solution of maleic anhydride was added to one flask. After 15 min. the contents of both flasks were diluted to the mark and the rotations observed. The levopimaric acid content of the oleoresin, L, was calculated as a percent of resin acids using equation 4:

$$\% L = 100 \frac{(\alpha_M - \alpha_0)V}{W\,\{([\alpha]_D)_L - M_A/M_L\,([\alpha]_D)_A\}} \quad (4)$$

in which α_M and α_0 are the observed rotations with and without maleic anhydride, V is the volume in milliliters, W is the weight in grams of resin acids in sample as calculated from the titer, $([\alpha]_D)_L$ and $([\alpha]_D)_A$ are the specific rotations of levopimaric acid and adduct, and M_A and M_L are the molecular weights of levopimaric acid and its adduct.

Acknowledgment. The authors wish to express their appreciation to Messrs. Ray V. Lawrence and Gordon S. Fisher for many helpful discussions during this work and to Mrs. Luella R. Lloyd for editing the manuscript.

OLUSTEE, FLA.

[CONTRIBUTION NO. 624 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION,
E. I. DU PONT DE NEMOURS AND CO.]

4-(2-Cyano-3-maleimidyl)arylamines and Related Colored Compounds

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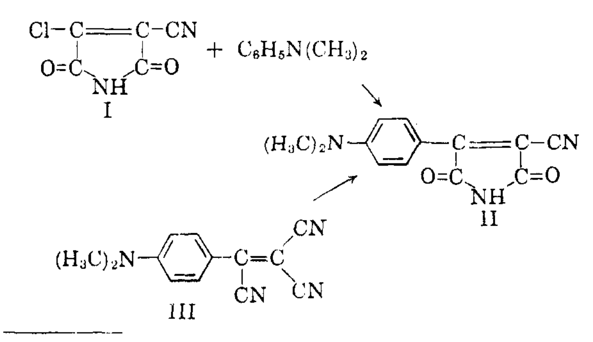
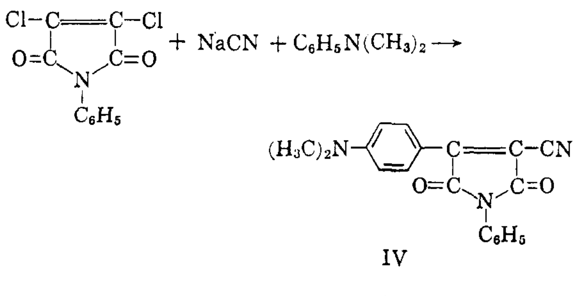
3-Chloro-2-cyanomaleimides react with tertiary arylamines by attacking the aromatic ring to give 4-(2-cyano-3-maleimidyl)arylamines, a new class of colored compounds. The same compounds can be obtained by the condensation of a dihalomaleimide and a metal cyanide in the presence of a tertiary arylamine. Dihalomaleic anhydrides and mucohalic acids can be substituted for the dihalomaleimides, and metal sulfinates can be used in place of metal cyanides to give analogous compounds.

Tetracyanoethylene reacts with primary and secondary aliphatic amines and with most primary and some secondary aromatic amines to give N-tricyanovinylamines.[1] However, the reaction of tetracyanoethylene and tertiary aromatic amines and certain secondary aromatic amines results in attack on the ring to give 4-tricyanovinylarylamines.[1] Tricyanovinyl chloride behaves much like tetracyanoethylene toward amines.[2] A recent publication[3] reported the reaction of 3-chloro-2-cyanomaleimide (I) with primary aromatic amines and a secondary aliphatic amine to give derivatives in which a hydrogen atom on the amine group had been replaced by a 2-cyano-3-maleimidyl residue. It has now been found that, like tetracyanoethylene and tricyanovinyl chloride, 3-chloro-2-cyanomaleimide (I) readily attacks the ring of tertiary atomatic amines to give 4-(2-cyano-3-maleimidyl)arylamines, a new class of colored compounds. For example, N,N-dimethylaniline and 3-chloro-2-cyanomaleimide (I) gave 4-(2-cyano-3-maleimidyl)-N,N-dimethylaniline (II), a bright red substance. N-Substituted 3-chloro-2-cyanomaleimides behave similarly.



Compound II is identical with the product obtained by the acid hydrolysis[4] of 4-(tricyanovinyl)-N,N-dimethylaniline (III), a dye whose structure was established by an unequivocal synthesis.[1]

4-(2-Cyano-3-maleimidyl)arylamines can be prepared also by the reaction of a dihalomaleimide, a tertiary aromatic amine, and sodium cyanide in a suitable solvent as illustrated in the preparation of 4-(N-phenyl-2-cyano-3-maleimidyl)-N,N-dimethylaniline (IV). Compounds of the formula VI are obtained conveniently by the addition of a salt of a sulfinic acid to a solution of a tertiary aromatic amine and a dibromo- or dichloromaleimide (V) in a suitable reaction medium. In these examples, the first step in the reaction



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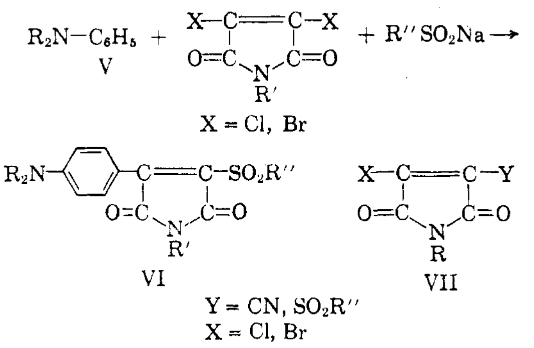
[1] B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *J. Am. Chem. Soc.*, **80**, 2806 (1958).

