TABLE II

EXPERIMENTAL RESULTS

Initial concentrations: $HClO_4$, 0.500 *M;* $KBrO_3$, 0.00500 *M*

Experiment	1	2	3	5
Init. $[H_2O_2]$, mole/liter $\times 10^2$	4.86	4.81	4.56	5.63
Init. [NaBr], mole/liter $\times 10^3$	15.6	7.80	3.90	0
Max. (HBrO), mole/liter $\times 10^9$	6.75	7.6	5.1	2.1
$[Br^-]$, mole/liter at HBrO max. $\times 10^3$	7.6	4.0	2.6	1.5
Time, min., at HBrO max.	3	4	4	27
V_c for HBrO max. $\times\cdot 10^4$	1.7	0.96	0.88	0.39
V_d for HBrO max. $\times 10^4$	2.8	3.2	2.0	0.89
$d[O_2]/dt$ at HBrO max. $\times 10^4$	2.6	2.8	2.0	1.5

In Table II are given the results of three other sets of experiments. It will be observed from columns 7, 8, 9, of this table, that when the maximum value of hypobromous acid is reached early in the experiment (where the loss in bromine has been negligible and consequently the measurements are reliable) the rate of oxygen evolution can be represented by reaction d. Since it is not necessary to assume oxygen evolution by reaction c, these results seem to indicate that the rate of the reduction of $HBrO_2$ by Br^- in these strongly acid solutions is considerably greater than the rate of reaction c. It appears, therefore, that in solutions in which the bromide ion concentration is at least 2.6×10^{-3} *M*, reaction c should be replaced by a new reaction $HBrO_2 + H^+ + Br^- = 2\ HBrO$.

In the case of experiment 5, the results are inconclusive. The observed rate is greater than the rate of reaction d, and the indications are that in these concentrations reaction c must be considered also. Unfortunately, however, the accumulated bromine was not appreciable in this experiment until the experiment was well advanced, and conditions were such that the experimental error was relatively high.

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NEW COMPOUNDS

The Acylation of Biphenyl with Dimethylcarbamyl Chloride

Biphenyl has been acylated with dimethylcarbamyl chloride in the Friedel–Crafts manner, without a solvent. Both the mono- and the diamide were obtained.

4-Biphenyl-N,N-dimethylcarboxamide.—Into a 2-l., 3-necked flask equipped with a condenser, mechanical stirrer, thermometer and a Glascol heater were placed 600 g. (3.9 moles) of biphenyl and 325 g. (3 moles) of dimethylcarbamyl chloride.[1] During twenty minutes 400 g. (3 moles) of anhydrous aluminum chloride was added in 50-g. portions, at such a rate that the reaction temperature did not exceed 120°. After all of the aluminum chloride had been added, the temperature was raised slowly to 150–170° and maintained in that range for four and one-half hours. The resulting mixture was cooled and poured onto ice. The unreacted biphenyl (146 g., 24.3% recovery) was removed by distillation, and the residue was recrystallized once from methanol to give 566 g. of amide, m. p. 93–96°, 84% based on dimethylcarbamyl chloride. The amide could also be purified by distillation at 175–180° (1 mm.). After further crystallization from methanol the compound melted at 105.5–106.5° cor.

Anal.[2] Calcd. for $C_{15}H_{15}ON$: N, 6.22. Found: N, 6.21, 6.36.

The amide was treated for six hours with sodium hydroxide in boiling methanol, and the salt was refluxed for five minutes with 20% sulfuric acid to give biphenyl-4-carboxylic acid, m. p. 226.5–228° cor. Gull and Turner[3] reported m. p. 228° for this compound.

Previously described Friedel–Crafts acylations with carbamyl chlorides have been limited to the use of carbamyl chloride itself,[4] and diphenylcarbamyl chloride.[5] Other mention was made of the use of disubstituted carbamyl chlorides, but no experimental data were given for such a reaction.[6]

4,4′-Biphenyl-N,N,N′,N′-tetramethyldicarboxamide.—The procedure was the same as that used for the monoamide, except that the reaction was carried out for nine hours at 150–180°. The resulting mixture was decomposed by pouring into hot water, and the product was recrystallized from benzene. From 308 g. (2 moles) of biphenyl, 535 g. (5 moles) of dimethylcarbamyl chloride and 668 g. (5 moles) of aluminum chloride there was obtained 350 g. of diamide, m. p. 187–205°, 59% based on biphenyl. Further recrystallizations gave m. p. 217–217.5° cor.

