

and a solid separated which was shown to be *n*-butyraldehyde-carbethoxyhydrazone by a comparison of infrared spectra and a mixed melting point determination.

The solution was diluted then with ether, washed repeatedly with 2 *N* hydrochloric acid, followed by sodium bicarbonate solution and water. After drying the solution and removing the solvents under reduced pressure at 0°, there was obtained 2.2 g. of a yellow liquid which possessed a sweet odor. It was stored at Dry Ice temperatures. An ethanol solution of this material showed a weak absorption maximum near 375 m $\mu$ ; no maximum was observed at 220 m $\mu$ . A sample of the compound was allowed to stand at room temperature and after a few hours an absorption maximum developed at 220 m $\mu$  which indicated the presence of an hydrazone. Upon working up this sample, a solid was obtained which had an infrared spectrum identical with that of *n*-butyraldehyde-carbethoxyhydrazone.

***t*-Butylhydrazine Hydrochloride.**—Essentially the method of Westphal<sup>7</sup> was followed. From 60 g. (1.9 moles) of anhydrous hydrazine and 180 g. (1.9 moles) of *t*-butyl chloride in 150 ml. of methanol there was obtained 12.1 g. (5%) of *t*-butylhydrazine hydrochloride which melted at 192–194° after repeated recrystallizations from methanol. Comparable yields of the hydrochloride were realized when the reaction was carried out in the presence of dimethylformamide. The yield was lowered slightly when dioxane was used as the solvent in the reaction.

**1-*t*-Butyl-2-carbethoxyhydrazine.**—A solution of 7.47 g. (0.06 mole) of *t*-butylhydrazine hydrochloride in 5 ml. of water was neutralized with 2.4 g. (0.06 mole) of sodium hydroxide in 3.6 ml. of water. This was added to a mixture of 20 ml. of pyridine and 80 ml. of water, and 6.5 g. (0.06 mole) of ethyl chloroformate was added dropwise with stirring. After all had been added, the reaction mixture was stirred for an additional hour, and then was extracted re-

peatedly with ether. The ether solution was dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was fractionated to give 6.3 g. (66%) of material which boiled at 75–77°/2–3 mm. and melted at 24–25°.

*Anal.* Calcd. for C<sub>7</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>: C, 52.47; H, 10.07. Found: C, 52.87; H, 10.12.

**Ethyl *t*-Butylazocarboxylate.**—A mixture of 1.6 g. (0.01 mole) of 1-*t*-butyl-2-carbethoxyhydrazine, 0.8 g. of anhydrous magnesium sulfate, and 10 ml. of benzene was stirred in an ice bath and 1.5 g. of silver oxide was added. Stirring was continued for 1 hr. at 20°, a further 1.5 g. of silver oxide was added, and the reaction was maintained for another hour. The mixture was filtered, the residue was washed with ether, and the combined solutions were evaporated to leave 1.4 g. of residue. This was purified by evaporative sublimation at room temperature at 0.7 mm. pressure. The material had a sweet odor, was yellow and a middle fraction boiled at 168–170°; m.p., –33 to –32°, *n*<sub>D</sub><sup>25</sup> 1.4155, *d*<sub>4</sub><sup>25</sup> 0.9317, molecular refractivity 42.48, calculated 42.56 (using the constants of Barrick, *et al.*,<sup>12</sup> for aliphatic azo compounds.

*Anal.* Calcd. for C<sub>7</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: C, 53.14, H, 8.92. Found: C, 53.32, 53.45; H, 9.52, 9.36.

A sample of the azo compound was heated under nitrogen in a flask attached to a gas buret. No appreciable change in volume was observed up to a bath temperature of 170°. The infrared spectrum of the heated residue was identical with that of the original material. The experiment was repeated in the presence of a small amount of *p*-toluenesulfonic acid. It was observed that a gas was evolved slowly even at room temperature under these conditions.

(12) L. D. Barrick, G. W. Drake, and H. L. Lochte, *J. Am. Chem. Soc.*, **58**, 160 (1936).

## Nitrosoanilines. II

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A variety of *N*-substituted *p*-nitrosoanilines were prepared by standard methods. A number of bulky groups such as phthalimido and benzothiazolythio have been incorporated as the aniline *N*-substituents. The phthalimidomethyl group contributes measurably to increased stability.