[2] C. L. Dickinson, D. W. Wiley, and B. C. McKusick, *J. Am. Chem. Soc.*, **82**, 6132 (1960).

[3] R. H. Wiley and S. C. Slaymaker, *J. Am. Chem. Soc.*, **80**, 1385 (1958).

[4] G. N. Sausen, V. A. Engelhardt, and W. J. Middleton, *J. Am. Chem. Soc.*, **80**, 2815 (1958).



V VI VII

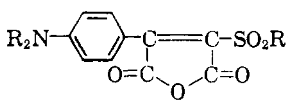
X = Cl, Br

Y = CN, SO_2R''

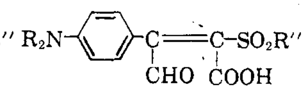
X = Cl, Br

is probably the replacement of one of the halogen atoms by a cyano or sulfonyl group, followed by condensation of the resulting halogen-substituted maleimide derivative (VII) with the tertiary aromatic amine. Secondary aromatic amines, dichloromaleimides, and sulfinates gave *N*-substitution reaction products.

It has also been found that the addition of a salt of a sulfinic acid to a solution of dibromo-, dichloro-, or difluoromaleic anhydride and a tertiary aromatic amine results in the formation of highly colored compounds of the general formula VIII. The structure of the maleic anhydride reaction product VIII ($R = CH_3$, $R'' = p\text{-}CH_3C_6H_4$) was established by conversion to the maleimide derivative (VI) ($R = CH_3$, $R' = C_6H_5$, $R'' = p\text{-}CH_3C_6H_4$) by reaction with aniline. The reaction has also been extended successfully to the mucobromic and mucochloric acids to give colored compounds assigned the structure IX. This assignment is based mainly on the recent study of the reaction of sodium nitrite and mucochloric acid.[5]



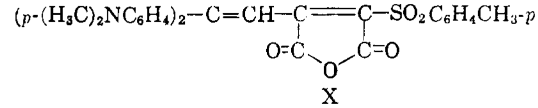
VIII



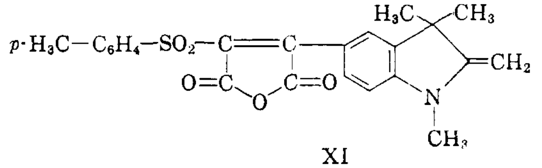
IX

The colored compounds of formulas II, VI, VIII, and IX give brilliant dyeings, ranging from orange to magenta, on fibers of materials such as cellulose acetate, polyethylene terephthalate, and polyacrylonitrile. The dyeings from compounds II, VI, and IX have good wash-fastness and sublimation-fastness and fair light-fastness, and they can be applied from a moderately acidic bath (*p*H 5-6) without serious decomposition. The anhydrides (VIII) hydrolyze rapidly in aqueous dye baths and must be applied from inert media such as methylene chloride.

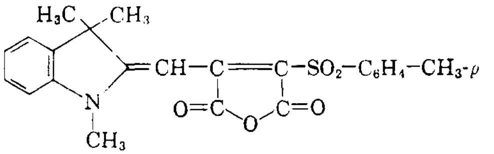
A number of compounds other than tertiary aromatic amines were condensed with 3-chloro-2-cyanomaleimide and dichloro-*N*-phenylmaleimides in order to obtain dyes of other shades. Phenols, hydrazones, and active-methylene compounds gave derivatives ranging in color from yellow to blue. Dichloromaleic anhydride and sodium *p*-toluenesulfinate reacted with 1,1-bis(4-dimethylaminophenyl)ethylene to give a blue compound (X), but reacted with 1,3,3-trimethyl-2-methyleneindoline to give two compounds, one blue and the other red. The blue product was assigned the structure XI and the red material was assigned the structure XII on the basis of spectral properties.



X



XI



XII

The 2-cyano- and 2-arenesulfonyl-3-maleimides absorb at somewhat longer wave lengths than corresponding 4-tricyanovinylarylamines. However, the tricyanovinylarylamines have molecular extinction coefficients nearly twice those of the maleimides. The arenesulfonyl-substituted maleic anhydrides have visible spectra very similar to the corresponding maleimides, especially when the maleimide structure is substituted on the nitrogen atom.

