pure product; m.p. 140–142°. The combined yield was 8.1 g. (94%). Recrystallization from 30% ethanol provided small colorless needles, m.p. 142–144°.

In some of the other preparations, the ester dissolved readily in the amine and no additional solvent was used. Heating on the steam-bath was employed with higher boiling and less reactive amines. These modifications are illustrated by the preparation of two diastereoisomers of **N-(2-acetoxyisopropyl)-1,4-benzodioxan-2-carboxamide** (compds. 8 and 9). A solution of 15 g. of I in 50 ml. of 2-amino-1-propanol was heated on the steam-bath for 2.5 hours, then allowed to stand at room temperature for five days. Excess aminopropanol was evaporated under reduced pressure. The thick oily residue, which could not be distilled without decomposition, was dissolved in 150 ml. of pyridine. The solution was treated with 80 ml. of acetic anhydride, gently heated on the steam-bath for 1.5 hours, cooled and poured into 500 ml. of ice-water. The mixture of diastereoisomers separated as a colorless crystalline solid; yield 15 g., m.p. 90–96°. It was recrystallized twice from benzene–ligroin, then once from aqueous ethanol to yield 4.8 g. (24%) of colorless short needles, m.p. 105–106°. Evaporation of the first benzene–ligroin mother liquor left a colorless solid melting at *ca.* 75°, which was recrystallized once from aqueous ethanol, then once from benzene–ligroin, providing 3.7 g. (18%) of the second isomer as colorless clusters of needles, m.p. 78–79°.

Compound 6 could not be crystallized and was purified by vacuum distillation. Some of the basic acids (compd. 7 and 11) were isolated as the hydrochlorides by saturating their solutions in anhydrous ether with dry hydrogen chloride and recrystallizing the salts from absolute ethanol–ether.

Method B.—The preparation of **N-ethyl-N-(β-diethylcarbamyl)-ethyl-1,4-benzodioxan-2-carboxamide** (compd. 12) serves to illustrate the acylation of secondary amines. Ten grams of 1,4-benzodioxan-2-carbonyl chloride (IV) in 50 ml. of methylene chloride was added slowly with stirring to 20 g. of N,N-diethyl-β-ethylaminopropionamide in 50 ml. of methylene chloride. The mixture was refluxed for two hours, evaporated under reduced pressure, and the residue added to dilute hydrochloric acid. The oil was extracted with ether, which was then washed with water and sodium bicarbonate solution, dried and evaporated. The oily product distilled at 190–192° (0.3 mm.); yield 11 g. (65%).

Method C.—This modification of method B was employed with aromatic and heterocyclic amines. It is illustrated by the preparation of **N-(2-pyridyl)-1,4-benzodioxan-2-carboxamide** (compd. 20). To a stirred solution of 12 g. of 2-aminopyridine in 150 ml. of boiling dry benzene was added 11.8 g. of IV in 50 ml. of benzene dropwise over one hour. The mixture was stirred and refluxed for another two hours, allowed to stand overnight and treated with cold water to dissolve the precipitated amine salt. The benzene layer was separated, washed with 50 ml. of 5% sodium bicarbonate solution, then with 50 ml. of 5% hydrochloric acid, and finally with 50 ml. of water, dried over magnesium sulfate and evaporated. The yield of pale yellow solid residue, m.p. 80–83°, was 11 g. (72%). Recrystallization from benzene–ligroin then 60% ethanol afforded small colorless needles, m.p. 84–86°.

Method D.—None of the preceding methods was successful in attempted preparations of **N-(2-benzimidazolyl)-1,4-benzodioxan-2-carboxamide** (compd. 26), which was therefore synthesized as follows: To a solution of 5.32 g. of 2-aminobenzimidazole in 80 ml. of dry pyridine was added with stirring and cooling in ice 8 g. of the acid chloride IV in small portions over one hour. The ice-bath was removed and stirring continued at room temperature for one hour, then with gentle heating on the steam-bath for 0.5 hour. The mixture was kept overnight, poured into 250 ml. of ice-water, and the colorless precipitate collected, washed with small portions of ice-water and dried at 60°; yield 10.7 g. (91%), m.p. 222–224°. Recrystallization from aqueous pyridine provided the analytical sample, m.p. 224–225°.