The chemical modification of butyl rubber with *N*, 4-dinitroso-*N*-methylaniline<sup>1</sup> to give filled vulcanizates with greatly improved properties<sup>2</sup> made it advisable to prepare new nitrosoanilines, preferably with higher melting points and exhibiting increased thermal stability. The initial phase of this investigation, as reported in a previous paper,<sup>3</sup> included the preparation of a variety of compounds possess-

ing the general formula  $\text{ON} \begin{array}{c} \text{R}' \\ | \\ \text{C}_6\text{H}_4 \\ | \\ \text{X} \end{array} \text{N}-\text{R}$ , wherein X = H, Cl, and –OC<sub>2</sub>H<sub>5</sub>; R and R' = H, alkyl

alkenyl, –CH<sub>2</sub>CH<sub>2</sub>CN, –CH<sub>2</sub>CH<sub>2</sub>OH, –CH<sub>2</sub>–CH<sub>2</sub>Cl, acid esters, and hetero groups.

The work reported herein involves the preparation of nitrosoanilines with R representing much larger or bulky groups. Inasmuch as the intermediates required for these preparations were not available, the synthesis of such substituted anilines was necessitated. These were of two general classes; (1) imide-formaldehyde-amine condensation products and (2) phthalimide- or 2-mercaptobenzothiazole-chloroamine reaction products. The first class was prepared by the procedures described by Winstead, Heine, and Blair<sup>4,5</sup> to give compounds of

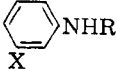
(1) Currently available in 33-1/3% active mixture with an inert filler under the Monsanto Chemical Co. tradename "Elastopar."

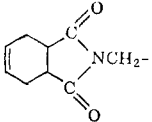
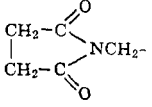
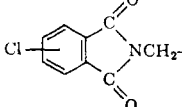
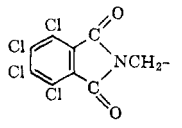
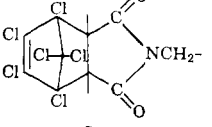
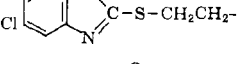
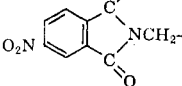
(2) H. M. Leeper, C. I. Gable, J. J. D'Amico, and C. C. Tung, *Rubber World*, **135**, 413 (1956).

(3) J. J. D'Amico, C. C. Tung, and L. A. Walker, *J. Am. Chem. Soc.*, **81**, 5957 (1959).

(4) M. B. Winstead and H. W. Heine, *J. Am. Chem. Soc.* **77**, 1913 (1955).

(5) H. W. Heine, M. B. Winstead, and R. P. Blair, *J. Am. Chem. Soc.* **78**, 672 (1956).

TABLE I  
*N*-SUBSTITUTED ANILINES 

Compound	R	Yield X crude, %	M.p., °C.	Empirical formula	Nitrogen, %		Chlorine, %		
					Calcd.	Found	Calcd.	Found	
I		H	83.5	161-162 <sup>a</sup>	C <sub>15</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>	10.93	11.03	...	...
II	"	Cl	91.7	113-115 <sup>a</sup>	C <sub>15</sub> H <sub>16</sub> ClN <sub>2</sub> O <sub>2</sub>	...	...	12.19	12.60
III		H	98.0	171-172 <sup>b</sup>	C <sub>11</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>	13.72	13.89	...	...
IV		H	61.0	133-134 <sup>a</sup>	C <sub>15</sub> H <sub>11</sub> ClN <sub>2</sub> O <sub>2</sub>	9.77	9.48	...	...
V		H	100.0	222-225 <sup>b</sup>	C <sub>15</sub> H <sub>5</sub> Cl <sub>4</sub> N <sub>2</sub> O <sub>2</sub>	36.32	36.10	...	...
VI		H	96.8	140.0- 141.5 <sup>a</sup>	C <sub>16</sub> H <sub>10</sub> Cl <sub>4</sub> N <sub>2</sub> O <sub>2</sub>	5.90	5.57	...	...
VII		H	77.9	Oil	C <sub>15</sub> H <sub>13</sub> ClN <sub>2</sub> S <sub>2</sub>	8.73	8.58	...	...
VIII		H	98.3	152-153 <sup>b</sup>	C <sub>15</sub> H <sub>11</sub> N <sub>3</sub> O <sub>4</sub>	14.14	14.13	...	...

