vents. The residual oil solidified on cooling. After recrystallization from *ca.* 30 ml. of hot benzene it weighed 0.97 g., m.p. 153–157°; an additional 0.18 g., m.p. 153–159°, was obtained by concentrating the benzene filtrate; total yield 55%. Recrystallization once from ethanol and once from acetone gave colorless plates, m.p. 167°. *Anal.* Calcd. for $C_{12}H_{10}N_4$: C, 68.55; H, 4.79. Found: C, 68.74; H, 4.48.

In a similar experiment in which 2.3 ml. of stannic chloride was substituted for aluminum chloride, a heavy, yellow precipitate formed immediately, and no gas evolution was detectable. The addition of 15 ml. of chloroform appeared to dissolve some of the solid, and started gas evolution. No crystalline product could be isolated by the foregoing work-up procedure, except for a small amount of unreacted ketone.

In an experiment with quantities identical to the successful one, the hydrogen azide solution was added to the solution of ketone and aluminum chloride at the rate of one drop in four seconds, with motor stirring. When worked up as before, there was obtained a crystalline solid, which when recrystallized from absolute ethanol gave 0.39 g. (19%) of crude tetrazole, m.p. 150–152°. Evaporation of the filtrate gave 1.14 g. of sticky, brown solid, which by recrystallization from benzene gave 0.2 g. (11%) of β-acetamidonaphthalene, m.p. 127–129° alone, and 130–132° when mixed with an authentic sample.

In an experiment identical with the first one except for the use of half the quantity of hydrogen azide (5 ml. of 1.4 *N*), there was obtained 0.47 g. (73% based on HN_3) of tetrazole, m.p. 158–159°.

1-Phenyl-5-methyltetrazole.—The first experiment described under β-acetonaphthone was repeated using 1.2 g. of acetophenone and the hydrogen azide obtained from 1.0 g. of sodium azide. There was obtained 0.54 g. (34% based on ketone; 42% based on NaN_3) of 1-phenyl-5-methyltetrazole, silky needles, m.p. 98–99° (reported[24] 98–99°).

To determine whether the tetrazole may have resulted from a secondary reaction induced by aluminum chloride on acetanilide first formed, 1.35 g. of acetanilide was treated in nitrobenzene solution with 2.7 g. of aluminum chloride and the hydrogen azide from 1.0 g. of sodium azide. After two hours the solvents were removed by steam distillation. The homogeneous, aqueous residue deposited no tetrazole on cooling; 0.32 g. of the characteristic leaves of crude acetanilide, m.p. 106–107°, was obtained by seeding. At the most, tetrazole could only have been present in the small amount necessary to lower the melting point to this extent.

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(24) A. G. Knoll, *Chem. Fabriken*, German Patent 540,409 (Feb. 12, 1927); *C. A.*, **26**, 3263^8 (1932).

ANN ARBOR, MICH.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BOSTON UNIVERSITY]

Preparation and Reactions of Bis-diazoalkanes

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Bis-nitrosoureido alkanes, bis-nitrosocarbamates and dinitroso diaza diketones have been made and decomposed to form bis-diazoalkanes which were not isolated, but were allowed to react with carboxylic acids, aldehydes, acetone, phenol and ethyl acetoacetate.

Bis-diazoalkanes have been reported by Petersen,(3) by Lieser and Beck(4a) and by Lettré and Brose,(4b) although none of these reports were available when our work was started.

Lieser and Beck prepared several bis-diazoalkanes by the treatment of an ethereal solution of the bisnitrosoureides, $NH_2CON(NO)(CH_2)_xN(NO)CONH_2$, where $x = 2–6$ and of the bis-nitrosocarbamates, $EtOOCN(NO)(CH_2)_xN(NO)COOEt$, where $x = 3–8$, with 40% aqueous potassium hydroxide at 0°. Ethereal solutions of the bis-diazoalkanes were allowed to react with phenol, β-naphthol or catechol, but neither yields nor analyses were given.

Lettré and Brose prepared ether solutions of bis-diazoalkanes from the bis-nitrosoureides, $H_2NCON(NO)(CH_2)_xN(NO)CONH_2$ where $x = 3–6$ and allowed these bis-diazoalkanes to react with benzoic acid and *p*-nitrobenzoic acid.

We have made bis-diazoalkanes not only from bis-nitrosoureido alkanes(3,4a,4b) and bis-nitrosocarbamates(3,4) but also from dinitroso diaza diketones which were made by a modification of the method used by Berenbom and Fones(5) for the preparation of diazomethane. It was hoped to make a bis-nitroso derivative of 1,6-bis-nitroguanidinohexane but this latter compound was so insoluble in concentrated acids at low temperature that the idea was abandoned.

The properties of the bis-nitroso compounds are listed in Table I.