PHILADELPHIA 44, PA.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

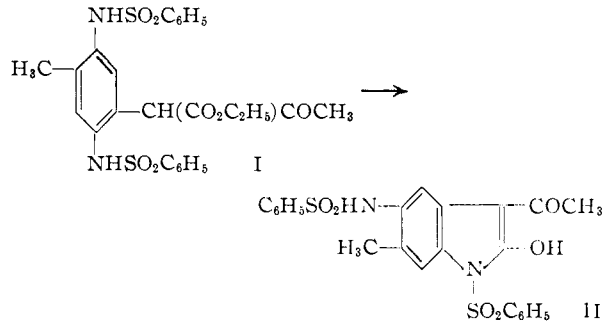
Quinone Imides. XXXVII. Conversion of *p*-Quinone Diimides to Indoles

BY ROGER ADAMS AND WILLIAM P. SAMUELS, JR.[1]

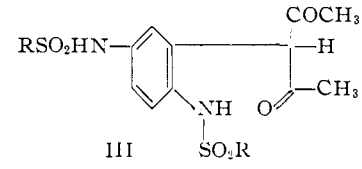
RECEIVED APRIL 13, 1955

Active methylene compounds have been added to several *p*-quinonebis-(dimethylsulfamiimides) and 1,4-naphthoquinonebis-(dimethylsulfamimide). Treatment of the resulting substituted diamides with 48% hydrobromic or 22% hydrochloric acid under reflux or cold concentrated sulfuric acid converts them to indoles.

The addition of active methylene compounds and in particular of β-diketones and β-ketoesters to quinone diimides has been studied previously.[2] However, the only reported cyclization of a compound of this type is the conversion of ethyl α-[2,5-dibenzenesulfonamido-4(?)-methylphenyl]-acetoacetate (I) to 3-acetyl-5-benzenesulfonamido-6(?)-methyloxindole (II) by heating it above its melting point; ring closure occurred with the loss of a molecule of ethanol.[2c] Examination of an active methylene adduct such as III reveals that by elimination of a molecule of water an indole derivative might result. If the 1-sulfonamido group of III were hydrolyzed to the amino group, the resulting aromatic amine would be of the type that previously has been demonstrated to cyclize readily to an indole.



This communication describes the results of experiments on the formation of indoles from such diamides.



(1) An abstract of a thesis submitted by William P. Samuels, Jr., to the Graduate College of the University of Illinois, 1955, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy; Standard Oil of California Fellow, 1952–1954.

(2) (a) R. Adams and W. Moje, THIS JOURNAL, **74**, 5557 (1952); (b) R. Adams and D. S. Acker, *ibid*, **74**, 5872 (1952); (c) R. Adams and D. C. Blomstrom, *ibid.*, **75**, 3403 (1953).