<sup>a</sup> Recrystallized from ethyl alcohol. <sup>b</sup> Insoluble in all common organic solvents.

the general structure  $M-\text{CH}_2\text{N}(\text{R})\text{C}_6\text{H}_4\text{X}$  with X = H,

Cl, or Br; R = H, alkyl,  $-\text{CH}_2\text{CH}_2\text{CN}$ , and  $-\text{CH}_2\text{CH}_2\text{COOCH}_3$ ; and M = succinimido, phthalimido, tetrahydrophthalimido, chlorophthalimido, tetrachlorophthalimido, and 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-ene-2,3-dicarboximido. The second type was prepared by the reaction of the sodium or potassium salts of the corresponding imide or mercaptobenzothiazole with the appropriate  $\beta$ -chloroethylaniline, using dimethyl formamide as solvent.

The *p*-nitroso-*N*-substituted anilines were prepared by the procedure described in the first paper of this series,<sup>3</sup> wherein the appropriate *N*-substituted aniline reacted in excess hydrogen chloride-methyl alcohol solution with sodium nitrite. The most critical factor in these reactions is the temperature as indicated in Table III.

The preparation of the *N,N*-disubstituted *p*-

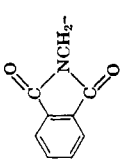
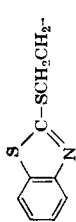
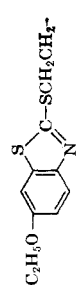
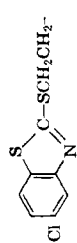
nitrosoanilines was essentially the same as employed in previous work.<sup>3</sup> The *N,N*-disubstituted aniline, in concentrated hydrochloric acid solution, was treated with an aqueous solution of sodium nitrite. Neutralization with sodium hydroxide yielded the desired products.

Reaction of *N*-(*m*-chloro-*p*-nitrosoanilinomethyl)-phthalimide (XVII) with the appropriate isocyanate in an inert solvent at room temperature produced the *p*-nitrosophenyl ureas.

### Discussion

When reference is made to the stability of organic compounds, properties often considered as indicative of good stability include high melting point, resistance to decomposition at extended periods of heating, long shelf life, and in some cases, high molecular weight. The nitrosoanilines described herein cannot be generally classified in such a clear manner. Little correlation exists between mo-

TABLE II

Compound	R	R'	X	Yield crude, %	M.p., °C.	Empirical formula	Nitrogen, %		Sulfur, %	
							Calcd.	Found	Calcd.	Found
IX		NCCH <sub>2</sub> CH <sub>2</sub> —	H	52.5	119–121 <sup>a</sup>	C <sub>18</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub>	13.76	13.73	...	...
X	"	H <sub>3</sub> COOCCH <sub>2</sub> CH <sub>2</sub> —	H	62.0	75–76 <sup>a</sup>	C <sub>19</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub>	8.28	8.50	...	...
XII		CH <sub>3</sub> CH <sub>2</sub> —	H	63.0	56–58 <sup>a</sup>	C <sub>17</sub> H <sub>18</sub> N <sub>2</sub> S <sub>2</sub>	8.91	8.79	...	...
XIII		CH <sub>3</sub> CH <sub>2</sub> —	H	64.6	Oil	C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> OS <sub>2</sub>	7.81	7.64	...	...
XIV		CH <sub>3</sub> CH <sub>2</sub> —	H	73.5	Oil	C <sub>17</sub> H <sub>17</sub> ClN <sub>2</sub> S <sub>2</sub>	8.03	7.76	...	...

<sup>a</sup> Recrystallized from ethyl alcohol.