The ultraviolet absorption spectra of three N,N′-dinitrosocarbamates and N,N′-dinitroso-1,2-diureidoethane were determined. The extinction coefficients of the dinitrosocarbamates (240–242) were very close to that of N,N′-dinitro-N,N′-dicarbethoxy-1,6-diaminohexane (238),(6) but appreciably lower than that for N,N′-dinitroso-1,2-eidoethane.

Bis-nitrosocarbamates and bis-nitrosoureido alkanes have been decomposed to form bis-diazo alkanes by treatment of a cold ether solution with solid potassium carbonate(3) or with a concentrated aqueous solution of potassium hydroxide.(4) The catalytic decomposition of nitroso-β-alkylamino ketones by means of sodium ethoxide in ethyl alcohol has been reported by Jones and Kenner.(7) We have found that the reaction with solid potassium carbonate is very slow in a cold room at 5.5°, requiring more than two weeks to go to completion, as evidenced by the cessation of the evolution of nitrogen.(8) The best method of decomposing the

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(1) Abstracted from a portion of the dissertation submitted by Carlos M. Samour in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Armstrong Cork Company Research Fellow, 1947–1949.

(3) Petersen, ORTS Report No. 694.

(4) (a) T. Lieser and G. Beck, *Ber.*, **83**, 137 (1950); (b) H. Lettré and U. Brose, *Naturwissenschaften*, **36**, 57 (1949).

(5) M. Berenbom and W. S. Fones, THIS JOURNAL, **71**, 1629 (1949).

(6) H. M. Curry and J. P. Mason, *ibid.*, **73**, 5449 (1951).

(7) E. C. Jones and J. Kenner, *J. Chem. Soc.*, 363 (1933).

(8) In this experiment, treating an absolute ethyl alcohol solution of N,N′-dinitroso-N,N′-dicarbethoxy-1,6-diaminohexane and benzaldehyde with solid potassium carbonate, we have made the assumption that the slow reaction is the decomposition of the bis-nitroso compound. This assumption appears to be justified by the fact that the same reaction is complete within 20 minutes when sodium hydroxide is used to decompose the bis-nitroso compound and also by the fact that, whenever the bis-diazoalkane was prepared in alcohol (or ether) solution and then added to the reactant, the reaction was rapid.

TABLE I

PROPERTIES OF BIS-NITROSO COMPOUNDS

Compound	Yield, %^{a}	M.p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
$(CH_2)_2[N(NO)CONH_2]_2$	76^b	182.9–183.9^c	41.2	40.9, 41.0
$(CH_2)_6[N(NO)CONH_2]_2$	77	138–139^d	32.3	31.9, 31.9
$(CH_2)_2[N(NO)COOC_2H_5]_2$	89	^{e}	21.4	21.2, 21.2
$(CH_2)_4[N(NO)COOC_2H_5]_2$	83	^{f}	19.3	19.1, 19.2
$(CH_2)_6[N(NO)COOC_2H_5]_2$	91	^{g}	17.6	16.4, 16.6
$(CH_2)_2[N(NO)COOCH_3]_2$	93	101.2–101.6	23.9	23.6, 23.6
$(CH_2)_4[N(NO)COOCH_3]_2$	88	87–87.4^h	21.4	21.1, 21.1
$(CH_2)_6[N(NO)COOCH_3]_2$	86	61.2–62.6^i	19.3	18.9, 19.0
$(CH_2)_2[N(NO)C(CH_3)_2CH_2COCH_3]_2$	10^b	153.2–154	17.8	17.8, 17.9
$(CH_2)_4[N(NO)C(CH_3)_2CH_2COCH_3]_2$	84^b	146.7–147.7	16.4	16.2, 16.2
$(CH_2)_6[N(NO)C(CH_3)_2CH_2COCH_3]_2$	98^b	83.5–84	15.1	15.2, 15.2

[a] All percentage yields were calculated from weight of product before recrystallization. Only small amounts of products were recrystallized for m.p. determinations and analyses. [b] Yields based on weight of diamine (or diamine hydrochloride). [c] Lieser and Beck[4a] reported m.p. of 170°; Lettré and Brose[4b] reported m.p. 173°. [d] Lieser and Beck[4a] reported m.p. of 130°; Lettré and Brose[4b] reported m.p. 150°. [e] n^{20}_D 1.4671, d^{25}_4 1.2385. [f] n^{20}_D 1.4626, d^{25}_4 1.1785. [g] n^{20}_D 1.4686, d^{25}_4 1.1154. [h] Petersen[3] reported m.p. of 87°, but gave neither yield nor analysis. [i] Petersen[3] reported m.p. of 60–62°, but gave neither yield nor analysis.

bis-nitroso compounds was simply to add one or two pellets of sodium hydroxide or potassium hydroxide to a cold, well-stirred absolute alcohol solution of the bis-nitroso compound and the compound which was to react with the bis-diazoalkane. If the bis-diazoalkane was to react with an acid or a phenol, the bis-nitroso compound was decomposed in an absolute alcohol solution, decanted from the sodium hydroxide and added slowly to an alcohol or ether solution of the acid or phenol. The basic form of the ion exchange resin known as Amberlite IR-400 was used as a substitute for solid sodium hydroxide. The reaction was much slower than when solid sodium hydroxide was used (three days *vs.* a few minutes) and the yield was poorer (57% *vs.* 72%) in the preparation of 7,14-eicosanedione. The data on the reactions of bis-diazoalkanes (formed *in situ*) with carboxylic acids, phenol, ethyl acetoacetate, aldehydes and acetone are given in Table II. No reaction was observed with *o*-chlorobenzaldehyde, 2,6-dichlorobenzaldehyde or acetophenone.