EXPERIMENTAL[6]

Preparation of 4-(2-cyano-3-maleimidyl)arylamines and related colored compounds. (Table I.). A. *Condensation of 3-chloro-2-cyanomaleimide and color-former.* A solution of 0.01 mole of 3-chloro-2-cyanomaleimide[3] and 0.01 mole of color-former in 25 ml. of a solvent was stirred at 25–40° for 1–3 hr. Suitable solvents included ethyl acetate, acetonitrile, dimethylformamide, and dimethylsulfoxide. If the maleimide dye crystallized, it was recovered by filtration and recrystallized. Otherwise, the reaction mixture was diluted with ice water, the precipitate was collected by filtration, washed with water, and crystallized. Specific examples are shown below.

B. *Condensation of a dihalomaleimide or dihalomaleic anhydride with a color-former and a metal cyanide or sulfinate.* Finely powdered sodium cyanide or sulfinate (0.01 mole) was added to a mechanically stirred suspension or solution of 0.01 mole of dihalomaleimide or dihalomaleic anhydride and 0.01 mole of color-former in 15–20 ml. of dimethyl formamide. The addition required about 5–10 min. and the stirring was continued at 15–35° for an additional 10–30 min. To isolate the reaction product, the reaction mixture was diluted with about 10 volumes of ice and water. When the product separated as a solid from the aqueous mixture, it was collected by filtration and washed with water. If a gummy maleimide reaction product separated, it often could

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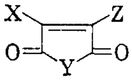
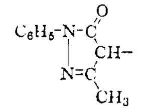
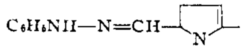
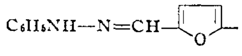
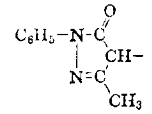
(5) P. E. Fanta, R. A. Stein, and R. M. W. Rickett, *J. Am. Chem. Soc.*, **80**, 4577 (1958).

(6) Melting points are not corrected.

TABLE I

PROPERTIES OF 4-(2-CYANO-3-MALEIMIDYL)ARYLAMINES AND RELATED COLORED COMPOUNDS OF FORMULA



X	Y	Z	Prepn. Method[a]	Yield, %	M.P.
4-$(NCCH_2CH_2)_2NC_6H_4$—	NH	CN	A	61	296–298
	NH	CN	A	45	226–228
	NH	CN	A	47	263
	NH	CN	A	91	
4-$Me_2NC_6H_5$—	N-C_6H_5	SO_2CH_3	B	11	222–224
4-$Me_2NC_6H_4$—	N-C_6H_5	$SO_2C_2H_5$	B	10	193–195
4-$Me_2NC_6H_4$—	N-C_6H_5	$SO_2CH_2C_6H_5$	B	7	183–185
4-$Me_2NC_6H_4$—	N-C_6H_5	$SO_2C_6H_4Cl$-4	B	21	195–196
4-$Me_2NC_6H_4$—	N-C_6H_4Cl-4	$SO_2C_6H_4CH_3$-4	B	16	198–200
4-$Me_2NC_6H_4$—	N-C_6H_4COOEt-4	$SO_2C_6H_4CH_3$-4	B	20	128–130
4-$Me_2NC_6H_4$—	N-C_6H_4-SO_2NH_2-4	$SO_2C_6H_4CH_3$-4	B	29	209–211
4-$Me_2NC_6H_4$—	N-$NHO_2SC_6H_4CH_3$-4	$SO_2C_6H_4CH_3$-4	B	37	205–207
4-$NCCH_2CH_2N(Me)C_6H_4$—	N-C_6H_3Cl-2-COOMe-5	$SO_2C_6H_4CH_3$-4	B	15	128–130
	N-C_6H_5	$SO_2C_6H_4CH_3$-4	B	37	167–169
$(4\text{-}Me_2NC_6H_4)_2C{=}CH$—	N-C_6H_5	$SO_2C_2H_5$	B	62	195–197
C_6H_5NMe—	N-C_6H_5	SO_2CH_3	B	73	188–189
C_6H_5NMe	N-C_6H_5	$SO_2C_6H_4CH_3$-4	B	79	207–209
4-$Me_2NC_6H_4$—	O	SO_2CH_3	C	71	165–166
4-$Me_2NC_6H_4$—	O	$SO_2C_2H_5$	C	49	153–155
4-$Me_2NC_6H_4$—	O	$SO_2C_4H_9$-n	C	57	139–141
4-$Me_2NC_6H_4$—	O	$SO_2CH_2C_6H_5$	C	16	173–174
4-$Me_2NC_6H_4$—	O	$SO_2C_6H_4Cl$-4	C	27	183–185
$(4\text{-}Me_2NC_6H_4)_2C{=}CH$—	O	$SO_2C_6H_4Cl$-4	C	28	209–210
4-$Me_2NC_6H_4$—	O	$SO_2C_6H_4CN$-2	C	17	232–233
4-$Me_2NC_6H_4$—	O	$SO_2C_6H_4NHAc$-4	C	41	206–207
4-$Me_2NC_6H_4$—	O	$SO_2C_6H_4NO_2$-4	C	10	213–214

[a] A, condensation of 3-chloro-2-cyanomaleimide and color-former; B, Condensation of dichloromaleimide, color-former, and sulfinate salt; C, Condensation of dichloromaleic anhydride, color-former and sulfinate salt. [b] In acetone. [c] Contains 1 CH_3COOH of crystallization. [d] Contains 1.5 CH_3OH of crystallization.

be induced to crystallize by trituration with methanol. However this technique could not be used with the maleic anhydride derivatives as they were rapidly converted to the light yellow methyl hydrogen maleate derivatives. In either case, the moist filter cake was dissolved in methylene chloride and the solution was dried with anhydrous magnesium sulfate. The filtrate was concentrated and ether or methanol was added to induce crystallization. Specific examples are given below.