TABLE III

Compound	N-Substituted aniline	X	Reaction temp., °C.	Reaction time, hr.	Yield crude, %	M.p., °C.	Nitrogen, %		Sulfur, %	
							Calcd.	Found	Calcd.	Found
XV	N-(Phthalimidomethyl)aniline <sup>a</sup>	H	25–45	4	99.0	184–186	14.94	14.51	...	...
XVI	N-(Phthalimidomethyl)- <i>m</i> -chloroaniline <sup>a</sup>	Cl	25–30	4	89.0	223–225 <sup>a</sup>	13.36	13.56	...	...
XVII	N-(Phthalimidomethyl)- <i>m</i> -bromoaniline <sup>a</sup>	Br	25–30	4	44.5	203–205 <sup>a</sup>	11.67	11.90	...	...
XVIII	I	H	25–30	4	58.0	100–102	14.72	14.66	...	...
XIX	II	Cl	10–20	4	92.6	65–66	13.14	12.89	...	...
XX	III	H	10–20	4	46.3	189–189.5 <sup>b</sup>	18.01	17.79	...	...
XXI	IV	H	25–33	4	95.3	165–165	13.32	13.19	...	...
XXII	V	H	15–20	4	71.5	>300	10.03	9.88	...	...
XXIII	VI	H	15–20	4	95.2	163–164 <sup>c</sup>	8.34	8.18	...	...
XXIV	VII	H	25–30	5	96.2	88–90	...	...	...	...
XXV	VIII	H	25–42	5	94.5	192.5–193.0	17.18	17.16	18.33	17.94

<sup>a</sup> Recrystallized from dimethylformamide–water.

<sup>b</sup> Recrystallized from ethyl acetate–acetone.

<sup>c</sup> Recrystallized from benzene–petroleum ether (b.p. 80–100°).

<sup>d</sup> Ref. 4.

lecular weight and thermal stability, while the higher melting materials were found to be generally more stable.

However, one class of compounds, the *p*-nitrosoanilinomethylimides, do show a marked increase in thermal stability over such materials as *N*, 4-dinitroso-*N*-methylaniline and *N*-methyl-*p*-nitrosoaniline. One notable exception in this regard is the use of tetrahydrophthalimide as the imide. All of the remaining imides follow the pattern of increased stability. This is illustrated in Table VI, in which two derivatives of phthalimide are compared with *N*,4-dinitroso-*N*-methylaniline and *N*-methyl-*p*-nitrosoaniline.

The thermal stability, determined by the method of Deason, *et al.*,<sup>6</sup> is seen to be greatly increased in the case of the two phthalimide derivatives, although both are quite active as modifiers for butyl rubber.<sup>7</sup> It is interesting to note that the chloro derivative is less stable thermally although it has a 40° higher melting point. All of the thermally stable imide derivatives have undergone no changes in melting point or assay after a shelf life of two years.

### Experimental<sup>8</sup>

*N*-(Anilinomethyl)cyclohexenedicarboximide (I), *N*-(*m*-chloroanilinomethyl)cyclohexenedicarboximide (II), *N*-(anilinomethyl)-succinimide (III), *N*-(anilinomethyl)-*ar*-chlorophthalimide (IV), *N*-(anilinomethyl)tetrachlorophthalimide (V), *N*-(anilinomethyl)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-hept-5-ene-2,3-dicarboximide (VI), and *N*-(anilinomethyl)-4-nitrophthalimide (VIII) were prepared by the procedure described by Winstead and Heine,<sup>4</sup> using the appropriate imides, formaldehyde, and primary aromatic amines. A good yield of relatively pure crude product was obtained in all cases. The data are summarized in Table I.

*N*-[*N*-(β-Cyanoethyl)anilinomethyl]phthalimide (IX) and methylphenyl-*N*-phthalimidomethyl-β-alaninate (X) were prepared by the procedure described by Heine, Winstead, and Blair,<sup>5</sup> using phthalimide, formaldehyde, and the appropriate *N*-substituted anilines. The data are summarized in Table II.

*N*-[2-(*N*-Ethylanilino)ethyl]phthalimide (XI).—A stirred mixture of 85.6 g. (0.5 mole) of potassium phthalimide, 300 ml. of *N*,*N*-dimethylformamide, 110.1 g. (0.50 mole) of *N*-(β-chloroethyl)-*N*-ethylaniline hydrochloride, and 28 g. (0.5 mole) of potassium hydroxide was heated at 140–150° for 24 hr. After cooling to 20°, the mixture was poured, with vigorous stirring, into 1500 g. of ice water and stirred for 1 hr. The resulting mixture was then 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*, an oil was obtained in 68% yield.