It was found that 1,6-bis-diazohexane can be used as a cross-linking agent for polyacrylic acid and polymethacrylic acid, yielding insoluble, infusible products.

Experimental Part

1,2-Bis-nitrosoureidoethane.—This compound was prepared from ethylenediamine, hydrochloric acid and urea, followed by nitrosation according to the procedure described by Arndt[9] for the preparation of nitrosomethylurea. The bis-nitrosoureidoethane rose to the surface as a crystalline foamy precipitate which was filtered at once with suction. The crystals were stirred twice to a paste with about 50 ml. of cold water, sucked dry, and dried over anhydrous calcium chloride in a desiccator. From 0.5 mole of ethylenediamine 78 g. of 1,2-bis-nitrosoureidoethane[10] was obtained. A sample for analysis was recrystallized from absolute ethyl alcohol.

1,6-Bis-nitrosoureidohexane.—A solution of 40.4 g. (0.2 mole) of 1,6-bis-ureidohexane (m.p. 195–196° prepared from hexamethylenediamine and potassium cyanate),[11] in 200 ml. of glacial acetic acid was cooled in an ice-bath and nitrosated with a saturated aqueous solution of 34.5 g. (0.5 mole) of sodium nitrite, about three hours being required for the reaction. The mixture was diluted with 500 ml. of water, filtered, the product washed with cold water and dried; 40 g. Small samples[12] were recrystallized from absolute ethyl alcohol.

Nitrosation of the N,N'-Dicarbalkoxydiaminoalkanes. Method A.—This procedure is similar to that used by Klobbie.[13] A solution of 0.3 mole of the N,N'-dicarbalkoxydiaminoalkane was dissolved in a mixture of 300 g. of concd. sulfuric acid and 200 ml. of water, cooled in an ice-salt-bath and nitrosated with a saturated aqueous solution containing 0.7 mole of sodium nitrite, the addition of the nitrite solution being done at such a rate that the temperature did not rise above 5°. In some experiments where the bis-nitroso compound was a solid, 200 ml. of water was added to facilitate stirring. If the product was a liquid, it was extracted with ether, washed with sodium bicarbonate until freed from acid, dried over sodium sulfate and ether removed by distillation at room temperature. If the product was a solid, it was removed by filtration, washed with water, dried and recrystallized from absolute alcohol. This procedure was used for the preparation of N,N'-dinitroso-N,N'-dicarbethoxy-1,2-diaminoethane and the three dinitrosodicarbomethoxy compounds listed in Table I.

Method B.—A solution of 0.1 mole of the N,N'-dicarbomethoxy-1,4-diaminobutane was dissolved in 200 ml. of glacial acetic acid and nitrosated at 0°. (The nitrosation of N,-N'-dicarbomethoxy-1,6-diaminohexane was done at 10–15°.) The solution was diluted with water and the product isolated as described in method A. An attempt was made to distil the N,N'-dinitroso-N,N'-dicarbethoxy-1,6-diaminohexane *in vacuo* at 5 mm. pressure. A liquid started to distil at 93°, then the temperature of the vapor rose to 155°, and an explosion resulted. Obnoxious fumes were given off. As a result, no further attempt was made to distil any of the bis-nitrosourethans. N,N'-Dinitroso-N,N'-dicarbethoxy-1,6-diaminohexane was purified by dissolving in ether, cooling with Dry Ice and acetone mixture, filtering off any unreacted dicarbamate and finally removing the ether under reduced pressure.

N,N'-Dicarbethoxy-1,4-diaminobutane.—N,N'-Dicarbethoxy-1,4-diaminobutane was prepared by adding 160 g. (1 mole) of liquid bromine to a stirred solution of 140 g. (3.5 moles) of sodium hydroxide, 200 ml. of water and 300 g. of ice in a three-necked, two-liter flask and then adding 72 g. (0.5 mole) of adipamide. The mixture was warmed on the steam-bath until clear, and heating was continued for a total of four hours. To the clear solution cooled in an

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(9) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 461.

(10) The 1,2-bis-nitrosoureidoethane showed no signs of decomposition when kept in a tightly closed dark bottle, even when kept for a year.