4-(2-Cyano-3-maleimidyl)-N,N-dimethylaniline (II). A. *From 3-chloro-2-cyanomaleimide.* A solution of 1.56 g. of 3-chloro-2-cyanomaleimide[3] and 1.24 g. of *N,N*-dimethylaniline in 25 ml. of ethyl acetate was stirred for 2 hr. and the red crystalline product was collected. The yield was 1.82 g. (74%). Crystallization from glacial acetic acid gave 1.8 g. (74%) of purple crystals, m.p. 308–310°; $\lambda_{max}^{ethanol}$ 518 mμ (ϵ 27,300).

Anal. Calcd. for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.76; H, 4.62; N, 17.53.

B. *From 4-(tricyanovinyl)-N,N-dimethylaniline.* A solution of 4.0 g. of 4-(tricyanovinyl)-*N,N*-dimethylaniline[1] in 35 ml. of concd. hydrochloric acid was stirred at room temperature for 1 day. The reaction mixture was poured over ice and II was collected, washed with water, and crystallized from acetic acid. The compound melted at 308–310°, alone or in admixture with a sample of the compound obtained from 3-chloro-2-cyanomaleimide and *N,N*-dimethylaniline; $\lambda_{max}^{ethanol}$ 518 mμ (ϵ 28,600).

Anal. Calcd. for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 65.17; H, 4.68; N, 17.48.

4-(2-Cyano-N-phenyl-3-maleimidyl)-N,N-dimethylaniline (IV). A mechanically stirred solution of 7.26 g. of dichloro-*N*-phenylmaleimide in 55 ml. of dimethylformamide and 7 g. of *N,N*-dimethylaniline was heated on a steam bath and

TABLE I (*Continued*)

Crystn. Solvent	$\lambda_{max}^{CH_2Cl_2}$ mμ	ϵ_{max} × 10⁻²	Formula	Carbon, %		Hydrogen, %		Additional Analysis, %		
				Calcd.	Found	Calcd.	Found	Element	Calcd.	Found
HOAc	484[b]	254	$C_{17}H_{13}N_5O_2$	63.95	64.81	4.08	4.00	N	21.94	21.83
HOAc	408[b]	105	$C_{15}H_{10}N_4O_3$	61.23	61.59	3.40	3.15			
HOAc	579[b]	250	$C_{16}H_{11}N_5O_2$[c]	59.15	58.93	4.12	4.09	N	19.18	18.57
HOAC	562[b]	248	$C_{16}H_{10}N_4O_3$	62.75	62.87	3.27	3.64	N	18.30	17.71
CH_2Cl_2–ether	538	235	$C_{19}H_{18}N_2O_4S$	61.59	61.36	4.90	4.96	N	7.57	7.70
CH_2Cl_2–ether	537	225	$C_{20}H_{20}N_2O_4S$	62.46	62.65	5.25	5.38	N	7.29	7.28
CH_2Cl_2–MeOH	545	233	$C_{25}H_{22}N_2O_4S$	67.22	67.12	4.97	5.00	S	7.19	6.95
CH_2Cl_2–MeOH	548	244	$C_{24}H_{19}ClN_2O_4S$	61.71	61.23	4.10	4.18	Cl	7.60	7.32
CH_2Cl_2–ether	545	240	$C_{25}H_{21}ClN_2O_4S$	62.41	62.46	4.39	4.46	S	6.67	6.73
CH_2Cl_2–ether	548	248	$C_{28}H_{26}N_2O_6S$	64.84	64.91	5.06	5.31	S	6.19	6.11
CH_2Cl_2–ether	552	226	$C_{25}H_{23}N_3O_6S_2$	57.10	57.21	4.41	4.75	S	12.21	12.05
CH_2Cl_2–MeOH	557	256	$C_{26}H_{25}N_3O_6S_2$	57.87	58.29	4.67	4.94	S	11.88	11.75
CH_2Cl_2–MeOH	515	225	$C_{29}H_{24}ClN_3O_6S$	60.24	60.57	4.17	4.42	Cl	6.14	5.96
CH_2Cl_2–MeOH	443	60	$C_{27}H_{21}N_2O_5S$[d]	62.49	62.41	4.97	4.85	S	5.86	5.94
CH_2Cl_2–ether	597	264	$C_{30}H_{31}N_3O_4S$	68.01	67.86	5.90	6.29	N	7.94	7.69
CH_2Cl_2–ether	395	59	$C_{18}H_{16}N_2O_4S$	60.64	60.63	4.52	4.76	S	9.00	8.91
CH_2Cl_2–MeOH	400	65	$C_{24}H_{20}N_2O_4S$	66.63	66.81	4.66	4.74	S	7.43	7.30
CH_2Cl_2–ether	546	295	$C_{13}H_{13}NO_5S$	52.85	52.97	4.44	4.44	S	10.86	10.86
CH_2Cl_2–ether	547	292	$C_{14}H_{15}NO_5S$	54.33	53.92	4.89	5.00	S	10.37	10.31
CH_2Cl_2–ether	546	295	$C_{16}H_{19}NO_5S$	56.93	57.23	5.68	5.55	S	9.51	9.52
CH_2Cl_2–ether	553	290	$C_{19}H_{17}NO_6S$	61.43	61.05	4.62	4.79	S	8.63	8.45
CH_2Cl_2–ether	555	318	$C_{18}H_{14}ClNO_5S$	55.15	55.44	3.59	3.68	Cl	9.05	9.05
CH_2Cl_2–ether	636	475	$C_{28}H_{25}ClN_2O_5S$	62.60	62.62	4.70	4.75	Cl	6.61	6.92
CH_2Cl_2–ether	536	338	$C_{19}H_{14}N_2O_5S$	59.65	59.73	3.69	3.67	N	7.33	7.59
CH_2Cl_2–ether	552	308	$C_{20}H_{18}N_2O_6S$	57.94	57.78	4.38	4.31	N	6.76	6.77
CH_2Cl_2–ether	565	336	$C_{18}H_{14}N_2O_7S$	53.70	53.88	3.51	3.72	N	6.97	6.46