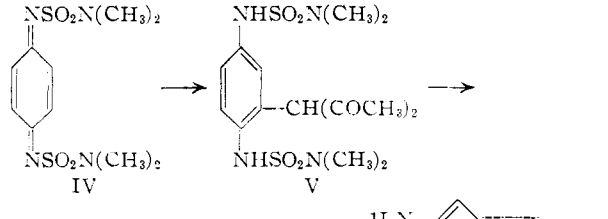
TABLE I

ADDUCTS OF ACTIVE METHYLENE COMPOUNDS AND QUINONE DIIMIDES

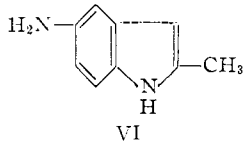
Adduct to quinone diimide IV	Crude yield, %	Pure m.p., °C.	Empirical formula	Analyses, % Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
Acetylacetone	100	197.5–198.5[a]	$C_{16}H_{24}N_4O_6S_2$	42.84	5.75	13.32	43.09	5.73	13.32
Benzoylacetone	100	173–175[b]	$C_{20}H_{26}N_4O_6S_2$	49.78	5.43	11.61	50.05	5.32	11.36
Ethyl acetoacetate	98	149.5–151.5[c]	$C_{16}H_{26}N_4O_7S_2$	42.65	5.82	12.43	42.34	5.77	12.68
Ethyl benzoylacetate	100	128–130[d]	$C_{21}H_{28}N_4O_7S_2$	49.20	5.51	10.93	48.90	5.33	10.59
Dibenzoylmethane	97	196.5–198[d]	$C_{25}H_{28}N_4O_6S_2$	55.13	5.18	10.29	55.34	5.30	10.55
2-Carbethoxycyclohexanone	98	143–145[e]	$C_{19}H_{30}N_4O_7S_2$	46.51	6.16	11.42	46.79	5.84	11.22
2-Carbethoxy-5-methylcyclohexanone	100	160–162[e]	$C_{20}H_{32}N_4O_7S_2$	47.60	6.39	11.13	47.72	6.64	11.23
2-Carbethoxycyclopentanone	94	155–156[c]	$C_{18}H_{28}N_4O_7S_2$	45.36	5.92	11.76	45.15	6.13	11.90
Adduct to 2-azido deriv. of IV									
Acetylacetone	97.5	140–171 d.[a]	$C_{15}H_{23}N_7O_6S_2$	39.04	5.02	21.25	39.33	5.14	21.11
Adduct to 2-benzenesulfonyl deriv. of IV									
Acetylacetone	90	187–188.5[c]	$C_{21}H_{28}N_4O_8S_3$	44.96	5.03	9.99	45.06	5.01	9.71
Adducts to 2-chloro deriv. of IV									
Acetylacetone	98	203.5–205.5[a]	$C_{15}H_{23}ClN_4O_6S_2$	39.60	5.10	12.32	39.86	5.05	12.06
Dibenzoylmethane	100	193.5–195.5[b]	$C_{25}H_{27}ClN_4O_6S_2$	51.94	4.53	9.69	51.92	4.44	9.39
Ethyl benzoylacetate	74[f]	176–178[b]	$C_{21}H_{27}ClN_4O_7S_2$	45.94	5.32	10.20	46.27	5.21	10.01
2-Carbethoxycyclopentanone	97	153–156[b]	$C_{18}H_{27}ClN_4O_7S_2$	42.31	5.33	10.96	42.59	5.52	10.77
2-Carbethoxycyclohexanone	97.5	147–148[b]	$C_{19}H_{29}ClN_4O_7S_2$	43.46	5.57	10.67	43.63	5.66	10.44
2-Carbethoxy-5-methylcyclohexanone	95	185.5–187.5[b]	$C_{20}H_{31}ClN_4O_7S_2$	44.56	5.80	10.39	44.85	5.89	10.14
Adducts to 2,3-dichloro deriv. of IV									
Acetylacetone	90[f]	143–145[b]	$C_{15}H_{22}Cl_2N_4O_6S_2$	36.81	4.53	11.45	37.10	4.40	11.45
Ethyl benzoylacetate	100	200.5–201.5[b]	$C_{21}H_{26}Cl_2N_4O_7S_2$	43.22	4.84	9.60	43.37	4.72	9.85
Adducts to quinone diimide XXIV									
cetylacetone	100	195.5–197.5[b]	$C_{19}H_{26}N_4O_6S_2$	48.49	5.57	11.91	48.49	5.45	11.68
Ethyl acetoacetate	79[f]	139–141[b]	$C_{20}H_{28}N_4O_7S_2$	47.99	5.64	11.19	47.85	5.57	10.93
Ethyl benzoylacetate	99	206–207[d]	$C_{25}H_{30}N_4O_7S_2$	53.36	5.38	9.96	53.25	5.52	9.77

[a] Recrystallized from ethyl acetate. [b] From ethyl acetate–cyclohexane. [c] From chloroform–cyclohexane. [d] From ethanol. [e] From benzene–cyclohexane. [f] Once recrystallized.

