colorless plates, m.p. 184°, identified by a mixed melting point.

3-Methyl-DAB yielded 7.2 g. (71%) of 3'-methyl-4'-[4,4'-bis-(dimethylamino)-benzhydryl]-DAB (IV), brownish-yellow needles, m.p. and mixed m.p. 217°.

Anal. Calcd. for $C_{32}H_{37}N_5$: C, 78.17; H, 7.59; N, 14.25. Found: C, 78.20; H, 7.61; N, 14.30.

Reductive fission of IV gave 3.2 g. (89%) of 2-methyl-4-amino-4',4"-bis-(dimethylamino)-triphenylmethane (VII) colorless plates, m.p. 154°, identified by a mixed melting point.

MAB yielded 6.5 g. (70%) of 4'-[4,4'-bis-(dimethylamino)-benzhydryl]-MAB (V), orange needles, m.p. 203°, undepressed by admixture with the authentic specimen.

Anal. Calcd. for $C_{30}H_{33}N_5$: C, 77.72; H, 7.18; N, 15.11. Found: C, 77.78; H, 7.19; N, 15.21.

Reductive fission of V gave 3.2 g. (93%) of 4-amino-4',4"-bis-(dimethylamino)-triphenylmethane (II), colorless plates, m.p. and mixed m.p. 152°.

Attempted Alkylation of Azobenzene and 4'-Methyl-DAB with Michler's Hydrol.—Reaction was carried out with 0.002 mole of an azo compound, 0.5 g. (0.002 mole) of Michler's hydrol and 10 ml. of 98% sulfuric acid at 40° for 10 hr.

In the case of azobenzene, the mixture was poured onto cracked ice. The yellow solid precipitated immediately. This material was filtered off, washed with water and dried. After three recrystallizations from benzene-light petroleum (b.p. 75–120°), 0.3 g. (75%) of azobenzene was recovered. On the other hand, the aqueous filtrate was neutralized and extracted with ether. By removal of ether from the extract, crude Michler's hydrol was recovered almost quantitatively.

In the case of 4'-methyl-DAB, the mixture was poured onto cracked ice. The resulting deep red mixture was neutralized to give yellow precipitate. This material was filtered off, washed with cold methanol and recrystallized from benzene. Recovered 4'-methyl-DAB weighed 0.4 g. (80%). The methanol washings were evaporated to dryness, and the residue was dissolved in 50% ethanol. The solution was decolorized with Norit S.X. 30 and concentrated under reduced pressure to give crude Michler's hydrol (0.4 g., 80%).

KYOTO, JAPAN

[CONTRIBUTION FROM THE ORGANIC CHEMICALS DIVISION, NITRO RESEARCH DEPARTMENT, MONSANTO CHEMICAL CO.]

Nitrosoanilines

BY JOHN J. D'AMICO, CHING CHEN TUNG AND LLOYD A. WALKER

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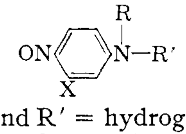
A variety of N- and *p*-nitroso-anilines were prepared by standard methods. Nitrosation of 3-anilinopropionitrile, β-anilinopropionic acid or ethyl β-anilinopropionate with sodium nitrite and methanolic hydrogen chloride was accompanied by alcoholysis, esterification or transesterification, yielding methyl β-(*p*-nitrosoanilino)-propionate (XLIII). The *para* rearrangement of the nitroso group in esters like XII and XIII catalyzed by hydrochloric acid–acetic acid took place with concurrent hydrolysis of the ester function; the corresponding nitrile XVIII was not hydrolyzed under the rearrangement conditions. Oxidation of the *p*-nitroso group in XLIII with dilute nitric acid occurred with simultaneous nitration to methyl β-(2,4-dinitroanilino)-propionate (XLVIII).

The discovery that Butyl rubber modified with N-methyl-N,4-dinitrosoaniline[1] gives a Butyl vulcanizate with improved low-temperature and resilience properties, increased 300% modulus, decreased hardness, increased electrical resistivity and better processing characteristics,[2] has made it desirable to prepare new structurally related nitroso compounds. Although a number of nitroso compounds have been prepared possessing the general formula where X = hydrogen, R =



alkyl or phenyl and R' = hydrogen, alkyl or nitroso, a limited number of examples were found containing other substituents. The purpose of this investigation was to vary the R, R' and X radicals and to determine whether these structural modifications enhanced the properties of the Butyl vulcanizate. The detailed evaluation data for these new compounds will be reported in forthcoming patents.

In the preparation of the nitroso-anilines some of the intermediates were not readily available. This necessitated their synthesis by the following known general methods: Employing the elegant procedure described by Moon,[3] 2,5-dichlorobenzothiazole was prepared by the reaction of 5-chloro-2-mercaptobenzothiazole with excess sulfuryl chloride. The acid hydrolysis of 3-anilinopropionitrile furnished the desired 3-anilinopropionamide. N-(2-Chloroallyl)-aniline (I), N-(3-chloro-2-butenyl)-aniline (II), N-(2-chloroallyl)-N-(2-methoxyethyl)-aniline (III), 1-(2,3,6-trichlorobenzyl)-4-phenylpiperazine (IV) and N,N'-diphenyl-2-butene-1,4-diamine (V) were prepared by the reaction of aniline, N-(2-methoxyethyl)-aniline or 1-phenylpiperazine with either 2,3-dichloro-1-propene, 1,3-dichloro-2-butene, 2,3,6-trichlorobenzyl chloride or 1,4-dichloro-2-butene. The reaction of aniline or N-methylaniline with 2-chlorobenzothiazole or 2,5-dichlorobenzothiazole gave 2-anilino-5-chlorobenzothiazole (VI), 2-(N-methylanilino)-benzothiazole (VII) and 5-chloro-2-(N-methylanilino)-benzothiazole (VIII), respectively. 5-Chloro-2-[2-(diethylamino)-ethylamino]-benzothiazole was obtained in 96% yield by the reaction of 2,5-dichlorobenzothiazole with N,N-diethyl ethylenediamine.

The N-nitroso N-substituted anilines were prepared by the reaction of the appropriate N-substituted aniline hydrochlorides in an aqueous or ethyl alcohol medium with aqueous sodium nitrite.