Anal.[2] Calcd. for $C_{18}H_{20}O_2N_2$: N, 9.45. Found: N, 9.40, 9.45.

When the reaction mixture was decomposed with ice and dried, an infusible, methanol-insoluble product containing 4.3% aluminum and 6.1% chlorine[2] was obtained. The use of hot water in the decomposition freed the amide of aluminum compounds.

Hydrolysis of the amide with sodium hydroxide in boiling amyl alcohol followed by acidification gave an acid which did not melt or sublime and was insoluble in the usual organic solvents. These characteristics have been reported for biphenyl 4,4′-dicarboxylic acid.[7]

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[1] Slocombe, Hardy, Saunders and Jenkins, THIS JOURNAL, **72**, 1888 (1950).

[2] The authors wish to thank Mr. W. B. Dunlap for these analyses.

[3] Gull and Turner, *J. Chem. Soc.*, 491 (1929).

[4] (a) Gattermann, *Ann.*, **244**, 30 (1888). Hopff and Ohlinger, "The Synthesis of Mono- and Dicarboxylic Acids from Aromatic Hydrocarbons and Carbamyl Chloride, with Special Consideration of Polycyclic Hydrocarbons," Off. Pub. Bd. Report P. B. 75249.

[5] Lellmann and Bonhoffer, *Ber.*, **20**, 2118 (1887).

[6] Hopff and Ohlinger, U. S. Patent 2,137,287; *C. A.*, **33**, 1759 (1939).

[7] Doebner, *Ber.*, **9**, 271 (1876).

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Tertiary Acetylenic Amines. II[1]

Parcell and Pollard reported a method for the synthesis of tertiary, acetylenic amines by the dehydrohalogenation of halo-alkenylamines with sodium amide in liquid ammonia.[2] The synthesis of 1-diethylaminopropyne-2 by

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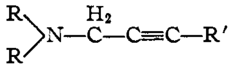
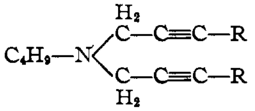
[1] This paper is abstracted from a portion of the Ph.D. Dissertation of R. F. Parcell, a project under the sponsorship of the Office of Naval Research.

[2] Parcell and Pollard, THIS JOURNAL, **72**, 2385 (1950).

TABLE I

PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR TWENTY TERTIARY, ACETYLENIC AMINES





