strength 0.1 F. The spectrophotometric pK_a values were obtained at two different wavelengths, agreement always being better than ± 0.03 units. The error in reported pK_a values is estimated to be less than $\pm 0.05 \text{ pK}_a$ units. Solubilities were determined spectrophotometrically at $27 \pm 2^{\circ}$ and are estimated to be accurate to within $\pm 5\%$.

Registry No.-1, 20336-15-6; 2, 38222-83-2; 38222-84-3; 4, 38222-85-4; 5, 2055-21-2; 6, 38222-86-5; 7, 38222-87-6; 8, 38222-88-7; 9, 38222-89-8; 10, 38222-90-1; 11a, 38222-91-2; 11b, 38222-92-3; 11c, 38222-93-4; 11d, 38222-94-5; 12a, 38222-95-6; 12b, 38222-96-7; 12c, 38222-97-8; 13, 38222-98-9; 14a, 38222-99-0; 14b, 38222-00-6; 14c, 38222-01-7; 15, 38223-02-8; 16a, 38222-03-9; 16b, 38223-04-0; pyridine, 110-86-1; 2,4,6-tri-tert-butylpyridine HAuCl4 salt, 29930-36-7; 4,4',6,6'-tetra-tert-butyl-2,2'-bipyridyl, 38223-05-1; 4-picoline, 108-894; 2,6-di-tert-butyl-4methylpyridine HAuCl₄ salt, 38218-84-7; 3-picoline, 108-

99-6; 2,6-di-tert-butyl-3-methylpyridine HAuCl₄ salt, 38295-40-8; 4-picolylamine, 3731-53-1; 3-picolylamine, 3731-52-0; 4-(2-dimethylaminoethyl)pyridine, 38223-06-2; 4-vinylpyridine, 100-43-6; 4-dimethylaminopyridine, 1122-58-3; 2-dimethylaminopyridine, 5683-33-0; 2-tert-butyl-6-dimethylaminopyridine HAuCl₄ salt, 38218-85-8; methyl iodide, 74-88-4; 2,6-di-tert-butylpyridine, 585-48-8; trimethylsulfoxonium iodide, 1774-47-6; trimethylsulfoxonium perchlorate, 38223-07-3.

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Amine Copper(I) Perchlorates. A Novel Class of Copper Species for Promoting Diazonium Ion Reactions

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Copper(I) perchlorates, complexed by heterocyclic amines, are effective at promoting homolytic cleavage of aryl diazonium salts in neutral medium. For 2-diazobenzophenone tetrafluoroborate the major products are 2,2'-dibenzoylbiphenyl (\sim 70%) and 9-fluorenone (\sim 30%). In the presence of cupric ion a high yield of 2hydroxybenzophenone is obtained; with hydrogen atom donors, e.g., ethanol, the major product is benzophenone.

The homolytic decomposition of aryl diazonium salts has been shown to be more effectively promoted by cuprous copper than by the metal itself.^{2,3} In fact, the replacement of metallic copper by cuprous oxide in the decomposition of 2-diazobenzophenone tetrafluoroborate (1) at 45° has demonstrated that by accelerating homolytic carbon-nitrogen bond scission, competition by the heterolytic pathway is essentially eliminated. Not all cuprous salts are, however, suitable as catalysts. Owing to the greater solvation energy of copper(II) ion, as compared to that of copper(I) ion, in water,⁴ all aquated copper(I) salts disproportionate to Cu(II) and Cu(0).⁵ Cuprous oxide, which had been the catalyst of choice,^{2,3} has the disadvantage of being effective in highly acidic medium only, owing to its insolubility in neutral water. Thus, diazonium ion decomposition requiring a neutral medium cannot be promoted by cuprous copper.

We have developed a series of relatively stable, soluble copper(I) salts, complexed by heterocyclic amines, which are effective in catalyzing homolytic diazonium ion decomposition in the pH range 2-6.

Results and Discussion

In the course of our investigations of anyl diazonium ion decompositions we have become interested in

(1) Taken from the dissertation of R. J. Michl submitted to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry (1971).

(2) A. H. Lewin, A. H. Dinwoodie, and T. Cohen, Tetrahedron, 22, 1527 (1966).

(3) A. H. Lewin and T. Cohen, J. Org. Chem., 32, 3844 (1967).
(4) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry,"
2nd ed, Interscience, New York, N. Y., 1966.