The reaction of the N,N-disubstituted aniline hydrochlorides with an aqueous sodium nitrite solution at 0–10°, followed by neutralization of the reaction mixture with 10% aqueous sodium hydroxide gave the N,N-disubstituted *p*-nitrosoanilines (XX-XXVIII). It was anticipated that

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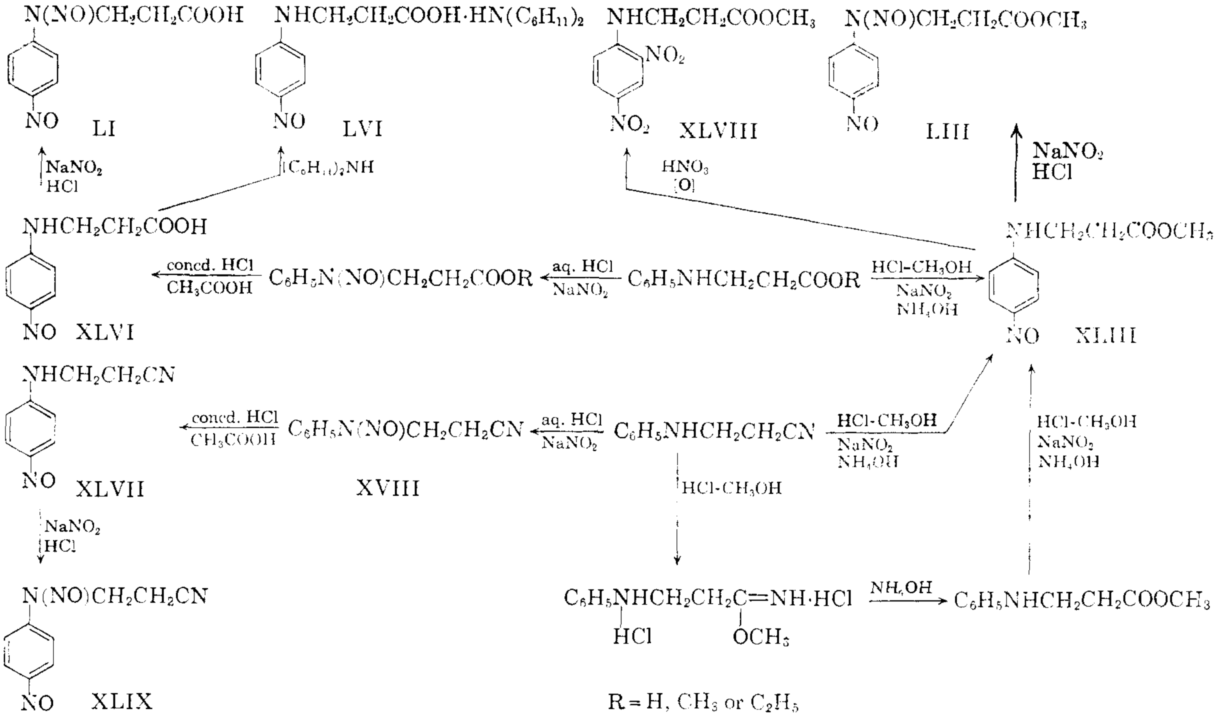
[1] Currently available in 33¹/₃% active mixture with an inert filler under the trade mark Elastopar.

[2] H. M. Leeper, C. L. Gable, J. J. D'Amico and C. C. Tung, *Rubber World*, **135**, 413 (1956).

[3] N. S. Moon, U. S. Patent 2,469,697.



R = H, CH₃ or C₂H₅

the reaction of N,N′-diethyl-N,N′-diphenyl-2-butene-1,4-diamine with sodium nitrite would yield the bis-*p*-nitroso derivative, but instead the mono-*p*-nitroso derivative (XXVIII) was obtained.

The N-substituted *p*-nitrosoanilines (XXIX-XLII) were obtained by the reaction of the appropriate N-substituted aniline in excess hydrogen chloride–methyl alcohol solution with sodium nitrite.

The reaction of a solution containing 3-(*o*-hydroxyanilino)-propionitrile, sodium hydroxide, sodium nitrite and water with dilute sulfuric acid at 0–10° furnished the desired 3-(2-hydroxy-5-nitrosoanilino)-propionitrile in 82.4% yield.

1-(*p*-Nitrosophenyl)-4-(2,3,6-trichlorobenzyl)-piperazine was obtained in 88.5% yield by the reaction of an aqueous solution of 1-(2,3,6-trichlorobenzyl)-piperazine hydrochloride with sodium nitrite.

Nitrosation of 3-anilinopropionitrile, β-anilinopropionic acid or ethyl β-anilinopropionate with sodium nitrite and methanolic hydrogen chloride was accompanied by alcoholysis, esterification or transesterification, yielding methyl β-(*p*-nitrosoanilino)-propionate (XLIII). For the alcoholysis reaction, proof of structure was elucidated by treating 3-anilinopropionitrile with an excess of hydrogen chloride–methyl alcohol solution to give N - (3 - imino - 3 - methoxypropyl) - aniline dihydrochloride which upon neutralization with concd. ammonium hydroxide yielded the intermediate methyl β-anilinopropionate. Nitrosation of 3-(*m*-toluidino)-propionitrile and 3-(α-naphthylamino)-propionitrile under the same conditions as employed for 3-anilinopropionitrile furnished methyl β - (3 - methyl - 4 - nitrosoanilino) - propionate (XLIV) and methyl β-(4-nitroso-1-naphthylamino)-propionate (XLV), respectively. Oxidation of the *p*-nitroso group in XLIII with dilute nitric acid occurred with simultaneous nitration to methyl β-(2,4-dinitroanilino)-propionate (XLVIII).

The *para* rearrangement of nitroso group in esters like XII and XIII catalyzed by hydrochloric acid–acetic acid took place with concurrent hydrolysis of the ester function, yielding β-(*p*-nitrosoanilino)-propionic acid (XLVI). However, 3-(N-nitrosoanilino)-propionitrile (XVIII) was not hydrolyzed under the rearrangement conditions and the product obtained was 3-(*p*-nitrosoanilino)-propionitrile (XLVII).

The reaction of the appropriate N-substituted *p*-nitrosoaniline hydrochlorides with an aqueous solution of sodium nitrite at 0–10° gave the corresponding N,4-dinitroso N-substituted anilines (XLIX-LV).

Dicyclohexylamine salt of β-(*p*-nitrosoanilino)-propionic acid (LVI) was obtained by the reaction of XLVI with dicyclohexylamine.

The reaction of XLVI or XLIII with toluene 2,4-diisocyanate or 4,4′-methylenediphenol isocyanate furnished the *p*-nitrosophenyl substituted ureas (LVII-LVIX).

The metal salts of N-substituted *p*-nitrosoanilines (LX-LXIV) were obtained by the reaction of an aqueous slurry of the sodium salt of the appropriate N-substituted *p*-nitrosoaniline with either nickel nitrate hexahydrate, zinc chloride, copper sulfate pentahydrate or cadmium sulfate. The reaction of an aqueous solution of the sodium salt of XLVI with copper sulfate pentahydrate gave the copper salt of β-(*p*-nitrosoanilino)-propionic acid tetrahydrate (LXV).

β - (2,4 - Dihydroxy - 3,5 - dinitrosophenyl)-propionic acid hydrate was obtained by the reaction of β-(2,4-dihydroxyphenyl)-propionic acid with nitrous acid.