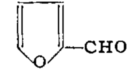
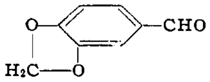
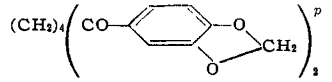
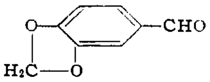
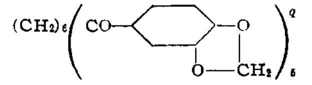
(11) Solonina, *Chem. Zentr.*, **68**, 849 (1897).

(12) In one instance when an attempt was made to transfer the bis-nitroso compound, after being stored for several months, into a beaker for recrystallization from absolute ethanol, the whole mass decomposed spontaneously with evolution of acrid fumes of oxides of nitrogen. The substance left in the beaker was a sticky solid.

(13) M. E. A. Klobbie, *Rec. trav. chim.*, **9**, 134 (1890).

TABLE II

PRODUCTS OBTAINED FROM BIS-DIAZOALKANES (NOT ISOLATED) AND VARIOUS REACTANTS

$(CH_2)_n$	$[N(NO)R]_2$			Yield,		Carbon, %		Hydrogen, %	
n	R	Reactant	Product	%^{a}	M.p., °C.	Calcd.	Found	Calcd.	Found
2	–COOEt	C_6H_5COOH	$(CH_2)_2(OCOC_6H_5)_2$	19^b	73.2–73.6^c				
6	–COOEt	C_6H_5COOH	$(CH_2)_6(OCOC_6H_5)_2$	68	55.8–56.5^d				
6	–COOEt	$(CH_2)_8(COOH)_2$	Polyester						
2	–COOMe	C_6H_5OH	$(CH_2)_2(OC_6H_5)_2$	72	98–98.5^e				
6	–COOEt	C_6H_5OH	$(CH_2)_6(OC_6H_5)_2$	76	82–83^f				
6	–COOEt	CH_3COCH_2COOEt	$(CH_2)_6[OC(CH_3){=}CHCOOEt]_2{}^g$	16		63.2	62.8	8.8	8.5
6	–COOEt	CH_3CHO	$(CH_2)_6(COCH_3)_2$	41	63.8–64.3^h				
6	–COOEt	$C_6H_{13}CHO$	$(CH_2)_6(COC_6H_{13})_2$	72^i	83.5–84	77.4	77.0	12.3	12.3
6	–COOEt		$(CH_2)_6(COC_4H_3O)_2{}^j$	87	122.7–123.4	70.1	70.1	6.6	6.8
2	–COOMe	C_6H_5CHO	$(CH_2)_2(COC_6H_5)_2$	28^k	144.9^l				
4	–COOEt	C_6H_5CHO	$(CH_2)_4(COC_6H_5)_2$	85	111.6–112.2^m				
6	–COOEt	C_6H_5CHO	$(CH_2)_6(COC_6H_5)_2$	90^n	90.8–91.2^o				
4	–COOEt			38	179.4–180.4	67.8	67.8	5.1	5.2
6	–COOEt			36	180.3–181.3	69.1	69.0	5.8	6.0
6	–COOEt	p-$CH_3OC_6H_4CHO$	$(CH_2)_6(COC_6H_4OMe)_2{}^r$	70	128.8–129.2	74.6	74.2	7.3	7.3
6	–COOEt	p-$(CH_3)_2NC_6H_4CHO$	$(CH_2)_6(COC_6H_4NMe_2)_2{}^s$	90	178.2–179.2	75.8	75.6	8.4	8.7
6	–CMe₂CH₂Ac	p-$(CH_3)_2NC_6H_4CHO$	$(CH_2)_6(COC_6H_4NMe_2)_2$	77	179–179.4				
6	–CMe₂CH₂Ac	p-$O_2NC_6H_4CHO$	$(CH_2)_6(COC_6H_4NO_2)_2{}^t$	92	135–136	62.5	62.5	5.2	5.4
6	–COOEt	m-$O_2NC_6H_4CHO$	$(CH_2)_6(COC_6H_4NO_2)_2{}^u$	90	131.2–132	62.5	62.5	5.2	5.4
6	–COOEt	CH_3COCH_3	$(CH_2)_4(CHMeCOMe)_2{}^v$	63		72.7	72.4	11.2	11.2

[a] All yields based upon the weight of dinitroso compound and calculated on the weight of the product before recrystallization. In most cases the product was quite pure without recrystallizing.

[b] Solid potassium carbonate used instead of sodium hydroxide pellets.

[c] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," Third Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 251, reported m.p. 73°.

[d] A. Franke, A. Kroupa and O. Schmid, *Monatsh.*, **66**, 406 (1932), reported m.p. 55.5–56°.

[e] E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 511, reported m.p. 98°.

[f] A. W. Solonina, *Ber.*, **26**, 2987 (1893), reported m.p. 83°.

[g] B.p. 115° (2.8 mm.), n^{20}_D 1.4471, d^{25}_4 0.9572.

[h] E. Blaise and A. Koehler, *Compt. rend.*, **148**, 491 (1908), reported m.p. 64°.