1.0 g. of finely powdered sodium cyanide was added during the course of 5 min. The reaction mixture was stirred and heated for an additional 35 min. The reaction mixture was diluted with ice and petroleum ether (b.p. 30–60°) and the precipitate was collected and washed with water and petroleum ether. The filter cake was dissolved in methylene chloride, the solution was dried with anhydrous magnesium sulfate, the filtrate was concentrated to a small volume, and anhydrous ether was added. The crystalline material was collected and recrystallized two additional times as previously described from methylene chloride–ether. The yield of purple powder, m.p. 223–225°, was 0.5 g. (16%); $\lambda_{max}^{CH_2Cl_2}$ 545 mμ (ε 29,000).

Anal. Calcd. for $C_{19}H_{15}N_3O_2$: C, 71.80; H, 4.77; N, 13.25. Found: C, 72.28; H, 5.09; N, 13.72.

4-(2-(4-Toluenesulfonyl)-N-phenyl-3-maleimidyl)-N,N-dimethylaniline. A. *From dichloro-N-phenylmaleimide.* Finely powdered anhydrous sodium *p*-toluenesulfinate (1.8 g.) was added in small portions to a stirred suspension of 2.4 g. of dichloro-*N*-phenylmaleimide in 15 ml. of dimethylformamide and 2.4 g. of *N,N*-dimethylaniline. After stirring at 25–35° for 10 min., the reaction mixture was diluted with petroleum ether and ice water and the gummy precipitate was collected. The gummy reaction product was stirred with a small amount of methanol whereupon a crystalline material was obtained. Crystallization from methylene chloride-ether gave 3.2 g. (71%) of glistening greenish-black plates, m.p. 198–200°; $\lambda_{max}^{CH_2Cl_2}$ 541 mμ (ε 23,600).

Anal. Calcd. for $C_{25}H_{22}N_2O_4S$: C, 67.23; H, 4.97; N, 6.28. Found: C, 67.20; H, 5.17; N, 6.56.

B. *From dibromo-N-phenylmaleimide.* The condensation of 0.33 g. of dibromo-*N*-phenylmaleimide, 1 g. of *N,N*-dimethylaniline, and 0.2 g. of sodium *p*-toluenesulfinate in 5 ml. of dimethylformamide was carried out essentially as described in the above preparation. The yield of glistening, greenish-black plates, m.p. 198–200°, alone or in admixture with the above sample, was 0.25 g. (56%); $\lambda_{max}^{CH_2Cl_2}$ 541 mμ (ε 23,600).

C. *From 2-(4-dimethylaminophenyl)-3-(4-toluenesulfonyl)-maleic anhydride.* Five grams of aniline was added to 0.19 g. of 2-(4-dimethylaminophenyl)-3-(4-toluenesulfonyl)maleic anhydride and the resulting mixture was stirred at room temperature for 5 min. The color of the reaction mixture changed from deep purple to light brown during this period, probably as a result of the formation of the maleanilic acid. The excess aniline was distilled from the reaction mixture at 1 mm. with a bath temperature of 75°. The resulting deep purple solid was dissolved in 20 ml. of glacial acetic acid and the resulting deep magenta solution was refluxed for 5 min. The acetic acid was removed by distillation under reduced pressure from a bath at 60° and the crystalline residue was stirred with cold water. Crystallization from methylene chloride–ether gave 0.2 g. (90%) of 4-(2-(4-toluenesulfonyl)-*N*-phenyl-3-maleimidyl)-*N*,*N*-dimethylaniline as glistening greenish-black crystals, m.p. 198–200°, alone or in admixture with a sample of the compound obtained from dichloro-*N*-phenylmaleimide, *N*,*N*-dimethylaniline, and sodium *p*-toluenesulfinate; $\lambda_{max}^{CH_2Cl_2}$ 541 mμ (ε 23,300).