TABLE I

N-NITROSO-N-SUBSTITUTED ANILINES, $C_6H_5N(NO)R$

Compound	N-Subst. aniline	R	Yield crude, %	M.p., °C.	Empirical formula	Nitrogen, % Calcd.	Nitrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found
IX	N-Allylaniline[b]	$—CH_2CH{=}CH_2$	90.5	Liquid	$C_9H_{10}N_2O$	17.27	17.05	...	...
X	N-(2-Chloroallyl)-aniline	$—CH_2CCl{=}CH_2$	88.5	Liquid	$C_9H_9ClN_2O$	...	...	18.03	18.62
XI	β-Anilinopropionic acid[c]	$—CH_2CH_2COOH$	90.1	70–72	$C_9H_{10}N_2O_3$	14.42	14.05	...	...
XII	Ethyl β-anilinopropionate[d]	$—CH_2CH_2COOC_2H_5$	93.0	Liquid	$C_{11}H_{14}N_2O_3$	12.61	12.37	...	...
XIII	Methyl β-anilinopropionate[c]	$—CH_2CH_2COOCH_3$	78.5	Liquid	$C_{10}H_{12}N_2O_3$	13.45	13.09	...	...
XIV	N-(2-Methoxyethyl)-aniline[e]	$—CH_2CH_2OCH_3$	85.5	Liquid	$C_9H_{12}N_2O_2$	15.52	15.42	...	...
XV	N-(3-Chloro-2-butenyl)-aniline	$—CH_2CH{=}CClCH_3$	84.0	Liquid	$C_{10}H_{11}ClN_2O$	...	...	16.85	16.77
XVI	Ethyl N-phenylglycinate	$—CH_2COOC_2H_5$	92.4	Liquid	$C_{10}H_{12}N_2O_3$	13.45	13.47	...	...
XVII	2-Anilino-5-chlorobenzothiazole	$—C_7H_3ClNS$[f]	90.1	233–234[a]	$C_{13}H_8ClN_3OS$	14.49	14.20	...	...

[a] Recrystallization from ethyl alcohol. [b] F. L. Carnahan and C. D. Hurd, THIS JOURNAL, **52**, 4586 (1930). [c] P. L. Southwick and L. F. Seivard, *ibid.*, **71**, 2532 (1949). [d] J. R. Thayer and S. M. McElvain, *ibid.*, **49**, 2862 (1927). [e] J. G. McNally and J. B. Dickey, U. S. Patent 2,381,071. [f] 5-Chloro-2-benzothiazolyl.

Experimental[4]

2,5-Dichlorobenzothiazole was prepared by the procedure described by Moon.[3] The product, a tan colored solid, m.p. 64–66°, was obtained in 95.9% yield.

Anal. Calcd. for $C_7H_3Cl_2NS$: N, 6.86; S, 15.71. Found: N, 6.67; S, 15.87.

3-Anilinopropionamide.—To 200 g. (1.36 moles) of 3-anilinopropionitrile was added dropwise 500 ml. of concd. sulfuric acid at 0–10°. The resulting solution was stirred for an additional hour and then allowed to stand at 25–30° for two days. This solution was added to 1,000 g. of crushed ice and while stirring was neutralized by the addition of concd. ammonium hydroxide. The reaction mixture was extracted with 500 ml. of ethyl ether. The ether extract was washed with water until the wash water was neutral to litmus and dried over sodium sulfate. Upon removal of ether *in vacuo*, a white solid, m.p. 55–56°, was obtained in 61% yield.

Anal. Calcd. for $C_9H_{12}N_2O$: N, 17.02; Found: N, 16.98.

N-(2-Chloroallyl)-aniline (I), N-(3-Chloro-2-butenyl)-aniline (II), N-(2-Chloroallyl)-N-(2-methoxyethyl)-aniline (III), 1-(2,3,6-trichlorobenzyl)-4-phenylpiperazine (IV) and N,N′-Diphenyl-2-butene-1,4-diamine (V).—To two moles of stirred aniline, N-(2-methoxyethyl)-aniline or 1-phenylpiperazine at 100° was added dropwise at 100–125°, one mole of 2,3-dichloro-1-propene, 1,3-dichloro-2-butene, 2,3,6,trichlorobenzyl chloride or one-half mole of 1,4-dichloro-2-butene. For compounds I, II and V the stirred reaction mixture was heated at 135–140° for four hours, whereas compounds III and IV were maintained at these temperatures for 24 hours. For I, II and III after cooling to 50°, 180 g. (1.13 moles) of 25% aqueous sodium hydroxide was added dropwise. After stirring for one hour and cooling to 25° the sodium chloride was removed by filtration. The top organic layer was separated, dried over alkali and distilled *in vacuo*. For compound IV, 440 g. (1.1 moles) of 10% aqueous sodium hydroxide was added to the cooled reaction mixture. The reaction mixture was stirred for 30 minutes and then cooled to 5°. The resulting semi-solid was collected by filtration, washed successively with 500 ml. of water and 300 ml. of heptane and air-dried at 25–30°. For compound V after cooling to 25°, 400 ml. of water was added to the reaction mixture and stirring was continued for an additional hour. The top organic layer was separated, washed with 200 ml. of water and dried over alkali. The excess aniline was removed by distillation at 2 mm.

2-Anilino-5-chlorobenzothiazole (VI), 2-(Methylanilino)-benzothiazole (VII) and 5-Chloro-2-(N-methylanilino)-benzothiazole (VIII).—To 214.3 g. (2.0 moles) of N-methylaniline or 186.3 g. (2.0 moles) of aniline at 80°, 169.6 g. (1.0 mole) of 2-chlorobenzothiazole or 204.1 g. (1.0 mole) of 2,5-dichlorobenzothiazole was added in small portions at 80–100° over a 10-minute period. The stirred reaction mixture was heated at 140–150° for six hours. After cooling to 90°, 500 ml. of water was added and stirring was continued for 30 minutes. After cooling to 25°, compound VI was collected by filtration, washed with water until free of chloride and air-dried at 50°.

Compound	Yield, %	B.p. °C.	B.p. Mm.	Nitrogen, % Calcd.	Nitrogen, % Found
I	69.2	130–131	15	8.36	8.34
II	44.2	147–149	17	7.71	7.75
III	19.1	152–154	11	6.20	6.44
IV	96.5	[a]		7.88	8.01
V	62.3	Viscous liquid		11.76	11.61

[a] M.p. 112–113° after recrystallization from ethyl alcohol.

For compounds VII and VIII the reaction mixture was extracted with 500 ml. of chloroform. The bottom chloroform layer was washed with 500 ml. of water and dried over sodium sulfate. The chloroform and excess N-methylaniline was removed *in vacuo*.

Compound	Yield, %	M.p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
VI	93.0	234–236	10.74	10.58	12.30	12.29
VII	93.3	66–67[a]	11.66	12.10	13.34	12.91
VIII	82.0	Oil	10.20	10.40	11.67	11.04

[a] Recrystallization from ethyl alcohol.