(5) R. G. R. Bacon and H. A. O. Hill, Quart. Rev. Chem. Soc., 19, 95 (1965).

carrying out homolytic reactions in neutral water. The 2-diazobenzophenone system was selected for study because of the considerable amount of reliable data already available concerning both the thermal^{3,6} and the copper-promoted⁸ reactions.

Cuprous oxide, reported to be an effective catalyst in acid solution,^{2,3} was found to promote homolytic decomposition of 2-diazobenzophenone tetrafluoroborate only at pH 1.25 or less. Other commercially available copper(I) salts (bromide, chloride, iodide, thiocyanate, and acetate) also failed to promote the reaction in neutral water. Copper(I) hydride,7 prepared by the procedure of Whitesides, et al.,8 was ineffective in catalyzing the decomposition.

Several known acetonitrile complexes of copper(I),⁹ as well as bis(2,9-dimethyl-1,10-phenanthroline)copper-(I) sulfate¹⁰ and two pyridinecopper(I) salts, were prepared and examined for suitability in promoting the homolytic decomposition of 1 in neutral water. The results, summarized in Table I, indicated that although two of the acetonitrile complexes were effective within the desired pH range (entries 1, 2) they formed copper (II), either by oxidation or by disproportionation, too rapidly to serve as useful catalysts. In the very stable phenanthroline complex (entry 5), on the other hand, copper(I) was stabilized to the point where it was in-

Soc., 3215 (1961). (10) C. J. Hawkins and D. D. Perrin, ibid., 2996 (1963); J. R. Hall, N. K. Marchant, and R. A. Plowman, Aust. J. Chem., 16, 34 (1963).

⁽⁶⁾ D. F. DeTar and D. I. Relyes, J. Amer. Chem. Soc., 76, 1680 (1954). (7) E. Wiberg and W. Henle, Z. Naturforsch. B, 7, 250 (1952); J. A.

 ⁽⁷⁾ E. Wieerg and W. Henle, Z. Natarijovsch. B. 1, 250 (1905).
 (8) G. M. Whitesides, J. San Filippo, Jr.; E. R. Stredowsky, and C. P. Casey, ibid., 91, 6542 (1969); G. M. Whitesides and J. San Filippo, ibid.,

^{92, 6611 (1970).} (9) B. J. Hathaway, D. G. Holahand, and J. D. Postlethwaite, J. Chem.

TABLE I

pH of the Reaction	OF COPPER(I) SALTS WITH
2-DIAZOBENZOPHENONE	TETRAFLUOROBORATE (1) ^a

No.	Salt	$_{\rm pH^b}$
1	$Tetrakis(acetonitrile)copper(I) perchlorate^{c}$	5.1
2	Tetrakis(acetonitrile)copper(I) nitrate ^{c,d}	5.5
3	Tetrakis(acetonitrile)copper(I) tetrafluoro- borate ^c	2.6
4	$(Acetonitrile)_x copper(I) sulfate^e$	2.0
5	(2,9-Dimethyl-1,10-phenanthroline)2-	i

6.2

- copper(I) sulfate 6 (Pyridine)_xcopper(I) nitrate^{c,e,f}
- 7 Tetrakis(pyridine)copper(I) perchlorate^{g,h}

^a The reaction consisted of adding 0.42 mmol of copper(I) salt to a stirred solution of 0.3 mmol of 2-diazobenzophenone tetrafluoroborate in 30 ml of water. Decomposition was moni-tored using the β -naphthol test: N. C. Cheronis and J. B. Entrokin, "Semimicro Qualitative Organic Analysis," Interscience, New York, N. Y., 1961. ^b The pH of the reaction was measured, using a pH meter, after the addition of the copper(I) complex to the diazonium salt. $^{\circ}$ The salt appeared as white crystals which turned blue on exposure to air. d This was the least stable of the acetonitrile complexes, turning blue rapidly on exposure to air. e The number of ligands (x) was presumed to be four, the most common coordination number of copper(I).⁴ ^f (Pyridine)_xcopper(I) nitrate was too unstable to react with the diazonium salt. ^g K. L. Chen and R. T. Twansato, Inorg. Nucl. Chem. Lett., 4, 499 (1968). h A. H. Lewin, R. J. Michl, P. Ganis, U. Lepore, and G. Avitabile, *Chem. Commun.*, 1400 (1971). ⁱ No reaction. (1971).