Compound	Yield, %	B. p., °C. (cor.)	B. p., Mm.	n^{25}_D	d^{25}_4	MR_D Calcd.	MR_D Found	N, % Calcd.	N, % Found
1-Dipropylaminopropyne-2	81	157.5–158.5	..[a]	1.4325	0.7986	45.70	45.26	10.06	10.09
1-Dipropylaminobutyne-2	81	70.0–70.5	10	1.4431	.8099	50.32	50.24	9.14	9.09
1-Dipropylaminopentyne-2	82.5	81.0–81.5	10	1.4423	.8040	54.94	55.09	8.37	8.42
1-Dipropylaminohexyne-2	75	94–95	10	1.4441	.8066	59.55	59.73	7.73	7.52
1-Dipropylaminoheptyne-2	76	108–109	10	1.4459	.8087	64.17	64.40	7.17	7.27
1-Dipropylaminoöctyne-2	77	120.5–121.5	10	1.4471	.8115	68.79	68.94	6.69	6.94
1-Diisopropylaminopropyne-2	81.5	152.5–153	..[a]	1.4385	.8017	45.70	45.64	10.06	10.19
1-Diisopropylaminobutyne-2	43	64–65	10	1.4482	.8209	50.32	49.97	9.14	9.03
1-Diisopropylaminopentyne-2	68	75.5–76	10	1.4470	.8146	54.94	54.94	8.37	8.38
1-Diisopropylaminohexyne-2	62	89–90	10	1.4490	.8182	59.55	59.44	7.73	7.75
1-Diisopropylaminoheptyne-2	62	103	10	1.4505	.8200	64.17	64.09	7.17	7.27
1-Diisopropylaminoöctyne-2	66	115.5–116.5	10	1.4515	.8203	68.79	68.79	6.69	6.71
1-Dibutylaminopropyne-2	89	77.5–78.5	10	1.4381	.8045	54.93	54.59	8.37	8.13
1-Dibutylaminobutyne-2	75	97.5–97.8	10	1.4465	.8139	59.55	59.46	7.73	7.73
1-Dibutylaminopentyne-2	76	107–107.2	10	1.4455	.8090	64.17	64.33	7.17	6.92
1-Dibutylaminohexyne-2	72	119.5–119.8	10	1.4472	.8813	68.79	68.98	6.69	6.65
1-Dibutylaminoheptyne-2	75.5	131.6–132.2	10	1.4483	.8127	73.41	73.63	6.27	6.26
1-Dibutylaminoöctyne-2	77	143.5–143.8	10	1.4498	.8144	78.03	78.32	5.90	5.84
N-*n*-Butyl-di-2-propynylamine	76.5	73–74	10	1.4567	.8512	48.31	47.71	9.39	9.36
N-*n*-Butyl-di-2-butynylamine	72	114.5–115.5	10	1.4778	.8616	57.56	58.20	7.90	7.80

[a] Boiling point at normal atmospheric pressure is given.

this method was described. Various alkyl halides were then coupled with the sodium acetylide of 1-diethylaminopropyne-2 to form a series of 1-diethylamino-2-alkynes. These reactions have been applied in the synthesis of three additional series of tertiary, monoacetylenic amines and in the synthesis of two tertiary, diacetylenic amines.

The physical constants and analytical data for the compounds prepared are summarized in Table I.

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A New Complex of Acetylsulfanilamide, Ethylenediamine and Copper

Complexes of several sulfa compounds with ethylenediamine and various metals have been reported.[1,2,3,4,5] Bacteriostatically inactive N^1-acetylsulfanilamide was chosen for the present investigation so that the bactericidal and fungicidal properties of its complex with ethylenediamine and copper could be studied; these studies will be reported at a later date.

The complex was prepared by adding 0.25 mole of finely powdered N^1-acetyl-sulfanilamide to a stirred solution of 0.10 mole of freshly prepared moist cupric hydroxide in 0.50 mole of ethylenediamine monohydrate. The resulting solution, filtered through glass wool, was poured into 2–3 times its volume of ethanol. After twenty-four hours the solid product was filtered by suction, washed with absolute ethanol and dried in a vacuum desiccator over sulfuric acid. The blue crystalline complex has a density of 1.4577 at 15° and melts at 190°. It is insoluble in ether, acetone, chloroform, benzene, cold ethanol and cold carbon bisulfide (gives copper sulfide when warmed with carbon bisulfide) but is soluble in ethylene glycol, propylene glycol, glycerol and hot ethanol. The complex is insoluble in cold 10% acetic acid but soluble in hot 10% acetic acid, water, 4% sodium hydroxide, 4% hydrochloric acid, glacial acetic acid, concd. hydrochloric acid, concd. sulfuric acid and 30% sodium hydroxide. Only the solutions in the more concentrated acids give the reactions of the cupric ion.

The analytical data indicate a complex containing N^1-acetylsulfanilamide, ethylenediamine and copper in the ratio 2:2:1.

Anal. Calcd.: N, 18.3; S, 10.5; Cu, 10.4. Found: N, 17.7; S, 10.9; Cu, 10.4.

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(1) J. Erdos, *Ciencia* (*Mex.*), **8**, 265 (1948).

(2) J. Erdos, *Anales escuela nacl. cienc. biol.* (*Mex.*), **5**, 105 (1948).

(3) J. Erdos and R. Ramirez, in press.

(4) J. Erdos and L. Ortiz, in press.

(5) J. Erdos and M. Bernea, in press.