5-Chloro-2-[2-diethylamino]-ethylamino]-benzothiazole.—To 71.2 g. (0.35 mole) of 2,5-dichlorobenzothiazole externally cooled by an ice-bath was added dropwise 88 g. (0.77 mole) of N,N-diethylethylenediamine. An exothermic reaction set in causing the temperature to rise to 80°. After the exothermic reaction had subsided, the stirred reaction mixture was heated at 120–125° for five hours. After cooling to 25°, 350 ml. of water was added and stirring continued for 30 minutes. The solid was collected by filtration, washed with water until free of chloride and air-dried at 25–30°. The crude product, m.p. 81–84°, was obtained in 96% yield. After recrystallization from heptane, it melted at 84–86°.

Anal. Calcd. for $C_{13}H_{18}ClN_3S$: N, 14.81; S, 11.30. Found: N, 14.59; S, 11.05.

N-Nitroso-N-substituted Anilines (IX–XVII).—To one mole of stirred N-substituted aniline and 400 g. of crushed ice was added dropwise 145 ml. of concd. hydrochloric acid. After cooling to 0°, a solution containing 80 g. (1.125 moles) of 95% sodium nitrite dissolved in 250 ml. of water was added dropwise at 0–10° over a 30-minute period. After stirring at 10–20° for one hour for all compounds except XVII the reaction mixture was extracted with 500 ml. of ethyl ether. The ether solution was washed with water until

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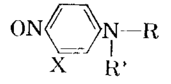
[4] All melting points were taken upon a Fisher-Johns block and are uncorrected.

TABLE II: N,N-DISUBSTITUTED *p*-NITROSOANILINES



Compound	N,N-Disubstituted aniline	R	R'	X	Yield crude, %	M.p., °C.	Empirical formula	Nitrogen, % Calcd.	Nitrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found	Sulfur, % Calcd.	Sulfur, % Found
XX	β,β-(Phenylimino)-dipropionitrile	$-CH_2CH_2CN$	$-CH_2CH_2CN$	H	98.0	138–140[a]	$C_{12}H_{12}N_4O$	24.55	24.19	...	...	...	...
XXI	2,2'-(Phenylimino)-diethanol	$-CH_2CH_2OH$	$-CH_2CH_2OH$	H	86.0	137–138[a]	$C_{10}H_{14}N_2O_3$	13.33	13.00	...	...	...	...
XXII	N-(2-Chloroethyl)-N-ethylaniline hydrochloride	$-C_2H_5$	$-CH_2CH_2Cl$	H	77.1	53–55[a]	$C_{10}H_{13}ClN_2O$	...	...	16.67	16.21	...	...
XXIII	*m*-Chloro-N,N-dimethylaniline	$-CH_3$	$-CH_3$	Cl	96.8	137–138[b]	$C_8H_9ClN_2O$	15.18	15.07	19.21	19.48	...	...
XXIV	*m*-Chloro-N,N-diethylaniline	$-C_2H_5$	$-C_2H_5$	Cl	50.0	74–75	$C_{10}H_{13}ClN_2O$	...	...	16.67	16.69	...	...
XXV	2-(N-Methylanilino)-benzothiazole and 250 ml. of ethyl alcohol	$-CH_3$	$-C_7H_4NS$[c]	H	91.0	70–72[a]	$C_{14}H_{11}N_3OS$	...	...	...	...	11.91	11.99
XXVI	N-(2-Chloroallyl)-N-(2-methoxyethyl)-aniline and 250 ml. of ethyl alcohol	$-CH_2CH_2OCH_3$	$-CH_2CCl{=}CH_2$	H	54.5	58–60[a]	$C_{12}H_{15}ClN_2O_2$	11.00	10.96	13.92	14.20	...	...
XXVII	5-Chloro-2-(N-methylanilino)-benzothiazole and 250 ml. of ethyl alcohol	$-CH_3$	$-C_7H_3ClNS$[d]	H	96.0	68–70[a]	$C_{14}H_{10}ClN_3OS$	...	...	11.67	12.07	10.56	10.83
XXVIII	N,N'-Diethyl-N,N'-diphenyl-2-butene-1,4-diamine	$-C_2H_5$	$-CH_2CH\;CHCH_2\underset{C_2H_5}{\underset{\vert}{N}}C_6H_5$	H	99.0	94–96[a]	$C_{20}H_{25}N_3O$	12.99	13.00	...	...	...	...

[a] Recrystallization from dilute ethyl alcohol. [b] Recrystallization from acetone. [c] 2-Benzothiazolyl. [d] 5-Chloro-2-benzothiazolyl.

the washings were neutral to litmus and dried over sodium sulfate. The ether was removed *in vacuo*.

For compound XVII, the reaction mixture was filtered, washed with water until the washings were neutral to litmus and air-dried at 25–30°. The data are summarized in Table I.

3-(N-Nitrosoanilino)-propionitrile (XVIII) and N,N'-Dinitroso-N,N'-diphenyl-2-butene-1,4-diamine (XIX).—To 146.2 g. (1.0 mole) of stirred 3-anilinopropionitrile or 119.2 g. (0.5 mole) of N,N'-diphenyl-2-butene-1,4-diamine and 600 ml. of ethyl alcohol at 0° was added dropwise at 0–10°, 145 ml. of concd. hydrochloric acid. To this stirred reaction mixture at 0° was added dropwise at 0–10° a solution containing 80 g. (1.125 moles) of 97% sodium nitrite in 250 ml. of water over a 30-minute period. The stirred reaction mixture was maintained at 0–5° for an additional two hours. The resulting solid was collected, washed with water until the wash water was neutral to litmus and air-dried at 25–30°. Compound XVIII, m.p. 50–51°, after recrystallization from ethyl alcohol, and XIX, m. p. 111–112°, after recrystallization from ethyl alcohol, were obtained in 91.5 and 88.4% yields, respectively.

Anal. Calcd. for $C_9H_9N_3O$ (XVIII): N, 23.99. Found: N, 23.75. Calcd. for $C_{12}H_{16}N_4O_2$ (XIX): N, 18.91. Found: N, 18.78.

5-Chloro-2-(2-diethylaminoethyl-N-nitrosoamino)-benzothiazole.—To 42.6 g. (0.15 mole) of stirred 5-chloro-2-[2-(diethylamino)-ethylamino]-benzothiazole and 500 g. of crushed ice was added dropwise 22 ml. of concd. hydrochloric acid. To this stirred reaction mixture at 0° was added dropwise 10.8 g. (0.15 mole) of 97% sodium nitrite dissolved in 38 ml. of water over a 15-minute period. The stirred reaction mixture was maintained at 0–10° for two additional hours. The resulting solid was collected, washed with water until the washings were neutral to litmus and air-dried at 25–30°. The crude product, m.p. 135–140°, was obtained in 96% yield. After recrystallization from ethyl alcohol it melted at 158–160°.