capable of reducing the diazonium ion and was therefore ineffective as a catalyst. Tetrakis(pyridine)copper(I) perchlorate (entry 7) seemed to meet all the required specifications; other heterocyclic amine complexes of copper(I) perchlorate were therefore investigated. Surprisingly, although the coordination compounds of heterocyclic amines with many transition metals are well known, only little work has been done on such copper(I) complexes.^{11,12} A series of perchlorate salts of copper(I) ligandated by pyridine, substituted pyridines, quinoline, and substituted quinolines was prepared by us, according to the procedure of Morgan.13

Effectiveness of these copper(I) perchlorate-amine complexes in promoting the homolytic decomposition of 1 was investigated and is examplified by the results obtained with tris(2-picoline)copper(I) perchlorate.¹⁴ The effects of adding copper(II) species and hydrogen-donating solvents are shown in Tables II and III.

Basically, our results parallel those for the cuprous oxide promoted decomposition of 1 in acid solution.³ Lewin and Cohen³ have shown that the addition of cupric ions as cupric nitrate to the reaction mixture led to increased phenol production. In our work, copper-(II) acetate hydrate was used, since it does not cause a large increase in acidity when dissolved in water as do most other copper(II) salts. Although cupric acetate was not so effective as cupric nitrate at low cupric ion concentration (entry 2, Table II) and the 200-fold increase in the ratio of 2-hydroxybenzophenone (3) to 9fluorenone (4) previously reported³ could not be achieved owing to the lesser solubility of cupric ace-

TABLE II

THE EFFECT OF THE ADDITION OF COPPER(II) ACETATE HYDRATE IN THE DECOMPOSITION OF 2-DIAZOBENZOPHENONE

TETRAFLUOROBORATE (1)^a

				Product yi 2-	elds, % ^{b-e}	
	Mmol of			Hydroxy-		
	cupric ion		Benzo-	benzo-	9-Fluo-	
	$[Cu(OAc)_2 \cdot$		phenone	phenone	renone	Ratio
No.	H_2O	$_{pH}$	(2)	(3)	(4)	of 3:4
1	0	6.2	1.0	1.0	28.0	0.04
2	3.5	6.0	1.0	d	24.0	
3	10.0		1.0	2.0	16.3	0.12
4	25.0		1.0	6.4	35.5	0.18
5	50.0		1.0	16.0	20.0	0.80
6	Satu- rated	5.2	2.0	39.0	12.6	3.10

^a Reaction of 0.6 mmol of 2-diazobenzophenone tetrafluoroborate and 1.22 mmol of tris(2-picoline)copper(I) perchlorate in 30 ml of water. ^b The yields were determined by vpc analysis vs. hexadecane as added internal standard. "The balance of the reaction was a fourth product, 2,2'-dibenzoylbiphenyl. ^d The product was present but as less than 1% of the overall reaction. • Overall yield was between 85 and 100%.

TABLE III The Effect of Hydrogen-Donating Solvents ON THE DECOMPOSITION OF 2-DIAZOBENZOPHENONE TETRAFLUOROBORATE (1)^a

		Product yields, % ^{b-a}				
		2- Hydroxy-				
No.	Composition of solution	Benzo- phenone (2)	benzo- phenone (3)	9-Fluo- renone (4)		
1	3 ml acetone 27 ml water	13.3	4.5	13.1		
2	15 ml acetone 15 ml water	10.5	7.2	1.5		
3	3 ml ethanol 27 ml water	46.5	d	10.5		
4	15 ml ethanol 15 ml water	77.0	d	2.0		
5	30 ml water	1.0	1.0	28.0		

^a Reaction of 0.6 mmol of 2-diazobenzophenone tetrafluoroborate and 1.0 mmol of tris(2-picoline)copper(I) perchlorate in 30 ml of solution. ^b The yields were determined by vpc analysis, vs. hexadecane as the added internal standard. ^c The balance of the reaction was the fourth product 2,2'-dibenzoylbiphenyl. ^d The product was detected but as less than 1% of the overall reaction. ^e Dimers were found: for acetone, 2,5-hexadione; and for ethanol, 2,3-butanediol. ^f Overall yield was between 85 and 100%.

tate,¹⁵ the right trend was observed, with a 75-fold increase in the ratio of 3 and 4 upon addition of cupric species (entries 1 and 6, Table II).