Adams and Shafer[3] found that the dimethylsulfamamido group can be hydrolyzed readily with 48% hydrobromic acid or 22% hydrochloric acid and consequently *p*-quinonebis-(dimethylsulfamimide) (IV) was selected for use in this investigation. When the adduct V, formed from acetylacetone and IV, was treated with these reagents it was converted readily into 5-amino-2-methylindole (VI) in 29 and 86.5% yields, respectively. The indole VI was identified through its acetyl derivative and by its chemical and physical properties.

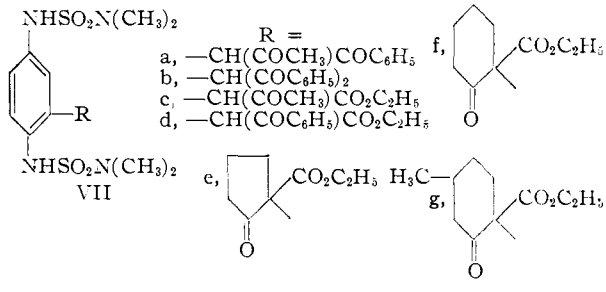


IV V



VI

To provide other diamides for conversion to indoles, benzoylacetone, dibenzoylmethane and the ethyl esters of acetoacetic, benzoylacetic, cyclopentanone-2-carboxylic, cyclohexanone-2-carboxylic and 5-methylcyclohexanone-2-carboxylic acids were added to the diimide IV (see Table I). All the products have the general structure VII.



VII

The addition of monosubstituted active methylene compounds to the diimide IV was in most cases unsatisfactory. Only the 2-carbethoxycycloalkanones added readily in good yield. Compounds such as ethyl *n*-butylacetoacetate, ethyl α-chloroacetoacetate and diethyl methylmalonate did not cause discharge of the color of the diimide solution and it therefore was assumed that no addition occurred. The reaction with 3-ethylpentane-2,4-dione gave an oil which could not be crystallized, but hydrolysis indicated addition had been effected.

With a substituent in the quinone nucleus of the *p*-quinone diimide, adducts of active methylene compounds were formed readily. The position of

(3) R. Adams and P. Shafer, THIS JOURNAL, **75**, 667 (1953).