[i] Using Amberlite IR-400 base instead of sodium hydroxide pellets, the yield was 57%. M.p. of the disemicarbazone, 146–148°. *Anal.* Calcd. for $C_{22}H_{44}N_6O_2$: N, 19.8. Found: N, 19.4.

[j] M.p. of the bis-2,4-dinitrophenylhydrazone 204.8–205.8° dec. *Anal.* Calcd. for $C_{28}H_{26}N_8O_{10}$: N, 17.7. Found: N, 17.7.

[k] Sodium methoxide used instead of sodium hydroxide pellets.

[l] A. F. Holleman, *Ber.*, **20**, 3361 (1887), reported m.p. 145°.

[m] M. L. Etaix, *Ann. chim. phys.*, [7] **9**, 372 (1896), reported m.p. 102–103°.

[n] Using solid potassium carbonate instead of sodium hydroxide, the yield was 46%.

[o] Ref. *m*, p. 389, m.p. 83–85°; m.p. of dioxime 192.1–193.2°. Etaix, ref. *m*, p. 390, m.p. 192–193°.

[p] M.p. of the bis-2,4-dinitrophenylhydrazone, 316–317° dec. *Anal.* Calcd. for $C_{32}H_{26}N_8O_{12}$: N, 15.7. Found: N, 15.8.

[q] M.p. of the bis-2,4-dinitrophenylhydrazone, 280.4–281.4°. *Anal.* Calcd. for $C_{34}H_{30}N_8O_{12}$: N, 15.1. Found: N, 14.9.

[r] M.p. of the bis-2,4-dinitrophenylhydrazone, 223.7–224.7°. *Anal.* Calcd. for $C_{34}H_{34}N_8O_{10}$: N, 15.7. Found: N, 15.4.

[s] *Anal.* Calcd.: N, 7.4. Found: N, 7.1. M.p. of the bis-2,4-dinitrophenylhydrazone 181.6–182.6°. *Anal.* Calcd. for $C_{36}H_{40}N_{10}O_8$: N, 18.9. Found: N, 18.7.

[t] *Anal.* Calcd.: N, 7.3. Found: N, 7.2.

[u] *Anal.* Calcd.: N, 7.3. Found: N, 7.2. M.p. of the bis-2,4-dinitrophenylhydrazone 244.9–246° dec. *Anal.* Calcd. for $C_{32}H_{28}N_{10}O_{12}$: N, 18.8. Found: N, 18.7.

[v] B.p. 109° (1.3 mm.), n^{25}_D 1.4452. M.p. of disemicarbazone 197.5–198°. Petersen[3] reported m.p. of 198°. *Anal.* Calcd. for $C_{14}H_{28}N_6O_2$: N, 19.7. Found: N, 19.6.

ice–salt-bath, was added slowly 114 g. (1.05 mole) of ethyl chlorocarbonate. The resulting solid was filtered, and recrystallized from a large amount of water to yield 112 g. (96.5%) of N,N′-dicarbethoxy-1,4-diaminobutane; m.p. 94.0–94.5°. A sample of the product was prepared from 1,4-diaminobutane dihydrochloride, sodium hydroxide and ethyl chlorocarbonate. It was recrystallized from water; m.p. 94.0–94.5°, mixed m.p. 94.0–94.5°.

Anal. Calcd. for $C_{10}H_{20}O_4N_2$: N, 12.1. Found: N, 12.0, 12.1.

4,4,13,13-Tetramethyl-N,N′-dinitroso-5,12-diaza-2,15-hexadecanedione.—This compound was prepared by a modification of the procedure used by Berenbom and Fones.[5] In a 500-ml. three-necked flask provided with a stirrer and a dropping funnel was placed a solution of 11.6 g. (0.1 mole) of hexamethylenediamine in 30 ml. of water. Twenty-four and one-half grams (0.25 mole) of pure mesityl oxide was added dropwise, with constant stirring, over a period of one hour. The solution was cooled in ice and the mixture was neutralized with glacial acetic acid at such a rate that the temperature of the reaction was kept below 5°. Twenty-seven and six-tenths grams (0.4 mole) of sodium nitrite, 40 ml. of water and 20 ml. of glacial acetic acid were added consecutively and the mixture stirred for two hours. During this time the reaction vessel was kept in ice for one hour and then in a water-bath at 35° for an additional hour. The flask was then cooled in an ice–salt-bath and 100 ml. of ice-water was added. A light orange solid separated out immediately. It was filtered, washed several times with water, dried, and recrystallized from absolute alcohol.

4,4,11,11-Tetramethyl-N,N′-dinitroso-5,10-diaza-2,13-tetradecanedione was made by the same procedure from putrescine dihydrochloride, using sufficient sodium hydroxide solution to liberate the diamine from its salt. The product was recrystallized twice from ethyl acetate.