The presence of hydrogen donors in the reaction mixture had been shown to lead to reduction of the diazonium salt, *i.e.*, to benzophenone (2).³ In our hands addition of acetone (entries 2, 3, Table III) and ethanol (entries 3, 4, Table III) to the reaction produced significant increases in the yield of benzophenone. Both 2.5hexadione and 2.3-butanediol were observed as by-products, as expected from the coupling of the hydrogen donor radicals.

The most striking difference between the products of reactions promoted by cuprous oxide and by tris(2picoline)copper(I) perchlorate lies in the fact that, whereas benzophenone (2), 2-hydroxybenzophenone

^{(11) &}quot;Gmelins Handbuch," No. 60, Verlag Chemie, Weinheim/Bergstr., (11) Ginemis Handburn, A.G. 1.
Germany, 1966.
(12) W. E. Hatfield and R. Whyman, "Transition Metal Chemistry,"
Vol. 5, R. L. Carlin, Ed., Marcel Dekker, New York, N. Y., 1969.
(13) H. H. Morgan, J. Chem. Soc., 2901 (1923).

⁽¹⁴⁾ A. H. Lewin, R. J. Michl, P. Ganis, and U. Lepore, J. Chem. Soc., Chem. Commun., ibid., 661 (1972),

^{(15) &}quot;Handbook of Chemistry and Physics," 50th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1969.

(3), and 9-fluorenone (4) accounted for about 86% of the product in the copper(I) oxide promoted decomposition of 2-diazobenzophenone tetrafluoroborate (1),³ (
m Scheme I) only 30% of the product could be accounted



for in this way in the analogous decomposition by tris-(2-picoline)copper(I) perchlorate. It was suspected that the balance of the product may be a dimer, and therefore the effect of dilution on the product composition was examined. It was found that the sum of the yields of benzophenone (2), 2-hydroxybenzophenone (3), and 9-fluorenone (4) increased from 30 to 50% at extreme dilution (Table IV), consistent with the fourth product being dimeric. Small concentration changes did not have any notable effect. In addition it may be

TABLE IV

THE EFFECT OF DILUTION ON THE PRODUCT COMPOSITION IN THE DECOMPOSITION OF 2-DIAZOBENZOPHENONE TETRAFLUOROBORATE (1)^a

			—Product y 2-	ields, % ^{b-d}	
Water, ml	Dilution factor	Benzo- phenone (2)	Hydroxy- benzo- phenone (3)	9-Fluo- renone (4)	Sum of $2+3+4$
30	1	1.0	1.0	28.0	30.0
60	2	1.0	1.0	29.6	31.6
90	3	1.0	2.2	32.8	36.0
150	5	1.0	4.7	44.2	49.9
300	10	1,0	3.4	42.7	48.1
800	27	1.0	3.8	44.4	49.2

^a Reaction of 0.6 mmol of 2-diazobenzophenone tetrafluoroborate with 1.0 mmol of tris(2-picoline)copper(I) perchlorate. ^b The yields were determined by vpc analysis vs. hexadecane as the added internal standard. ^c The balance of the reaction was a fourth product, 2.2'-dibenzoylbiphenyl. ^d Overall yield was between 85 and 100%.

noted that an increase in the sum of the yields of benzophenone (2), 2-hydroxybenzophenone (3), and 9fluorenone (4) had been observed in the presence of large amounts of cupric species (Table II) as well as in the presence of hydrogen donors (Table III). It therefore appeared likely that the intermediate radical A was implicated, dimerizing to give 2,2'-dibenzoylbiphenyl (5) or reacting with radical B to give 5-(2benzoylphenyl)hydrofluorenone (6) (Scheme II).



A high-boiling material was isolated from the product mixture which had neither azo stretch^{16,17} nor bands typical for aliphatic or allylic hydrogens in the ir. The mass spectrum had major peaks at m/e 257, 105, and 77. An authentic sample of 2,2'-dibenzoylbiphenyl, prepared via the Ullmann biaryl synthesis of 2-iodobenzophenone,^{18,19} had ir and mass spectra identical with those of the material isolated from the product mixture. The dimer was therefore assigned the structure 2,2'-dibenzoylbiphenyl (5).