*Anal.* Calcd. for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: N, 9.52; Found: N, 9.01.

2-(β-Anilinoethylthio)-5-chlorobenzothiazole (VII), 2-(β-(*N*-Ethylanilino)ethylthio)benzothiazole (XII), 2-[β-(*N*-Ethylanilino)ethylthio]-6-ethoxybenzothiazole (XIII), 2-[β-(*N*-Ethylanilino)ethylthio]-5-chlorobenzothiazole (XIV).—To a stirred mixture of 0.5 mole of 2-mercapto-5-chlorobenz-

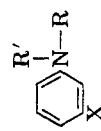


TABLE IV

*N,N*-DISUBSTITUTED *p*-NITROSOANILINES

Compound	N,N'-Disubstituted aniline	X	Yield crude, %	M.p., °C.	Empirical formula	Nitrogen, %		Chlorine, %		Sulfur, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
XXVI	<i>N</i> -Methyl- <i>N</i> -(phthalimido-methyl)aniline <sup>b</sup>	H	99.0	163–167 <sup>a</sup>	C <sub>16</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>	14.23	13.98	...	...	...	...
XXVII	<i>N</i> -Ethyl- <i>N</i> -(phthalimido-methyl)aniline <sup>b</sup>	H	89.5	173–175 <sup>a</sup>	C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>	13.58	13.35	...	...	...	...
XXVIII	IX	H	52.0	135–137	C <sub>18</sub> H <sub>14</sub> N <sub>4</sub> O <sub>3</sub>	16.76	16.66	...	...	...	...
XXIX	X	H	20.8	133–134	C <sub>19</sub> H <sub>17</sub> N <sub>3</sub> O <sub>5</sub>	11.44	11.22	...	...	...	...
XXX	<i>N</i> -Ethyl- <i>N</i> -(phthalimido-methyl)- <i>m</i> -chloroaniline <sup>b</sup>	Cl	81.6	163–169	C <sub>17</sub> H <sub>14</sub> ClN <sub>2</sub> O <sub>2</sub>	12.22	12.58	...	...	...	...
XXXI	XI	H	49.5	173–175	C <sub>18</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub>	13.00	12.54	...	...	...	...
XXXII	XII	H	87.4	127–128	C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub>	12.23	12.16	...	...	18.67	18.89
XXXIII	XIII	H	63.7	118–120	C <sub>19</sub> H <sub>21</sub> N <sub>3</sub> O <sub>5</sub>	10.84	11.02	...	...	...	...
XXXIV	XIV	H	93.9	142–143	C <sub>17</sub> H <sub>16</sub> ClN <sub>3</sub> O <sub>5</sub>	...	...	9.38	9.66	...	...

<sup>a</sup> Recrystallized from ethyl alcohol-acetone. <sup>b</sup> Ref. 5.

(6) W. R. Deason, W. E. Koerner, and R. H. Munch, *Ind. Eng. Chem.* **51**, 997 (1959).

(7) J. J. D'Amico (to Monsanto Chemical Co.), U. S. Patent 2,927,930 (March 8, 1960).

(8) All melting points were taken upon a Fisher-Johns block and are uncorrected.

TABLE V

Compound	R	R'	X	Yield crude, %	M.p., °C.	Empirical formula	—Nitrogen, %—	
							Calcd.	Found
XXXV		C <sub>6</sub> H <sub>5</sub> -	Cl	81.0	118-122 <sup>a</sup>	C <sub>22</sub> H <sub>18</sub> ClN <sub>4</sub> O <sub>4</sub>	12.90	12.60
XXXVI			Cl	71.4	121-126 <sup>a</sup>	C <sub>24</sub> H <sub>18</sub> ClN <sub>5</sub> O <sub>6</sub>	14.30	14.11
XXXVII			Cl	75.8	120-124 <sup>a</sup>	C <sub>30</sub> H <sub>20</sub> ClN <sub>4</sub> O <sub>5</sub>	12.37	12.46

<sup>a</sup> Insoluble in all common organic solvents.