4,4,9,9-Tetramethyl-N,N′-dinitroso-5,8-diaza-2,11-dodecanedione was made by the same procedure starting with 60% aqueous solution of ethylenediamine, except that the glacial acetic acid was added slowly during the nitrosation reaction. No solid was obtained. Extraction with ether followed by removal of the ether gave a viscous liquid. This was dissolved in isopropyl alcohol and cooled in a Dry Ice–acetone-bath. The yellow precipitate was filtered, dried, and recrystallized twice from ethyl acetate.

1,6-Bis-nitroguanidinohexane.—This compound was made by using a modification of the procedure used by McKay and Wright[14] for the preparation of N-methyl-N′-nitroguanidine.

An alkaline solution of 20.2 g. (0.2 mole) of nitroguanidine[15] in 150 ml. of water containing 12 g. (0.21 mole) of

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[14] A. F. McKay and G. F. Wright, THIS JOURNAL, **69**, 3028 (1947).

[15] T. L. Davis, "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1947, p. 399.

potassium hydroxide was prepared. The solution was warmed to 40° and 18.9 g. (0.1 mole) of hexamethylenediamine dihydrochloride in 50 ml. of water was added to the above solution with stirring. The reaction was left for two hours at the end of which time a finely divided precipitate was obtained. The mixture was then cooled and the precipitate filtered, washed and dried; weight 24.6 g. (84.8%), m.p. 221.3–222.8°. The compound was found to be insoluble in many solvents including ethanol, methanol, tetrahydrofuran, chloroform, ether and aqueous acid. The 1,6-nitroguanidinohexane was recrystallized from dimethylformamide, using decolorizing charcoal, by adding ethyl alcohol to the hot filtrate and allowing the mixture to cool overnight in a refrigerator; m.p. 227.5–228.2° (cor.) dec.

Anal. Calcd. for $C_8H_{18}O_4N_8$: N, 38.6. Found: N, 37.8.

Ultraviolet Absorption Spectra.—All spectrophotometric measurements were made with dilute ethanol solutions in 1-cm. quartz cells in the Beckman quartz spectrophotometer, model DU. The solutions were dilute enough (0.0001 *M*) so that the readings obtained were within the range of 10–80% transmission. The ethanol used as the solvent was purified according to the procedure of Castille and Henri.[16] The data obtained are presented in Table III. The data on N,N'-dinitro-N,N'-dicarbethoxy-1,6-diaminohexane are included for comparison.

TABLE III

Compound	λmax, mμ	x
N,N'-Dinitroso-N,N'-dicarbethoxy-1,6-diaminohexane	241	11900
N,N'-Dinitroso-N,N-dicarbomethoxy-1,6-diaminohexane	242	11320
N,N'-Dinitroso-N,N'-dicarbomethoxy-1,2-diaminoethane	240	11460
N,N'-Dinitroso-1,2-diureidoethane	249	13040
N,N'-Dinitro-N,N'-dicarbethoxy-1,6-diaminohexane	238[a]	12070[a]

[a] H. M. Curry and J. P. Mason, THIS JOURNAL, **73**, 5449 (1951).

Reactions of Bis-diazoalkanes with Acids, Enols and Carbonyl Compounds.—The bis-diazoalkanes were made in suitable solvents and were allowed to react with the desired compound without being isolated. Of the following four procedures used, the best results were obtained by procedure A.

Procedure A. **7,14-Eicosanedione.**—To a 250-ml. three-necked flask, equipped with a mercury-seal stirrer, thermometer, calcium chloride tube, and surrounded with an ice-bath, was added a solution of 2 g. (0.0125 mole) of N,N'-dinitroso-N,N'-dicarbethoxy-1,6-diaminohexane and 2.9 g. (0.025 mole) of freshly distilled *n*-heptaldehyde in 40 ml. of absolute ethyl alcohol (dried over calcium hydride and distilled). To the resulting cold solution (2°) was added one pellet of sodium hydroxide. After a few minutes the temperature rose slowly to 40° and then dropped. When the solution reached room temperature the pellet of sodium hydroxide was removed, the solution concentrated and cooled in an ice–salt-bath, and the resulting colorless crystalline plates filtered, washed first with petroleum ether (b.p. 30–60°), then with water and dried; 2.8 g. (72%). A sample for analysis was recrystallized from absolute ethyl alcohol.

Procedure B. **1,6-Dibenzoylhexane.**—To a cold solution of 15.9 g. (0.05 mole) of N,N'-dinitroso-N,N'-dicarbethoxy-1,6-diaminohexane and 10.6 g. (0.1 mole) of freshly distilled chlorine-free benzaldehyde in 100 ml. of dry ethyl alcohol in a 500-ml. flask equipped with a soda-lime tube and surrounded with a mixture of ice and salt, was added 2 g. of solid anhydrous potassium carbonate. At the end of five hours, the flask was removed and placed in the cold room at 5.5°. By the end of two weeks a large amount of crystalline plates had appeared, but the reaction was incomplete, as evidenced by bubbles of gas coming out of the solution. At the end of one month no more evolution of gas was observed. The mixture was filtered and the crystals washed several times with water to remove the potassium carbonate, and then dried.