The fact that dimer formation is extensive in reactions promoted by copper(I) perchlorate ligandated by heterocyclic amines, but is essentially negligible in cuprous oxide promoted decomposition, may be due to the difference in cuprous copper concentration. The concentration of cuprous ion from dissolution of cuprous oxide in 0.1 N H₂SO₄³ is constant at 0.014 M,²⁰ whereas the initial concentration of cuprous copper in experiments with tris(2-picoline)copper(I) perchlorate is ca. 0.035 M. Since the rate of formation of radical A is a function of the concentration of cuprous copper, higher concentrations are A are more likely to be achieved with tris(2-picoline)copper(I) perchlorate²¹ than with cuprous oxide, favoring dimerization of A. The effect of cuprous copper concentration on the extent of dimer (5) formation are consistent with the above explanation, as seen in Table V. At high copper(I) concentration (entry 1, Table V) the product is almost exclusively the dimer 5; a distinct trend toward diminished dimerization is observed with decreasing cuprous copper concentrations. At low copper(I) concentrations (entries

(16) L. J. Bellamy, "Infrared Spectra of Complex Molecules," 2nd ed,
Wiley, New York, N. Y., 1958.
(17) P. Bassignana and C. Cogrossi, *Tetrahedron*, 20, 236 (1964).

(18) A. E. Tschitschibabin and P. G. Ssergejeff, Ber., 59, 654 (1926).
(19) R. G. R. Bacon and W. S. Lindsay, J. Chem. Soc., 1382 (1958).
(20) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hail,

Englewood Cliffs, N. J., 1961, p 187.

(21) These may be localized by complexation with the metal species.

AMINE COPPER(I) PERCHLORATES

TABLE V		TABLE	\mathbf{v}
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THE EFFECT OF CHANGING THE COPPER(I)/DIAZONIUM SALT RATIO IN THE DECOMPOSITION OF 2-DIAZOBENZOPHENONE TETRAFLUOROBORATE (1)^a

				(-)		
			Prod	uct yields,	% ^{b-d}	
	Molarity of	Ratio of		2-		
	tris(2-picoline)-	copper(I)	Dames	Hydroxy-	0. Elua	
	copper(1)	nium	phenone	phenone	Fenone	Sum of
No.	M	salt	(2)	(3)	(4)	2 + 3 + 4
1	0,200	10.0	0	0	13.8	13.8
2	0.134	6.7	0	0	21.5	21.5
3	0.100	5.0	1.2	0.7	23.2	25.1
4	0.067	3.3	0	0	22.0	22.0
5	0.050	2.5	1.2	1.4	28.9	31.5
6	0.034	1.7	1.0	1.0	28.0	30.0
7	0.023	1.2	1.0	1.0	31.8	33.8
8	0.020	1.0	4.6	2.5	29.6	36.7
9	0.017	0.8	1.5	2.5	36.8	40.8
10	0.014	0.7	1.0	4.5	21.0	26.5
11	0.010	0.5	T	ncomple	te react	ion

^a Reaction of 0.6 mmol of 2-diazobenzophenone tetrafluoroborate (1) in 30 ml of water. ^b The yields were determined by vpc analysis, vs. hexadecane as the added internal standard. ^c The balance of the reaction was the fourth product, 2,2'dibenzoylbiphenyl (5). ^d Overall yield was between 85 and 100%.

10, 11, Table V) the reaction becomes very sluggish and may no longer proceed by a homolytic pathway only, as suggested by the increased yield of phenol **3**.

It is noteworthy that the decomposition of 2-diazobenzophenone tetrafluoroborate (1) failed to go to completion when the ratio of copper(I) to diazonium salt dropped to 0.5 (entry 11, Table V). This observation is in accord with the proposed mechanism³ (Scheme I), since, according to this mechanism, copper(I) is not a true catalyst because only the reactions to produce 2hydroxybenzophenone (3) and possibly 9-fluorenone²² (4) regenerate copper(I).

Since the aminecopper(I) perchlorates were effective in promoting diazonium ion decompositions in the pH range 2–6, whereas copper(I) oxide was effective at rather high acidity (pH 1) only, the effect of pH on the product composition was investigated. By use of appropriate buffers, the pH of the 2-diazobenzophenone tetrafluoroborate decomposition reaction catalyzed by tris(2-picoline)copper(I) perchlorate was varied between 6 and 2. Analysis of the product composition indicated a negligible pH effect (Table VI).