1,1-Bis(4-dimethylaminophenyl)-2-(2-methanesulfonyl-N-phenyl-3-maleimidyl)ethylene. Sodium methanesulfinate (1.2 g.) was added to a mechanically stirred solution of 1.2 g. of dichloro-*N*-phenylmaleimide and 1.3 g. of 1,1-bis(4-dimethylaminophenyl)ethylene in 10 ml. of dimethylformamide. After stirring for 5 min. at 25–30°, the deep blue reaction mixture was diluted with water and ice. The crystalline product was collected, washed, and dried. Two recrystallizations from methylene chloride–ether gave 1.3 g. (51%) of deep purple, felt-like needles, m.p. 196–198°; $\lambda_{max}^{CH_2Cl_2}$ 595 mμ (ε 26,600).

Anal. Calcd. for $C_{29}H_{29}N_3O_4S$: C, 67.53; H, 5.67; S, 6.22. Found: C, 67.78; H, 5.78; S, 6.04.

2-(4-Dimethylaminophenyl)-3-(4-toluenesulfonyl)maleic anhydride. A. *From dichloromaleic anhydride.*[7] A solution of 5.0 g. of dichloromaleic anhydride in 30 ml. of dimethylformamide was cooled to 15° and 7.2 g. of *N*,*N*-dimethylaniline was added. Finely powdered anhydrous sodium *p*-toluenesulfinate (5.4 g.) was added in small portions with stirring at 20–25° during the course of 2 min. Stirring was continued for an additional 5 min. during which time the reaction product separated in crystalline form. The reaction mixture was diluted with water and petroleum ether, and the crystals filtered off. The filter cake was washed with cold water and then petroleum ether. The crude product was dissolved in methylene chloride, the methylene chloride solution was dried with anhydrous magnesium sulfate, concentrated to a small volume, and anhydrous ether added. The compound crystallized almost immediately in the form of black needles. After cooling, the needles were collected, washed with ether, and, after drying, weighed 8 g. (72%), m.p. 182–184°; $\lambda_{max}^{CH_2Cl_2}$ 552 mμ (ε 30,800).

Anal. Calcd. for $C_{19}H_{17}NO_5S$: C, 61.43; H, 4.62; N, 3.77. Found: C, 61.87; H, 4.80; N, 3.84.

B. *From dibromomaleic anhydride.*[7] The condensation of 2.56 g. of dibromomaleic anhydride, 2.4 g. of *N*,*N*-dimethylaniline, and 1.8 g. of sodium *p*-toluenesulfinate in 10 ml. of dimethylformamide essentially as described above gave 1.2 g. (32%) of black needles, m.p. 182–184°, alone or in admixture with the above preparation.

C. *From difluoromaleic anhydride.*[8] The condensation of 1.34 g. of difluoromaleic anhydride, 2.4 g. of *N*,*N*-dimethylaniline, and 1.8 g. of sodium *p*-toluenesulfinate essentially as described in the above preparation gave 0.2 g. (5%) of black needles, m.p. 182–184°, alone or in admixture with a sample of the compound prepared from dichloromaleic anhydride.

4,4-Bis(4-dimethylaminophenyl)-1-(4-toluenesulfonyl)-1,3-butadiene-1,2-dicarboxylic anhydride (X). Sodium *p*-toluenesulfinate (0.18 g.) was added in small portions to a stirred solution of 0.27 g. of 1,1-bis(4-dimethylaminophenyl)ethylene and 0.17 g. of dichloromaleic anhydride in 10 ml. of dimethylformamide at 25°. After stirring for an additional period of 5 min., the reaction mixture was diluted with ice water, and the crude material was collected and crystallized twice from methylene chloride–ether. The yield of glistening, bronze crystals was 0.45 g. (87%), m.p. 208–210°; $\lambda_{max}^{CH_2Cl_2}$ 630 mμ (ε 40,800).

Anal. Calcd. for $C_{29}H_{28}N_2O_5S$: C, 67.40; H, 5.47; N, 5.43; S, 6.21. Found: C, 67.57; H, 5.79; N, 5.62; S, 6.11.