Anal. Calcd. for $C_{13}H_{17}ClN_4OS$: N, 17.91; S, 10.25. Found: N, 18.46; S, 10.21.

N,N-Disubstituted *p*-Nitrosoanilines (XX–XXVIII).—To the stirred N,N-disubstituted aniline (0.25 mole), 200 g. of ice-water and 105 ml. of concd. hydrochloric acid was added dropwise (sub-surface) at 0–10° a solution containing 18.5 g. (0.26 mole) of 97% sodium nitrite in 30 ml. of water. After stirring the reaction mixture for one hour at 10–20°, 10% aqueous sodium hydroxide was added dropwise until a *p*H 8 was obtained. After stirring for one hour at 10–20°, the resulting solid was collected, washed with one liter of cold water and air-dried at 25–30°.

For XXVIII the procedure was the same as described above except the following reactants were employed: 58.9 g. (0.2 mole) of N,N'-diethyl-N,N'-diphenyl-2-butene-1,4-diamine, 168 ml. of concd. hydrochloric acid, 2,000 g. of ice-water and 32 g. (0.45 mole) of 97% sodium nitrite dissolved in 100 ml. of water.

The data are summarized in Table II.

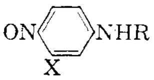
N-Substituted *p*-Nitrosoanilines (XXIX–XLII).—To the stirred 40% hydrogen chloride–methyl alcohol solution at 0°, the amine (1.0 mole) was added in small portions at 0–15° over a 15–30 minute period. After cooling to 5°, 80 g. (1.12 moles) of 97% sodium nitrite was added in one portion. External cooling was removed and the temperature of the stirred reaction mixture was allowed to rise to the specified temperature indicated in Table III. The stirred reaction mixtures were maintained at these temperatures from 4 to 24 hours.

For XXXI, XXXIII, XXXIV, XXXVI and XL the reaction mixture was filtered and N-substituted *p*-nitrosoaniline hydrochloride was washed with 500 ml. of ethyl ether. The hydrochloride salt was added to 2,000 g. of stirred ice-water and concd. ammonium hydroxide was added dropwise at 0–20° until a *p*H 8 was obtained. The reaction mixture was stirred for an additional hour at 10–20° and the resulting solid was collected, washed with one liter of cold water and air-dried at 25–30°.

For the remaining compounds the reaction mixture was added to 2,000 g. of ice-water. After stirring for 15 minutes, concd. ammonium hydroxide was added dropwise at 0–20° until *p*H 8 was obtained. This was followed by addition of 500 ml. of heptane and the reaction mixture was stirred at 10–20° for an additional hour. The solid was collected by fil-

TABLE III

N-SUBSTITUTED *p*-NITROSOANILINES



Compound	N-Subst. aniline	R	X	Mole ratio 40% HCl/ CH_3OH–amine	Reaction temp., °C.	Time reacn., hr.	Yield crude, %	M.p., °C.	Empirical formula	Nitrogen, % Calcd.	Nitrogen, % Found
XXIX	N-Cyclohexylaniline	$—C_6H_{11}$	H	6:1	20–25	4.0	44.0	94–95	$C_{12}H_{16}N_2O$	13.72	13.80
XXX	N-2-Chloroallylaniline	$—CH_2CCl{=}CH_2$	H	6:1	10–15	5.0	55.0	85–87[a]	$C_9H_9ClN_2O$	14.25	14.40
XXXI	2-Anilinoacetamide	$—CH_2CONH_2$	H	6:1	20–25	5.0	24.0	150–151[a]	$C_8H_9N_3O_2$	23.45	23.61
XXXII	3-Anilinopropionamide	$—CH_2CH_2CONH_2$	H	6:1	25–30	4.0	78.5	173–174[a]	$C_9H_{11}N_3O_2$[c]	21.75	21.10
XXXIII	N-Ethyl-*m*-chloroaniline	$—C_2H_5$	Cl	6:1	25–30	24.0	57.0	110–112	$C_8H_9ClN_2O$	15.17	15.46
XXXIV	N-Ethyl-*m*-phenetidine	$—C_2H_5$	OC_2H_5	6:1	10–15	4.0	35.6	120–122[b]	$C_{10}H_{14}N_2O_2$	14.42	14.24
XXXV	2-Anilinoethanol	$—CH_2CH_2OH$	H	6:1	25–30	4.0	78.8	93–94[a]	$C_8H_{10}N_2O_2$	16.86	16.70
XXXVI	2-Nitrodiphenylamine	$—C_6H_4NO_2$[f]	H	6:1	15–20	5.0	56.9	173–174[a]	$C_{12}H_9N_3O_3$	17.28	17.64
XXXVII	3-Ethylamino-*p*-cresol	[d]	[d]	8:1	25–30	5.0	55.0	149–150[a]	$C_9H_{12}N_2O_2$	15.55	15.43
XXXVIII	N-Methylcyclohexylmethylaniline	$C_8H_{15}N$[g]	H	7:1	20–25	24.0	83.9	95–97[a]	$C_{14}H_{20}N_2O$	12.06	11.72
XXXIX	N-Cyclohexylmethylaniline	$—CH_2C_6H_{11}$	H	6:1	20–25	17.0	22.5	101–102[a]	$C_{13}H_{17}N_2O$	12.91	12.22
XL	N-Methyl-*m*-chloroaniline	$—CH_3$	Cl	10:1	25–30	4.0	85.0	128–130[e]	$C_7H_7ClN_2O$	18.15	18.36
XLI	2,4-Dichlorobenzylaniline	$—C_7H_5Cl_2$[h]	H	11:1	15–25	4.0	93.0	143–146[b]	$C_{13}H_{10}Cl_2N_2O$	9.96	9.99
XLII	Ethyl N-phenylglycinate	$—CH_2COOC_2H_5$	H	6:1	15–25	4.0	85.3	85–90[e]	$C_{10}H_{12}N_2O_3$	13.46	13.31

[a] Recrystallization from ethyl alcohol. [b] Recrystallization from benzene. [c] Calcd. H, 5.70. Found: H, 6.04. [d] 5-Ethylamino-2-nitroso-*p*-cresol. [e] With decomposition; decomposed when attempted to recrystallize. [f] 2-Nitrophenyl. [g] Methylcyclohexylmethyl. [h] 2,4-Dichlorobenzyl.

tration, washed with 500 ml. of cold water and air-dried at 25–30°. The data are summarized in Table III.