Conclusions

The aminecopper(I) perchlorates synthesized are effective in promoting homolytic decomposition of aryl diazonium salts in neutral solution. In dilute solution (ca. 0.002 M) in diazonium salt with a copper(I) to diazonium salt ratio of ca. 0.8, the results obtained are analogous to those obtained at pH 1 with cuprous oxide.³ Thus, the copper(I)-promoted reaction of 2diazobenzophenone tetrafluoroborate (1) yields primarily (a) 9-fluorenone (4) in pure water; (b) benzophenone (2) in the presence of hydrogen atom donors; and (c) ligand transfer product (e.g., 2-hydroxybenzophenone, 3) in the presence of cupric species with transferable ligands (e.g., aquated cupric ions). The dimer, 2,2'-dibenzoylbiphenyl (5), is produced at high copper(I) concentrations. Copper(I) has been shown

(22) 9-Fluorenone may be produced from B via air oxidation.

TABLE	VI
TUDUC	× 1

Тне	Effect	OF	ALTERING	the pH	OF	THE	Decomposition
01	F 2-DIAZ	OBI	NZOPHENO	NE TETE	LAF.	LUOR	OBORATE $(1)^a$

ъ ц	Benzophenone	Product yield, % ^{b-} 2-Hydroxy- benzophenone	9-Fluorenone
pn	(2)	(3)	(*)
6.0	1.0	1.0	28.0
5.0	1.2	d	28.3
4.0	1.0	d	34.4
2.0	1,0	2.0	31.1

^a Reaction of 0.6 mmol of 2-diazobenzophenone tetrafluoroborate and 1.22 mmol of tris(2-picoline)copper(I) perchlorate in 30 ml of buffered solution. ^b The yields were determined by vpc analysis vs. hexadecane as the added internal standard. ^c The balance of the reaction was a fourth product, 2,2'-dibenzoylbiphenyl. ^d The product was present but as less than 1% of the overall reaction. ^e Overall yield was between 85 and 100%.

not to be a true catalyst, in agreement with the previously proposed mechanism,² since a nearly equimolar amount is required to complete the reaction.

Experimental Section

Physical Measurements.—Infrared spectra in the wavenumber range $4000-600 \text{ cm}^{-1}$ were obtained with a Perkin-Elmer Model 521 spectrophotometer using potassium bromide pellets.

pH Measurements were read with a Beckman Model 76 expanded-scale pH meter. The meter was standardized with buffer solutions purchased from Fisher Scientific.

Mass spectra were recorded on a Perkin-Elmer Hitachi RMU 6 mass spectrophotometer. The samples were normally run at 80 eV.

Gas chromatographic analysis was done on a Varian Aerograph Model A 90-P3 with a linear temperature programmer. The product mixture (benzophenone, 2-hydroxybenzophenone, and 9-fluorenone) was analyzed on a 6-ft 18% Apeizon L column (on 70/80 Anakrom ABS) at 210° with a helium flow rate of 50 ml/min. Analysis of 2,2'-dibenzoylbiphenyl was performed on a 6-ft 25% SE-30 column (on 70/80 Anakrom ABS) at various program rates from 50 to 320°, at a helium flow rate of 30 ml/ min. Hexadecane (Metro Scientific) was used as the internal standard and the products were all calibrated vs. this standard.

Buffers.—The following buffers were obtained from Fisher Scientific and used directly: pH 6 monopotassium phosphatesodium hydroxide, 0.05 M; pH 5 potassium biphthalate-sodium hydroxide, 0.05 M; pH 4 potassium biphthalate, 0.05 M; pH 2 potassium chloride-hydrochloric acid, 0.05 M. **2-Diazobenzophenone Tetrafluoroborate**²³—To a solution of

2-Diazobenzophenone Tetrafluoroborate²³—To a solution of 0.99 g (5 mmol) of 2-aminobenzophenone (Aldrich) in 30 ml of ethanol containing 2.65 g (15 mmol) of fluoroboric acid (Baker, 50% in H₂O) which was stirred and cooled to 0° was added 0.65 g (5.5 mmol) of isoamyl nitrite dropwise, keeping the temperature between 0 and 1°. The reaction mixture was stirred at 0° for 15 min, during which time precipitation took place. At the end of 15 min, 150 ml of ice-cold ether was added and the mixture was stirred at 0° for 30 min longer. The white precipitate (80% yield) was filtered and stored in a vial which was tightly capped and refrigerated.