TABLE VI  
COMPARISON OF THERMAL STABILITY OF *p*-NITROSOANILINES<sup>a</sup>

	Mol. wt.	M.p., °C.	T <sub>1</sub> , <sup>b</sup> °C.	T <sub>2</sub> , <sup>c</sup> °C.
<i>N</i> ,4-Dinitroso- <i>N</i> -methylaniline	165.15	95-96	68.0	91.5
<i>N</i> -Methyl- <i>p</i> -nitrosoaniline	136.15	117-118	37.5	55.0
<i>N</i> -( <i>p</i> -Nitrosoanilinomethyl)phthalimide	281.26	184-186	112.5	133.5
<i>N</i> -( <i>m</i> -Chloro- <i>p</i> -nitrosoanilinomethyl)-phthalimide	315.71	223-225	98.5	120.5

<sup>a</sup> See ref. 6. <sup>b</sup> T<sub>1</sub> = Temperature at which heat evolution = 10 cal./min./kg. <sup>c</sup> T<sub>2</sub> = Temperature at which heat evolution = 100 cal./min./kg.

othiazole, 2-mercaptobenzothiazole, or 2-mercapto-6-ethoxybenzothiazole, 400 ml. of water, and 160 g. (1.0 mole) of 25% sodium hydroxide solution was added 0.5 mole of *N*-( $\beta$ -chloroethyl)aniline hydrochloride or *N*-( $\beta$ -chloroethyl)-*N*-ethylamine hydrochloride in one portion at 25°. The resulting mixture was stirred at 50-60° for 6 hr., after which time it was cooled to 15° and 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. The ether was removed *in vacuo* to yield the desired products. The data for VII is given in Table I while the remainder are described in Table II.

***p*-Nitroso-*N*-substituted Anilines (XV-XXV).**—To 868 g. (10.0 moles) of 42% hydrogen chloride-methyl alcohol solution at 0-5° was added, with vigorous stirring, 1 mole of the appropriate *N*-substituted aniline in small portions over a 15-30-min. period. The addition was accompanied by a rise in temperature to 15-20°. After cooling the reaction mixture 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 reaction mixture was allowed to rise to that specified in Table III. The stirred reaction mixtures were maintained at these temperatures for 4 to 5 hr.

The reaction mixture was added to 2000 g. of ice water, stirred for 5-15 min., and concentrated ammonium hydroxide was then added dropwise at 0-20° until pH 8 was obtained. After stirring the mixture for 1 hr. at 10-20°, the precipitated product was collected by filtration, washed with water until the wash water was neutral to litmus, and air-dried at 25-30°. The data are summarized in Table III.

***N*,*N*-Disubstituted *p*-Nitroso Anilines (XXVI-XXXIV).**—To 150 g. (1.5 moles) of concentrated hydrochloric acid at 0-10° was added, with vigorous stirring, 0.25 mole of the

appropriate *N*,*N*-disubstituted aniline in one portion, after which a temperature rise to 15-20° was observed. The mixture was cooled to 0° and 20 g. (0.281 mole) of 97% sodium nitrite dissolved in 50 ml. of water was added dropwise over a period of 15-30 min. at 0-10°. Stirring was then continued for 1 hr. at 0-10°. The mixture was then poured into 500 g. of ice water, stirred for 10-15 min., and 25% sodium hydroxide solution was added dropwise at 0-10° to the well stirred mixture until pH 8 was obtained. After stirring for 1 hr. at 10-20°, the resulting solid was collected by filtration, washed with water until the wash water was neutral to litmus, and air-dried at 25-30°. The data are summarized in Table IV.

***N*-(*m*-Chloro-*N*,4-dinitrosoanilinomethyl)phthalimide (XXXVIII).**—To a stirred mixture of 14 g. (0.044 mole) XVI and 150 g. glacial acetic acid, cooled to 15°, was added 10.0 g. (0.1 mole) of 37% aqueous hydrochloric acid over a period of 10 min. To the resulting solution there was added a solution of 4.0 g. (0.057 mole) of 98% sodium nitrite in 10 ml. of water over a period of 15 min., the temperature being maintained at 20-25°. After stirring for 3 hr. at 25-29°, the solution was cooled to 10° and 500 ml. of water was added to precipitate a light tan solid. The mixture was stirred at 15-20° for 30 min., after which time the solid was removed by filtration, washed with water until the washings were neutral to litmus, and dried over calcium chloride in a vacuum desiccator. Recrystallization from ethyl alcohol produced 9.9 g. (65.4%) of the desired product, a light tan solid, m.p. 152-154°.