3-(2-Hydroxy-5-nitrosoanilino)-propionitrile.—To a stirred solution containing 81.1 g. (0.50 mole) of 3-(*o*-hydroxyanilino)-propionitrile, 21.2 g. (0.52 mole) of sodium hydroxide, 40 g. (0.56 mole) of 97% sodium nitrite and 1500 ml. of water was added dropwise (sub-surface) at 0–10°, 118 g. of concd. sulfuric acid dissolved in 300 ml. of water. The time required for this addition was four hours. The resulting solid was collected, washed with one liter of water and air-dried at 25–30°. The product, a purple colored solid, m.p. 102–104°, was obtained in 82.4% yield. After recrystallization from ethyl acetate–heptane it melted at 108–110°.

Anal. Calcd. for $C_9H_9N_3O_2$: N, 21.98. Found: N, 21.64.

1-(*p*-Nitrosophenyl)-4-(2,3,6-trichlorobenzyl)-piperazine.—To a stirred solution containing 35.6 g. (0.1 mole) of 1-(2,3,6-trichlorobenzyl)-4-phenylpiperazine, 42 ml. of concd. hydrochloric acid and 100 g. of ice-water was added dropwise at 0–10° a solution containing 8 g. (0.112 mole) of 97% sodium nitrite in 15 ml. of water. After stirring at 0–10° for 20 minutes, 25% sodium hydroxide was added dropwise until *p*H 8 was obtained. The resulting solid was collected by filtration, washed successively with 500 ml. of water and heptane and air-dried at 25–30°. The product, a dark green solid, m.p. 85–87° with decomposition after recrystallization from ethyl alcohol was obtained in 88.5% yield.

Anal. Calcd. for $C_{17}H_{16}Cl_3N_3O$: Cl, 27.67. Found: Cl, 27.56.

Methyl β-(*p*-Nitrosoanilino)-propionate (XLIII). Method I.—To 1,000 g. (8.45 moles) of 31% hydrogen chloride–methyl alcohol solution at 0° was added dropwise 253 g. (1.41 moles) of methyl β-anilinopropionate. After cooling the stirred reaction mixture to 10°, 113 g. (1.59 moles) of 97% sodium nitrite was added in one portion. External cooling was removed and the temperature of the stirred reaction mixture was allowed to rise to 25° over a one hour period. The stirred reaction mixture was maintained at 25–30° for four hours. The resulting solid was collected, washed with 500 ml. of ethyl ether and air-dried at 25–30° for two hours. The solid was dissolved in 3 liters of water. To this stirred solution, concd. ammonium hydroxide was added dropwise until *p*H 8 was obtained. After stirring for 30 minutes the solid was collected by filtration, washed with one liter of water and air-dried at 25–30°. The product, a green colored solid, m.p. 107–109°, was obtained in 88.2% yield.

Anal. Calcd. for $C_{10}H_{12}N_2O_3$: N, 13.41. Found: N, 13.31.

Method II.—This relation was carried out in the same manner as described in method I except 233 g. (1.41 moles) of β-anilinopropionic acid was used. The product, m.p. 107–109°, was obtained in 72.6% yield. Mixed melting point with the product obtained from method I gave no depression.

Anal. Calcd. for $C_{10}H_{12}N_2O_3$: N, 13.41. Found: N, 13.35.

Method III.—This reaction was carried out in the same manner as described for method I except 272.5 g. (1.41 moles) of ethyl β-anilinopropionate was employed. The product, m.p. 100–105°, was obtained in 79% yield. After recrystallization from ethyl alcohol it melted at 107–109° and mixed melting point with the product obtained from method I or II gave no depression.

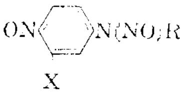
Anal. Calcd. for $C_{10}H_{12}N_2O_3$: N, 13.41. Found: N, 13.26.

Method IV.—To 183 g. (1.5 moles) of 30% hydrogen chloride–methyl alcohol solution at 3° was added in small portions at 3–10°, 36.6 g. (0.25 mole) of 3-anilinopropionitrile over a 15-minute period. The stirred reaction mixture was cooled to 5° and 20 g. (0.28 mole) of 97% sodium nitrite was added in one portion. External cooling was removed and the temperature of the stirred reaction mixture was allowed to rise to 40° over a 30-minute period. After cooling to 30°, the temperature was maintained at 25–30° for 3.5 hours. The reaction mixture was transferred to a four-liter beaker containing 1500 g. of ice-water. After stirring for 30 minutes, concd. ammonium hydroxide (80 g.) was added dropwise to the stirred solution until a *p*H 8 was obtained. Stirring was continued for an additional hour. The resulting solid was collected, washed with 500 ml. of water and air-dried at 25–30°. The product, a green colored solid, m.p. 102–107°, was obtained in 92.3% yield. After recrystallization from methyl alcohol it melted at 107–109°, and the mixed melting point with product obtained from method I, II or III gave no depression.

Anal. Calcd. for $C_{10}H_{12}N_2O_3$: N, 13.41. Found: N, 13.22.

Proof of Structure for Method IV. N-(3-Imino-3-methoxypropyl)-aniline Dihydrochloride.—To 303 g. (2.9 moles) of 35% hydrogen chloride–methyl alcohol solution at 5° was added 71 g. (0.48 mole) of 3-anilinopropionitrile. External cooling was removed and the temperature of the stirred reaction mixture was allowed to rise to 25° over a 30-minute period and then maintained at 20–25° for 5 hours. The resulting solid was collected by filtration, washed with 500 ml. of ethyl ether and air-dried at 25–30°. The product, a white solid, was obtained in 99% yield.

TABLE IV

N,4-DINITROSO-N-SUBSTITUTED ANILINES 

Compound	R	X	Yield crude, %	M.p., °C.	Empirical formula	Nitrogen, % Calcd.	Nitrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found
XLIX	CH_2CH_2CN	H	97.0	84–85[a]	$C_9H_8N_4O_2$	27.44	27.31	. . .	. . .
L	$CH_2CCl{=}CH_2$	H	22.2	89–90	$C_9H_8ClN_3O_2$	. . .	. . .	15.71	15.31
LI	CH_2CH_2COOH	H	72.0	102–103[b]	$C_9H_9N_3O_4$	18.83	19.12	. . .	. . .
LII	$CH_2CH_2CONH_2$	H	83.5	119–120[c]	$C_9H_{10}N_4O_3$[d]	. . .	. . .	. . .	. . .
LIII	$CH_2CH_2COOCH_3$	H	89.5	60–61	$C_{10}H_{11}N_3O_4$	17.72	17.55	. . .	. . .
LIV	C_2H_5	OC_2H_5	30.2	90–92[b]	$C_{10}H_{13}N_3O_3$	18.82	18.68	. . .	. . .
LV	CH_2CH_2OH	H	65.0	101–102[c]	$C_8H_9N_3O_3$[e]	21.53	21.36	. . .	. . .

[a] Recrystallization from isopropyl alcohol. [b] Recrystallization from ethyl alcohol. [c] Recrystallization from methyl alcohol. [d] Calcd.: C, 48.65. Found: C, 48.40. [e] Calcd.: C, 49.23; H, 4.65. Found: C, 49.56; H, 4.82.