2-(4-Toluenesulfonyl)-3-(1,3,3-trimethyl-2-methylene-5-indolinyl)maleic anhydride (XI). Five grams of dichloromaleic anhydride and 5.3 g. of sodium *p*-toluenesulfinate were added at approximately equivalent rates to a stirred solution of 5.2 g. of 2-methylene-1,3,3-trimethylindoline in 80 ml. of dimethylformamide at 5°. The resulting deep brown solution was stirred at 5° for an additional period of 15 min. and then diluted with ice and water. The resulting gummy precipitate was dissolved in methylene chloride, the solution was dried with anhydrous magnesium sulfate and was concentrated to a small volume. The addition of anhydrous ether precipitated nearly black crystals whereas the mother liquor was deep red. The crystalline material was collected and washed with ether. Crystallization from methylene chloride–ether was repeated until the mother liquor was free of the red compound. The yield of blue compound, m.p. 104–106°, was 2.7 g. (19%); $\lambda_{max}^{CH_2Cl_2}$ 650 mμ (ε 25,000). The infrared spectrum showed absorption at 3.3 μ (=CH), 5.55, 5.65 μ (anhydride carbonyls), 5.95 μ (exocyclic =CH_2), 7.2, 7.3 μ (*gem*-dimethyl) and 7.7, 8.75 μ (sulfone).

Anal. Calcd. for $C_{23}H_{21}NO_5S$: C, 65.21; H, 5.00; N, 3.31; S, 7.58. Found: C, 64.46; H, 5.06; N, 3.39; S, 7.23.

2-(4-Toluenesulfonyl)-3-[(1,3,3-trimethyl-2-indolinyl)methylene]maleic anhydride (XII). The reddish-blue mother liquors from the above preparation were treated with decolorizing charcoal whereupon a bright red ethereal solution of the second compound was obtained. The ethereal solution was concentrated to a small volume and cooled in a solid carbon dioxide–acetone mixture whereupon bright red crystals were obtained. Two additional crystallizations from ether gave 0.8 g. (6%) of bright red crystals, m.p. 110–112°; $\lambda_{max}^{CH_2Cl_2}$ 505 mμ (ε 31,000). The infrared spectrum showed absorption at the same values as listed above expect that there was no absorption in the exocyclic =CH_2 region around 5.95 mμ.

Anal. Calcd. for $C_{23}H_{21}NO_5S$: C, 65.21; H, 5.00; N, 3.31; S, 7.58. Found: C, 65.59; H, 5.40; N, 3.35; S, 7.34.

3-Formyl-2-(4-toluenesulfonyl)-5,5-bis(4-dimethylaminophenyl)-2,4-pentadienoic acid. The condensation of 2.66 g. of 1,1-bis(4-dimethylaminophenyl)ethylene, 2.42 g. of mucobromic acid, and 1.8 g. of sodium *p*-toluenesulfinate in 20 ml. of dimethylformamide at 50° gave 2 g. (39%) of nearly black powder, m.p. 115–117°, $\lambda_{max}^{CH_2Cl_2}$ 520 mμ (ε 12,400), after crystallization from a mixture of methylene chloride–ether–methanol.

Anal. Calcd. for $C_{29}H_{30}N_2O_5S$: C, 67.14; H, 5.83; N, 5.41; S, 6.19. Found: C, 67.56; H, 6.11; N, 5.87; S, 5.61.

Preparation of N-substituted dibromo- and dichloromaleimides (Table II). The *N*-substituted dibromo- and dichloromaleimides can be prepared by the condensation of the appropriate primary amine and the dihalomaleic anhydride in an inert solvent such as ether or methylene chloride to give the maleamic acid followed by treatment with thionyl chloride to effect ring closure. However, a more convenient method consists in the condensation of the halogenated maleic anhydride and the primary amine in glacial acetic acid solution, as disclosed in a recent publication[9] without

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[7] A. Salmony and H. Simonis, *Ber.*, **38**, 2583 (1905).

[8] M. S. Raasch, R. E. Miegel, and J. E. Castle, *J. Am. Chem. Soc.*, **81**, 2678 (1959).