*Anal.* Calcd. for C<sub>15</sub>H<sub>9</sub>ClN<sub>4</sub>O<sub>4</sub>: N, 16.25; Found: N, 16.08.

***p*-Nitrosophenyl Substituted Ureas (XXXV-XXXVII).**—To a stirred mixture of 63.0 g. (0.20 mole) of XVI and 300 ml. of *n*-heptane at 25-30° was added 0.22 mole of phenyl

isocyanate, tolyl 2,4-diisocyanate, or bis(*p*-isocyanato)-diphenylmethane in one portion. The resulting mixture was stirred at 25–30° for 20 hr. The precipitated solids were collected by filtration, washed with 50 ml. of cold *n*-heptane, and air-dried at 25–30°. The data are summarized in Table V.

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## Oxidation–Reduction Potentials and Absorption Spectra of Polycyclic Aromatic Quinones<sup>1</sup>

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Oxidation–reduction potentials, carbonyl, and ultraviolet and visible (240–600-m $\mu$  range) absorption frequencies of sixteen polycyclic aromatic quinones are reported. All available oxidation–reduction potential data of unsubstituted aromatic quinones are summarized and several new generalizations noted.

Oxidation–reduction potentials of polycyclic aromatic quinones normally provide a precise measure of both the oxidizing power of the quinone and the reducing intensity of the hydroquinone. These oxidation–reduction potentials, however, have also been used to account for the tendency of many aromatic compounds to give addition rather than substitution products.<sup>2,3</sup> Thus Fieser and Price<sup>4</sup> have correlated the velocity of the phenanthrene–bromine addition reaction for various phenanthrene derivatives with the magnitude of the redox potential of the corresponding *o*-quinone, while Badger<sup>5</sup> has used redox potentials as a measure of the stability of dihydro compounds having the same nuclear bond structure as the corresponding quinones. Waters<sup>6</sup> has found redox potentials also useful as guides to the position of substitution in polycyclic aromatics while Josien and co-workers<sup>7</sup> have indicated the relationship between the carbonyl vibration frequency of a compound and its oxidation–reduction potential. The utility of oxidation–reduction potential data in interpreting the behavior of tautomers of hydroxy- and aminoquinones is well documented.<sup>8</sup> Most recently, a linear relationship has been demonstrated between oxidation–reduction potentials and the rate of catalytic hydrogenation of *p*-quinones and their alkylated derivatives.<sup>9</sup>

Conversely Iball's<sup>10</sup> measurement of the oxidation–reduction potentials of sixteen carcinogenic and noncarcinogenic benz[*a*]anthracene-7,12-dione derivatives plus dibenz[*a,h*]- and dibenz[*a,j*]anthracene-7,14-diones showed that substituent position on the benz[*a*]anthracene nucleus had a marked effect on the oxidation potential, but that there was no apparent correlation between potential and carcinogenic potency.

The Branch-Calvin relation<sup>11</sup> between the corrected normal potential of an aromatic quinone and the number of Kekulé structures in the hydroquinone and quinone has led Carter<sup>12</sup> to an empirical equation for the calculation of resonance energies of polycyclic aromatic hydrocarbons. Coulson<sup>13</sup> has demonstrated the smooth curve relationship of these corrected redox potentials with experimental bond lengths, while other investigators have expanded this list to include bond localization energies<sup>14,15</sup> and bond orders.<sup>5,11,14,16</sup> Our most recent demonstrated qualitative correlation between corrected redox potentials of aromatic *o*- and *p*-quinones and both the position and ease of initial ozone attack in unsubstituted aromatic hydrocarbons<sup>17</sup> necessitated a review of all known potentials in the field.<sup>18</sup>

In this paper we report specifically on the measurement of oxidation–reduction potentials, car-

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