational free energies ($\Delta G°$) of the simple alkyl groups are the basic quantities needed for the conformational analysis of cyclohexane ring systems. Prior to our studies, the conformational free energy of the methyl group was well established by thermodynamic methods,[4] while corresponding values for the ethyl[5] and isopropyl[5,6] were only very approximately known. Theory[7] indicates that the conformational free energies of the alkyl groups should increase in the order, methyl < ethyl < isopropyl < *t*-butyl, but the differences between the first three members of the

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[1] Paper XLV: N. L. Allinger, M. A. Miller, L. W. Chow, R. A. Ford, and J. C. Graham, *J. Am. Chem. Soc.*, **87**, 3430 (1965).

[2] This investigation was supported by Public Health Service Research Grant A-5836 from the National Institute of Arthritis and Metabolic Diseases.

[3] Abstracted from the Ph.D. Dissertation submitted to the Graduate School of Wayne State University by L. A. Freiberg, March 1962. A preliminary communication outlining the present work was published earlier: N. L. Allinger, L. A. Freiberg, and S. Hu, *J. Am. Chem. Soc.*, **84**, 2836 (1962).

[4] (a) E. J. Prosen, W. H. Johnson, and F. D. Rossini, *J. Res. Natl. Bur. Std.*, **39**, 173 (1947); (b) J. E. Kilpatrick, H. G. Werner, C. W. Beckett, K. S. Pitzer and F. D. Rossini, *ibid.*, **39**, 523 (1947); (c) C. W. Beckett, K. S. Pitzer, and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 2488 (1947).

[5] (a) D. S. Noyce and L. J. Dolby, *J. Org. Chem.*, **26**, 3619 (1961); (b) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955); (c) A. R. H. Cole and P. R. Jefferies, *J. Chem. Soc.*, 4391 (1956).

[6] (a) N. Mori, and F. Suda, *Bull. Chem. Soc. Japan*, **36**, 227 (1963); (b) H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Koninkl. Ned. Akad. Wetenschap, Proc.*, **64B**, 161 (1961).

[7] (a) N. L. Allinger and S.-E. Hu, *J. Am. Chem. Soc.*, **84**, 370 (1962); (b) *J. Org. Chem.*, **27**, 3417 (1962).