Procedure for the Decomposition of the Diazonium Salt.—All the decomposition reactions were highly reproducible. When reactions were repeated and analyzed on the vpc, deviations of no more than 0.5% could be noted provided that the peaks were sufficiently large. For the small peaks (products of less than 5% of the reaction) large errors of 1-2% were apparent. All the products were stable under the reaction conditions. The internal standard, hexadecane, was always added in the same amount (0.088 ml, 0.3 mmol) to every reaction after it had been worked up.

The reactions were carried out as follows. The copper(I) catalyst was added to a solution of the diazonium salt in water, with stirring. If the reaction was to be performed in the presence of hydrogen donors, copper(II) ion, etc., they were added to

(23) J. Lipowitz and T. Cohen, J. Org. Chem., 30, 3891 (1965).

the water before addition of the diazonium salt and the copper(I)catalyst. A β -naphthol test was done on all the reactions to ascertain that all the diazonium salt had decomposed. When the reaction was complete, as indicated by a negative β -naphthol test, the reaction mixture was extracted three times with 150 ml of methylene chloride. If the reaction was performed in acidic solution, the combined organic extract was washed with saturated NaHCO₃ and water before drying. The combined organic extracts were then dried over anhydrous magnesium sulfate and concentrated at reduced pressure.

Copper(I) Hydride.^{7,8}—Copper(I) hydride was prepared by the reaction of lithium aluminum hydride with copper(I) iodide in pyridine; however, the resulting CuH was impure and stable when exposed to air. In a procedure reported by Whitesides⁸ using dissobutylaluminum hydride and copper(I) chloride in place of LiAlH4 and CuI, a pure product of CuH was obtained. The material, which was light brown, decomposed in about 10 min after being dried from ether. This, however, was enough time for us to carry out experiments.

2-Iodobenzophenone.18,19-o-Iodobenzoyl chloride (Fisher, reagent grade) 50 g (0.188 mol), in 200 ml of dry benzene was gradually treated with 28 g (0.211 mol) of powdered anhydrous aluminum chloride, and the mixture was refluxed for 2 hr. After hydrolysis of the complex, o-iodobenzophenone along with other products was obtained as a nearly colorless liquid (34 g, 59%), bp 143° (0.3 mm), which solidified and gave needles, mp 32.5°, from hexane.

2,2'-Dibenzoylbiphenyl.-o-Iodobenzophenone, 20 g (0.065 mol), and 18 g (0.284 g-atom) of electrolytic copper (Fisher) in 40 ml of dimethylformamide were heated under reflux for 2 hr. The product was taken up in chloroform, the solvents were removed, and the solid residue was recrystallized from cyclo-hexane, yielding 9.0 g (76%) of 2,2'-dibenzoylbiphenyl as white needles, mp 167°.

Registry No.-1, 342-62-1; 2, 119-61-9; 3, 117-99-7; 4, 486-25-9; 5, 24018-00-6; salt 1, 14057-91-1; salt 2, 37847-53-3; salt 3, 15418-29-8; salt 4, 37821-06-0; salt 7, 37821-07-1; copper(II) acetate monohydrate, 6046-93-1; 2-iodobenzophenone, 25187-00-2.

Reaction of Acetaldehyde with Mono- and Binuclear Organoaluminum Compounds at Low Temperature

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Studies of the reaction of pentaalkyldialuminum alkali metal oxide and its nitrogen and sulfur analogs with acetaldehyde at -78, -20, and 0° are reported and compared with AlR₃ alone and with mononuclear complexes AlR_{3} Do. AlR_{4} gave addition and reduction products as the primary reaction and some secondary reaction The reactivity of AlR₃ Do decreased with respect to both of the primary and secondary reactions with products. increase in the strength of the complex. Pentaalkyldialuminum complexes have high reactivity concerning the primary reaction, but have very low activity for the secondary reactions. The results can best be understood by a bimetallic cyclic transition state. With [R₂AlZLi] · [AIR'_a], R' addition and R addition occurred simultaneously, indicating a slow alkyl exchange process through a bridging alkyl.