Procedure C. **1,2-Dibenzoylethane.**—To a cold suspension of 7.02 g. (0.03 mole) of N,N'-dinitroso-N,N'-dicarbomethoxy-1,2-diaminoethane in 100 ml. of dry ethyl alcohol and surrounded with an ice-bath, was added slowly, with constant stirring, 3.24 g. (0.06 mole) of sodium methoxide. The resulting cold deep orange solution was filtered and 6.36 g. (0.06 mole) of benzaldehyde was added. The solution was allowed to stand overnight at room temperature. A small water-soluble precipitate was removed by filtration, and the alcohol was distilled. The resulting residue consisted of a viscous, reddish-brown liquid and crystals. The liquid was extracted with ether, in which the crystals were found to be insoluble; 2 g. (28%).

Procedure D. **7,14-Eicosanedione.**—In a 250-ml. flask, equipped with a calcium chloride tube, was placed a solution of 2 g. (0.0125 mole) of N,N'-dinitroso-N,N'-dicarbethoxy-1,6-diaminohexane and 2.86 g. (0.025 mole) of *n*-heptaldehyde in 50 ml. of dry ethyl alcohol. To the solution was added 5 g. of Amberlite IR-400 base. The decomposition was slow, as shown by a slow evolution of gas. The flask was allowed to stand for three days at room temperature when no more evolution of gas was observed and the solution was light yellow in color. The mixture was filtered, and the resin washed five times with 10-ml. portions of absolute alcohol. The combined solutions were concentrated to 10 ml., cooled in an ice–salt-bath, and the resulting colorless crystalline plates filtered, washed with petroleum ether, water and dried; 2.2 g. (56.7%).

3,8-Dimethyl-2,9-decanedione.—Petersen[3] suggested that the product of the reaction between 1,6-bis-diazohexane and acetone would be 2,11-dodecanedione. According to the accepted mechanism for this reaction, the product should be 3,8-dimethyl-2,9-decanedione. That this latter compound was actually obtained was shown by oxidizing it to 2,7-dimethyloctanedioic acid. The diketone was made by procedure B, the reaction being completed in 48 hours in the refrigerator. A mixture of 1 g. of the ketone and 20 ml. of 2% sodium hydroxide solution was cooled in an ice-bath and 3 g. of bromine was added. The mixture was stirred for 30 minutes at 2° and for an additional 30 minutes at 60°. When cool, it was extracted with ether to remove bromoform and any unreacted diketone. The aqueous solution was acidified, extracted three times with ether, the ether extract dried over sodium sulfate and then evaporated to dryness; 0.2 g. This solid was completely soluble in 10% sodium bicarbonate solution. After three recrystallizations from ligroin, it started to melt at 107.8°, but the melt was not clear until a temperature of 116.2° was reached. Four recrystallizations from water gave a product which melted at 130.5–131.5°,[17] and which gave a mixed melting point of 105–125° (sintering at 95°) with sebacic acid.

Cross-linking of Polyacrylic Acid with 1,6-Bis-diazohexane.—In a 250-ml. three-necked flask, equipped with a stirrer, thermometer, and surrounded with an ice-bath, was placed a solution of 4.3 g. (0.06 mole of monomer) of polyacrylic acid in 44 ml. of water. To this cold solution (+2°) was slowly added an alcoholic solution of 1,6-bis-diazohexane prepared from 9.6 g. (0.03 mole) of N,N'-dinitroso-N,N'-dicarbethoxy-1,6-diaminohexane in 60 ml. of alcohol and two pellets of sodium hydroxide. The reaction was very vigorous, and during the addition there was a constant evolution of gas as the solution became colorless. The solution became more and more viscous as more of the bis-diazohexane was added. At the end of the addition, the mixture was poured into 200 ml. of water and acidified with a few drops of dilute hydrochloric acid. The cross-linked product precipitated out as a fine solid. The mother liquor was decanted and the precipitate washed several times with water and dried; 4 g.

The cross-linked product was found to be insoluble in hot water and only slightly soluble in ethyl alcohol. On heating it did not soften or melt.

To 1 g. of the partially cross-linked polyacrylic acid was added 20 ml. of absolute ethyl alcohol and the mixture heated over the steam-bath to effect solution. However, not all dissolved. The mixture was filtered, and a solution of 1,6-bis-diazohexane prepared from 1 g. (0.0031 mole) of N,N'-dinitroso-N,N'-dicarbethoxy-1,6-diaminohexane in 20 ml. of alcohol and one pellet of sodium hydroxide, was added slowly to the alcoholic solution of the partially cross-

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(16) A. Castille and V. Henri, *Bull. soc. chim. biol.*, **6**, 299 (1924).

(17) C. C. Steele, THIS JOURNAL, **53**, 283 (1931).

linked polyacrylic acid. There was an immediate reaction with the formation of a precipitate. It was separated by centrifuging. The resulting product is a solid, which does not fuse. Thus, the partially cross-linked polymer can be further cross-linked by dissolving in alcohol and adding the bis-diazoalkane to it with stirring.