TABLE V

p-NITROSOPHENYL SUBSTITUTED UREAS

Compound	Structure	Yield crude, %	M.p., °C.	Empirical formula	Nitrogen, % Calcd.	Nitrogen, % Found
LVII	$RNHCON(C_6H_4NO)CH_2CH_2COOCH_3$	94.5	86–90[a]	$C_{19}H_{18}N_4O_5$	14.65	14.93
LVIII	$RNHCON(C_6H_4NO)CH_2CH_2COOH$	53.0	150–155[a]	$C_{18}H_{16}N_4O_5$	15.21	14.77
LVIX	$[-CH_2C_6H_4NHCON(C_6H_4NO)CH_2CH_2COOCH_3]_2$	99.0	110–112[a]	$C_{35}H_{34}N_6O_8$	12.61	12.78

[a] With decomposition; R = 3-isocyanto-*p*-tolyl.

TABLE VI

METAL SALTS OF N-SUBSTITUTED *p*-NITROSOANILINE 

Compound	R	M	Yield crude, %	Empirical formula	Metal, % Calcd.	Metal, % Found
LX	$-CH_2CH_2COOCH_3$	Ni	28.4	$C_{20}H_{22}N_4O_6Ni$	12.40	13.00
LXI	$-C_6H_5$	Zn	98.0	$C_{24}H_{18}N_4O_2Zn$	14.22	13.80
LXII	$-CH_2CH_2COOCH_3$	Zn	71.0	$C_{20}H_{22}N_4O_6Zn$	13.63	13.80
LXIII	$-C_6H_5$	Cu	99.0	$C_{24}H_{18}N_4O_2Cu$	13.87	14.00
LXIV	$-CH_3$	Cd	99.0	$C_{14}H_{14}N_4O_2Cd$	29.37	28.80

Anal. Calcd. for $C_{10}H_{14}N_2O.2HCl$: N, 11.20; Cl, 28.20. Found: N, 10.87; Cl, 27.65.

Methyl β-Anilinopropionate.—To a stirred solution containing 115 g. (0.46 mole) of N-(3-imino-3-methoxypropyl)-aniline dihydrochloride in 1000 g. of ice-water, concd. ammonium hydroxide was added dropwise until *p*H 8 was obtained. After stirring for an additional 10 minutes at 0–10°, the solid was collected, washed with cold water until the wash water was neutral to litmus and air-dried at 20–25°. The product, m.p. 37–38°, was obtained in 84% yield. A mixed melting point with an authentic sample gave no depression.

Methyl-β-(*p*-Nitrosoanilino)-propionate (LXIII).—This procedure was the same as described in method I except 253 g. (1.41 moles) of methyl β-anilinopropionate derived from N-(3-imino-3-methoxypropyl)-aniline was employed. The product, m.p. 107–109°, was obtained in 82.5% yield. Mixed melting point with the product derived from method I, II, III or IV gave no depression.

Anal. Calcd. for $C_{10}H_{12}N_2O_3$: N, 13.41. Found: N, 13.31.

Methyl β-(3-Methyl-4-nitrosoanilino)-propionate (XLIV) and Methyl β-(4-Nitroso-1-naphthylamino)-propionate (XLV).—This procedure was the same as described in method IV except one mole of 3-(*m*-toluidino)-propionitrile or 3-(α-naphthylamino)-propionitrile, ten moles of 30% hydrogen chloride–methyl alcohol solution and 80 g. (1.12 moles) of 97% sodium nitrite were used.

Compound	M.p., °C.	Yield crude, %	Empirical formula	Nitrogen, % Calcd.	Nitrogen, % Found
XLIV	62–63[a]	52.0	$C_{11}H_{14}N_2O_3$	12.61	12.83
XLV	150–155[a]	90.0	$C_{14}H_{14}N_2O_3$[b]	10.85	10.65

[a] Recrystallization from methyl alcohol. [b] Calcd.: C, 65.10. Found: C, 64.43.

β-(*p*-Nitrosoanilino)-propionic Acid (XLVI). Method V.—To a stirred solution containing 48.6 g. (0.25 mole) of β-(N-nitrosoanilino)-propionic acid (XI) and 183 ml. of glacial acetic acid was added in one portion 73 ml. of concd. hydrochloric acid. An exothermic reaction set in causing a temperature rise from 25 to 41° over a 30-minute period. The stirred reaction mixture was maintained at 25–30° for 24 hours. The solid was collected by filtration and washed with 500 ml. of ethyl ether. After drying for two hours the solid was added to 375 g. of ice-water. To this stirred solution concd. ammonium hydroxide (19 g.) was added dropwise until a *p*H 7.5 was obtained. The reaction mixture was stirred for an additional hour and filtered. The solid was washed with 400 ml. of cold water and air-dried at 25–30°. The product, a green colored solid, m.p. 153–157°, was obtained in 89.6% yield. After recrystallization from ethyl alcohol it melted at 163–164°.

Anal. Calcd. for $C_9H_{10}N_2O_3$: N, 14.42. Found: N, 14.36.

Method VI.—The same procedure described in method V was used except the following reactants were employed: 104.1 g. (0.5 mole) of methyl β-(N-nitrosoanilino)-propionate (XIII), 366 ml. of glacial acetic acid, 146 ml. of concd. hydrochloric acid, 750 g. of ice-water and 35 g. of concd. ammonium hydroxide. The product, a green colored solid, m.p. 155–157°, was obtained in 78.5% yield. After recrystallization from ethyl alcohol it melted at 163–164°. A mixed melting point with product obtained from method V gave no depression.

Anal. Calcd. for $C_9H_{10}N_2O_3$: N, 14.42. Found: N, 14.23.

Method VII.—The same procedure as described in method V was used except 56.6 g. (0.25 mole) of ethyl β-(N-nitrosoanilino)-propionate (XII) was replaced for the β-(N-nitrosoanilino)-propionic acid. The product, a green colored solid, m.p. 154–157°, was obtained in 76.3% yield. After recrystallization from ethyl alcohol it meltedat 163–164°. A mixed melting point with product obtained from method V or VI gave no depression.

Anal. Calcd. for $C_9H_{10}N_2O_3$: N, 14.42; H, 5.19; C, 55.66. Found: N, 14.50; H, 5.16; C, 55.86.

3-(*p*-Nitrosoanilino)-propionitrile (XLVII).—The same procedure described for the preparation of β-(*p*-nitrosoanilino)-propionic acid (method V) was employed except 43.8 g. (0.25 mole) of 3-(N-nitrosoanilino)-propionitrile XVIII was replaced for the β-(N-nitrosoanilino)-propionic acid. The product, a green colored solid, m.p. 127–129°, was obtained in 67.5% yield. After recrystallization from ethyl alcohol it melted at 132–133°.