Our recent works on the polymerization catalyst revealed that the reaction products from trialkylaluminum with alkali metal hydroxide¹⁻⁴ and lithium amide^{2,3,5} in a molar ratio of 2:1 gave highly isotactic polyacetaldehyde with desired properties.⁴ Extensive studies on the syntheses in the pure state⁶ and nmr spectroscopy⁷ on the structures in solution have elucidated that the organoaluminum compound produced can be represented as a series of binuclear complexes of the formula $[R_2AlZM] \cdot [AlR_3]$ with high complex stability when Z = O or NR', in which R_2AlZM serves as a donor and AlR_3 as an acceptor.

In order to study both the active species for initiation and the side reactions by the organoaluminum catalyst in the polymerization, detailed studies on the reaction with acetaldehyde were carried out at -78 (polymerization temperature), -20, and 0° (higher than the ceiling temperature of the polymerization). The binuclear organoaluminum compound was found to exhibit a characteristic reactivity of the AIR group as compared with trialkylaluminums and their mononuclear complexes. Our results may contribute also to fill the gaps in our knowledge of the reactions of organoaluminum reagents with carbonyl compounds,⁸⁻¹⁰ in which reaction intermediates involving two metals have been presumed for a few cases.¹¹⁻¹³ On the basis of the reaction of acetaldehyde with $[R_2AlZM] \cdot [AlR'_3]$ new information on the intramolecular alkyl-alkyl and "alkyl-alkoxyl" exchange reactions is also obtained.

Results and Discussion

Trialkylaluminums.—On the basis of the results with AlEt₃, AlMe₃, and Al-i-Bu₃ (Table I), the reaction process of acetaldehyde can be summarized in Scheme I, which involves primary and secondary reactions.¹⁴ In the primary reaction AlR₃ reacts with acetaldehyde in two ways; widely known Grignard addition (a) and reduction (b). The organoaluminum alkoxides derived from the primary reaction acts as the reagent for

 (8) (a) H. Gilman and K. E. Marple, Reel. Trav. Chim. Pays-Bas, 55, 518 (1936);
 (b) H. Meerwein, G. Hinz, H. Majert, and H. Sönke, J. Prakt. Chem., 147, 226 (1936).

(9) (a) K. Ziegler in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold, New York, N. Y., 1960, p 240; (b) H. Lehmkuhl and K. Ziegler in Hauben-Weyl's "Methoden der Organischen Chemie," Bd. 13/4, Metal-lorganische Verbindungen, Al, Ga, In, Tl. S.1, 1969.
 (10) T. Eicher in "The Chemistry of the Carbonyl Group," S. Patai,

Ed., Wiley, New York, N. Y., 1966, p 677.

(11) E. C. Ashby, J. Laemmle, and H. M. Neaman, J. Amer. Chem. Soc., 90. 5179 (1968).

- (13) S. Pasynkiewicz and E. Sliva, J. Organometal. Chem., 3, 121 (1965). (14) Similar reaction products have been observed with substituted benz-
- aldehyde recently: Y. Baba, Yuki Gosei Kayaku Kyokai Shi, 27, 264 (1969).

⁽¹⁾ H. Tani, T. Aovagi, and T. Araki, J. Polum. Sci., Part B-2, 921 (1964). (2) H. Tani, T. Araki, N. Oguni, and T. Aoyagi, *ibid.*, Part B-4, 97 (1966).

⁽³⁾ H. Tani, T. Araki, N. Oguni, T. Aoyagi, K. Hayakawa, and M. Mi-

kumo, Preprints of papers presented at International Symposium on Macro-molecular Chemistry, Tokyo-Kyoto, Japan, 1966, Vol. I, p 193. (4) T. Aoyagi, T. Araki, and H. Tani, J. Polym. Sci., Part A-1, 10, 2325

^{(1972).} (5) H. Tani and N. Oguni, ibid., Part B-3, 123 (1965).

⁽⁶⁾ T. Aoyagi, T. Araki, N. Oguni, M. Mikumo, and H. Tani, Inorg. Chem., to be published.

⁽⁷⁾ T. Aoyagi, T. Araki, N. Oguni, and H. Tani, ibid., in press.

⁽¹²⁾ E. A. Jeffery and T. Mole, Aust. J. Chem., 23, 715 (1970)