Polymethacrylic acid reacted similarly with 1,6-bis-diazohexane.

BOSTON, MASSACHUSETTS

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Free Radical Aromatic Substitution. II. The Relative Reactivities of the Phenyl Halides toward Phenyl Radical Attack[1,2]

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Benzoyl peroxide has been thermally decomposed in equimolecular binary mixtures of pyridine with chlorobenzene, bromobenzene and iodobenzene. The relative reactivities of these solvents toward phenyl radical attack (determined by comparing the ratios of halobiphenyls to phenylpyridines formed in the competitive reactions) have been found to be iodobenzene 1.1, pyridine 1.0, chlorobenzene 0.9 and bromobenzene 0.9. The mixtures of isomeric biaryls formed are predominantly ortho with the meta and para isomers in approximately statistical ratio to each other. The percentages of the ortho, meta and para isomers in the isolated biaryl are significant despite the concomitant formation of large quantities of high molecular weight products, for when one of these isolated biaryls is partially converted to tarry substances by means of additional benzoyl peroxide, the residual binuclear fraction is found to consist of the original percentages of isomers. Some evidence of the mechanism of formation of the high molecular weight products has also been obtained.

A complete understanding of the mechanism of substitution of aromatic nuclei by free radicals (*e.g.*, the Hey and Gomberg reactions) will require knowledge of the influences of substituents initially present in the parent nuclei. For example, the relative activating or deactivating effects of such substituents must be determined. Several types of competitive reactions are available for determining these effects.[4] It was decided in the present work to decompose a free radical reagent (benzoyl peroxide) in equimolecular binary mixtures of pyridine with various phenyl halides and compare the ratios of yields of phenylpyridines to halobiphenyls as a measure of the reactivities of the parent solvents. This general method has been previously applied by Grieve and Hey.[5] Pyridine was selected as the reference solvent to which the reactivities of the phenyl halides would be related because the solubility of the pyridine derivatives in aqueous acid facilitates their purification.

When the phenyl radical reacts with such aromatic compounds, isomeric biaryls result from attack upon the various positions in the ring relative to the substituent initially present. It was decided in the present work to determine these ratios of isomers for several reasons.

1. Such substitution has been described as invariably ortho–para although only recently[6–8] have many accurate quantitative data been reported upon which to base such a conclusion. Additional data could be readily obtained in the present work.

2. The products of free radical aromatic substitution are usually quite complex. Only by determining the isomers present in the biaryls produced can the purity of the fractions be established.

3. In using competitive reactions of this type, there is always a possibility that the two mononuclear solvents may associate with each other so that the measured reactivities are not those of the discrete mononuclear species but of larger aggregates. If a single solvent is used as a reference material throughout a series of reactions, association with the competitive reagents would probably (although not necessarily) affect the ratios of isomeric products formed from the reference material. In other words, in the present work if the phenylpyridine fractions obtained are always of the same isomer composition regardless of the nature of the competitive halobenzene reagent, an absence of association of pyridine with the competitive solvent would be indicated.

In all free radical aromatic substitutions, large quantities of high molecular weight tars are obtained. These tars may be formed by polysubstitution of the initial biaryl products but this mechanism has not been proved. If polysubstitution is the principal cause of formation of the high molecular weight products, then the following two effects might result: (a) The composition of the isomeric biaryl mixtures initially produced (*e.g.*, *o*-, *m*- and *p*-chlorobiphenyls) might be altered by polysubstitution, for one of the isomers (*e.g.*, *p*-chlorobiphenyl) might be more reactive than the others. Therefore the yields of isomeric biaryls isolated as products would not be representative of the reactivities of the corresponding positions in the parent benzene compounds. In the present work it was decided to measure directly the effect of polysubstitution on the isomeric biaryl mixtures. (b) The ratios of phenylpyridines to halobiphenyls formed in the competitive reactions might not be a true measure of the relative reactivities of the two mononuclear solvents, for the biaryls produced from one might be more susceptible to polysubstitution than the biaryls produced from the other. Therefore the ratios of phenylpyridines to halobiphenyls would be altered by polysubstitution. In

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(1) This paper is partially based upon a thesis submitted by Earl C. Gregg, Jr., to the Graduate School, Western Reserve University, in partial fulfillment of the requirements for the doctor's degree.

(2) Presented at the Buffalo meeting of the American Chemical Society, March, 1952.

(3) Research Corporation Predoctoral Fellow, 1952–1953.

(4) R. L. Dannley and M. Gippin, THIS JOURNAL, **74**, 332 (1952).

(5) W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 1797 (1934).

(6) D. F. DeTar and H. J. Scheifele, THIS JOURNAL, **73**, 1442 (1951).

(7) D. H. Hey, *J. Chem. Soc.*, 1974 (1952).

(8) D. R. Augood, D. H. Hey and G. H. Williams, *ibid.*, 44 (1953).