Anal. Calcd. for $C_9H_9N_3O$: H, 5.18; C, 61.70; N, 23.99; mol. wt., 175.2. Found: H, 4.97; C, 61.85; N, 23.91; mol. wt., 172.7.

Methyl β-(2,4-Dinitroanilino)-propionate (XLVIII).—To a stirred solution of 30 ml. of concd. nitric acid and 90 ml. of water, 40 g. (0.19 mole) of methyl (*p*-nitrosoanilino)-propionate (XLIII) was added in ten portions at 40–50° over a 15-minute period. The stirred reaction mixture was maintained at 40–50° for an additional 20 minutes, poured into 1,000 g. of ice-water and neutralized with concd. ammonium hydroxide until a *p*H 8 was obtained. The solid was collected by filtration, washed with water until the washings were neutral to litmus and air-dried at 25–30°. The product, a light brown solid, m.p. 69–70°, was obtained in 79.2% yield. After recrystallization from ethanol it melted at 72–73°.

Anal. Calcd. for $C_{10}H_{11}N_3O_6$: N, 15.61. Found: N, 15.98.

N,4-Dinitroso N-Substituted Anilines (XLIX-LV).—To a stirred slurry containing 0.2 mole of the appropriate N-substituted *p*-nitrosoaniline and 1000 g. of ice-water, 24 ml. of concd. hydrochloric acid was added in one portion. To this stirred solution at 0° was added dropwise at 0–10°, 14.4 g. (0.203 mole) of 97% sodium nitrite dissolved in 30 ml. of water over a 30-minute period. To the resulting slurry 200 ml. of heptane was added and stirring was continued for one hour at 10–20°. The solid was collected, washed successively with 500 ml. of cold water and heptane and air-dried at 25–30°. The data are summarized in Table IV.

Dicyclohexylamine Salt of β-(*p*-Nitrosoanilino)-propionic Acid (LVI).—To a stirred slurry containing 19.4 g. (0.1 mole) of β-(*p*-nitrosoanilino)-propionic acid (XLVI) in 200 ml. of dry benzene was added in one portion 36.3 g. (0.2 mole) of dicyclohexylamine. After stirring for four hours at 25–30°, the solid was collected, washed with 200 ml. of ethyl ether and air-dried at 25–30°. The product, a green colored solid, m.p. 162–167° with decomposition, was obtained in 99% yield.

Anal. Calcd. for $C_{21}H_{33}N_3O_3$: N, 11.19. Found: N, 10.95.

***p*-Nitrosophenyl Substituted Ureas (LVII-LVIX).**—To 0.2 mole of β-(*p*-nitrosoanilino)-propionic acid (XLVI) or methyl β-(*p*-nitrosoanilino)-propionate (XLIII) in 300 ml. of heptane was added in one portion 0.22 mole of toluene 2,4-diisocyanate or 4,4′-methylenediphenol isocyanate. The stirred reaction mixture was maintained at 25–30° for 24 hours. The product was collected by filtration and air-dried at 25–30°. The data are summarized in Table V.

Metal Salts of N-Substituted *p*-Nitrosoanilines (LX-LXIV).—To a stirred slurry containing 0.2 mole of the appropriate N-substituted *p*-nitrosoaniline, 32 g. (0.2 mole) of 25% aqueous sodium hydroxide and 1000 ml. of water was added in one portion a solution containing 0.1 mole of either nickel nitrate hexahydrate, zinc chloride, copper sulfate pentahydrate or cadmium sulfate (3 $CdSO_4 \cdot 8H_2O$) in 500 ml. of water. The reaction mixture was stirred for one hour at 25–30°. The solid was collected, washed with water until the washings were neutral to litmus and air-dried at 25–30°. The data are summarized in Table VI.

Copper Salt of β-(*p*-Nitrosoanilino)-propionic Acid (LXV).—To a stirred solution containing 19.4 g (0.1 mole) of β-(*p*-nitrosoanilino)-propionic acid (XLVI), 16 g. (0.1 mole) of 25% aqueous sodium hydroxide and 500 ml. of water was added in one portion 12.5 g. (0.05 mole) of copper sulfate pentahydrate dissolved in 500 ml. of water. After stirring for one hour at 25–30°, the solid was collected by filtration, washed with water until the washings were neutral to litmus and air-dried at 25–30°. The product, a green colored solid, was obtained in 49.7% yield.

Anal. Calcd. for $C_{18}H_{18}N_4O_6Cu \cdot 4H_2O$: Cu, 12.17. Found: Cu, 11.60.

β-(2,4-Dihydroxy-3,5-dinitrosophenyl)-propionic Acid Hydrate.—To a stirred suspension at 0° containing 45.6 g. (0.25 mole) of β-(2,4-dihydroxyphenyl)-propionic acid, 29 g. of concd. hydrochloride acid, 150 ml. of ethyl alcohol and 500 ml. of water was added dropwise at 0–10° a solution containing 40 g. (0.56 mole) of 97% sodium nitrite in 100 ml. of water. After stirring for an additional hour at 0–10° the solid was collected, washed with cold water until free of chloride and air-dried at 25–30°. The product, m.p. 110–115° with decomposition, was obtained in 46.6% yield. After recrystallization from water it melted at 128–130° with decomposition.

Anal. Calcd. for $C_9H_8N_2O_6 \cdot H_2O$: N, 10.53. Found: N, 10.67.

Acknowledgment.—The writers wish to acknowledge their indebtedness to Messrs. R. O. Zerbe, T. W. Bartram and D. Mullins for assistance during the course of this investigation. Grateful acknowledgment also is made for the analyses by Mr. E. E. Null.

NITRO, W. VA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

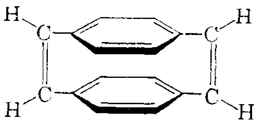
Macro Rings. XIX. Olefinic Paracyclophanes[1]

BY DONALD J. CRAM AND KENNETH C. DEWHIRST

RECEIVED FEBRUARY 14, 1959

A number of classically-conjugated olefinic paracyclophanes have been prepared based on the ring systems of [4.4]paracyclophane and of [2.2.2]paracyclophane. The peculiar geometry and symmetry properties of [4.4]paracyclophane which contains four double bonds is discussed. The spectral properties of these compounds are reported and correlated with their configurations.

An earlier paper[2] reported the preparation of unsaturated derivatives of [2.2]paracyclophane such as I, which serve as extreme examples of steric inhibition of resonance. This paper reports the preparation and properties of a number of paracyclophanes which contain double bonds in the bridges connecting the aromatic nuclei. These compounds are all based on the [2.2.2]paracyclophane (II) or



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[1] This work was supported in part by a grant from the Upjohn Co.

[2] K. C. Dewhirst and D. J. Cram, THIS JOURNAL, **80**, 3115 (1958).