TABLE II

PREPARATION OF *N*-SUBSTITUTED DIBROMO- AND DICHLOROMALEIMIDES

N-Substituent	Yield, %	M.P.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found
CH_2CH_2OH	75	100–101	$C_6H_5Cl_2NO_3$	34.29	34.22	2.40	2.51	33.78	33.86
C_6H_5	87	204–206	$C_{10}H_5Cl_2NO_2$	49.59	49.96	2.13	2.26	29.30	29.47
C_6H_5	80	166–168	$C_{10}H_5Br_2NO_2$	36.25	36.47	1.52	1.78	48.31[a]	48.62[a]
C_6H_{11}(cyclo)	70	140–142	$C_{10}H_{11}Cl_2NO_2$	48.39	48.91	4.47	4.53	28.60	28.46
C_6H_5Cl-4	85	191–194	$C_{10}H_4Cl_3NO_2$	43.41	43.55	1.46	1.87	38.49	38.07
$C_6H_3Cl_2$,3-4	93	206–208	$C_{10}H_3Cl_4NO_2$	38.60	38.79	0.97	1.13	45.62	45.82
$C_6H_4CH_3$-4	89	192–194	$C_{11}H_7Cl_2NO_2$	51.57	51.29	2.76	2.80	28.05	27.59
$C_6H_4OCH_3$-4	74	206–207	$C_{11}H_7Cl_2NO_3$	48.54	49.06	2.59	2.73	26.07	25.95
CH_2COOH	69	196–197	$C_6H_3Cl_2NO_4$	32.14	32.39	1.35	1.56	31.66	31.25
C_6H_4COOH-2	91	237–239	$C_{11}H_5Cl_2NO_4$	46.16	46.46	1.76	1.78	24.80	24.07
C_6H_4COOH-3	92	289–290	$C_{11}H_5Cl_2NO_4$	46.16	46.12	1.76	1.87	24.80	24.16
C_6H_4COOH-4	91	>305	$C_{11}H_5Cl_2NO_4$	46.16	45.96	1.76	1.93	24.80	24.35
C_6H_4-$COOC_2H_5$-4	77	197–200	$C_{13}H_9Cl_2NO_4$	49.68	49.52	2.89	2.83	22.58	22.58
C_6H_4-SO_2NH_2-4	94	>300	$C_{10}H_6Cl_2N_2O_4S$	37.38	37.87	1.88	2.02	22.09	21.91
NHC_6H_5[b]	80	173–175	$C_{10}H_6Cl_2N_2O_2$	46.69	46.68	2.35	2.32	27.60	27.43
$NHO_2SC_6H_4CH_3$-4	71	164–166	$C_{11}H_8Cl_2N_2O_4S$	39.39	39.24	2.41	2.68	21.16	21.02
C_6H_3Cl-2-$COOCH_3$-5	84	156–157	$C_{12}H_6Cl_3NO_4$	43.05	43.45	1.81	1.93	31.81	31.55
$C_6H_3CH_3$-2-$COOCH_3$-5	82	121–122	$C_{13}H_9Cl_2NO_4$	49.68	50.05	2.89	2.77	22.58	22.54

[a] Bromine analysis. [b] Maleimide structure based on infrared spectrum with carbonyl absorptions at 5.55 μ and 5.75 μ. Dichloro-*N*-phenylmaleimide had similar infrared spectrum.

details. The procedure used to prepare the *N*-substituted dihalomaleimides consisted in the addition of 0.1 mole of the amino compound in 25–30 ml. of glacial acetic acid to a solution of 0.1 mole of the dihalomaleic anhydride in 50–75 ml. of glacial acetic acid at room temperature. The temperature was gradually increased to reflux and the refluxing was continued for 15–30 min. In most cases the *N*-substituted dihalomaleimide separated in crystalline form during the reflux period or on cooling. Sometimes it is necessary to dilute the cooled reaction mixture with water to obtain the maleimide. All of the maleimides in Table II were converted to colored maleimide derivatives, representative examples of which are listed in Table I.

WILMINGTON, DEL.

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(9) Imperial Chemical Industries Ltd., Australia. Application **33,896** (1958).

[CONTRIBUTION FROM THE CHEMISTRY RESEARCH LABORATORY OF THE DEPARTMENT OF SURGERY, UNIVERSITY OF WASHINGTON, SCHOOL OF MEDICINE]

Derivatives of Fluorene. XIV. *N*-(Ring)-Fluorenylmaleimides[1]

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A series of *N*-(ring)-fluorenylmaleamic acids and maleimides is reported and some sulfhydryl addition compounds with the latter. Substituents with differing electron withdrawing or donor properties, it is speculated, might lead to compounds with differing biological activities. *N*-2-(7-Fluorofluorenyl)isomaleimide was produced in equal quantity with the normal maleimide in a standard cyclization procedure. No other instance of isomaleimide formation was observed. Infrared and ultraviolet spectral data are included and discussed. Solutions of at least some of these substances are unstable in absolute ethanol.

N-Fluorenylmaleimides and the corresponding maleamic acids have not been described in the literature. In a program developing many series of fluorene derivatives which might have interesting biological properties, we have prepared a number of maleimides[2] and maleamic acids with electron donor or withdrawing groups in various positions on the molecule. It seemed likely that such changes would give a series of compounds with differences, for example, in ease of reaction with sulfhydryl compounds. Alteration of biological activity might thus result.[3]

In general, procedures were standard and yields excellent. Typical reactions are illustrated in the experimental section. Table I lists products and analyses. *N*-2-(7-Fluorofluorenyl)maleamic acid was cyclized in the usual way to yield approximately equal quantities of normal maleimide and isomale-

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[2] A series of *N*-(9-fluorenyl)maleimides will be described shortly in a separate communication.

[3] Upon finding that injection of a small amount of *N*-ethylmaleimide, as suggested by its *in vitro* effect, suppresses gastric secretion in the Shay rat, we tried several other maleimides including *N*-2-fluorenylmaleimide. The latter was fully as depressant on a mole basis as *N*-ethylmaleimide: T. L. Fletcher, H. L. Buchman, A. W. Dahl, J. E. Jesseph, and H. N. Harkins, *J. Med. Pharm. Chem.*, **1**, 275 (1959).