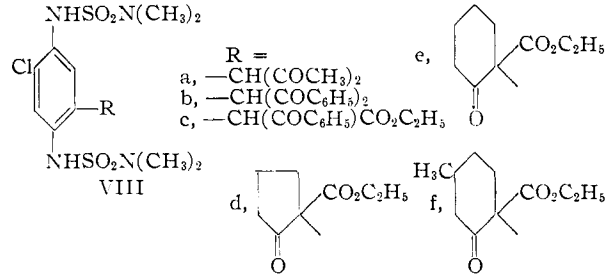
TABLE II

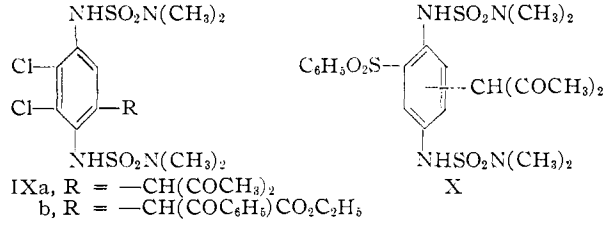
CONVERSION OF ACTIVE METHYLENE ADDUCTS TO INDOLES BY MEANS OF HYDROCHLORIC ACID

Active methylene adduct	Reflux, hr.[a]	Deriv. of 5-aminoindole	Crude yield, %	Pure m.p., °C.	Empirical formula	Analyses, % Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
V	2[b]		29								
V	4	2-Methyl-	86.5	157–159	$C_9H_{10}N_2$	73.91	6.96	19.17	73.97	6.90	10.13
VIIc	24	2-Methyl-	86.5								
VIIa	24	2-Methyl-	87								
VIId	7	2-Phenyl-	88.5	231.5–233	$C_{14}H_{12}N_2$	80.74	5.81	13.45	80.53	6.09	13.67
VIIf	12	6-Amino-1,2,3,4-tetrahydrocarbazole	79	152–154[d]	$C_{12}H_{14}N_2$	77.39	7.58		77.60	7.50	
VIIg	4	6-Amino-3-methyl-1,2,3,4-tetrahydrocarbazole	86.5	173–175	$C_{13}H_{16}N_2$	77.96	8.05	13.99	78.13	7.87	13.95
VIIIa	12	6(?)-Chloro-2-methyl-	71	196–197[c]	$C_9H_9ClN_2$	59.84	5.02	15.51	59.73	5.04	15.36
X	20	6(?)-Benzenesulfonyl-2-methyl-	55	188.5–190	$C_{15}H_{14}N_2O_2S$	62.91	4.93	9.79	63.01	4.88	9.49
IXa	4	6,7-Dichloro-2-methyl-	83.5	195.5–197.5	$C_9H_8Cl_2N_2$	50.26	3.75	13.03	50.47	3.70	13.17
IXb	89	6,7-Dichloro-2-phenyl-	55	176–178	$C_{14}H_{10}Cl_2N_2$	60.67	3.64	10.11	61.07	3.54	10.12

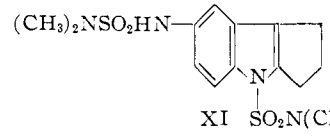
[a] Experiments were carried out with 22% hydrochloric acid under reflux. [b] Minutes; 48% hydrobromic acid was used in place of hydrochloric acid. [c] Purified by sublimation followed by recrystallization from anhydrous benzene. All other indoles were purified by sublimation. [d] Perkin and Plant, *J. Chem. Soc.*, 119, 1825 (1921), m.p. 152°.

the entering group was not established, but in most cases it is probably *para* to the ring substituent. Acetylacetone, dibenzoylmethane and the ethyl esters of benzoylacetic, cyclopentanone-2-carboxylic, cyclohexanone-2-carboxylic and 5-methylcyclohexanone-2-carboxylic acids were added to the 2-chloro diimide (general formula VIII); acetylacetone and ethyl benzoylacetate to the 2,3-dichloro diimide (general formula IX); and acetylacetone to the 2-benzenesulfonyl diimide X. Adducts could not be obtained from the 2,5-dichloro diimide. Single products in good yields usually were obtained. Only with the 2-azido diimide did the reaction lead to a mixture of isomeric adducts.

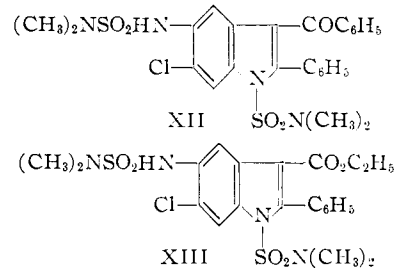




The character of the substituted indoles formed from the adducts was dependent on whether the cyclization was effected by 22% hydrochloric acid or by cold concentrated sulfuric acid. All the adducts described above except VIIb and VIIIe and f were subjected to the hydrochloric acid treatment. The cyclizations by this method usually were accompanied by the removal from the indole of both dimethylsulfamoyl groups and the substituent in the 3-position (acetyl, benzoyl or carbethoxy) (see Table II). However, several exceptions were found. In the cyclization of adduct VIIe neither dimethylsulfamoyl group was removed, only the carbethoxy group; 7-dimethylsulfamamido-4-dimethylsulfamoylcyclopent[b]indole (XI) was isolated in 63% yield. From adducts VIIIb and c



neither the dimethylsulfamoyl groups nor the substituent in the 3-position were removed; the indoles XII and XIII were isolated in yields of 88 and 84%, respectively.



Cold concentrated sulfuric acid proved to be a much milder reagent (see Table III). Its reaction was studied with adducts V, VIIb, d and e, and VIIIa, c, d. Cyclization occurred without removal of the 5-dimethylsulfamamido group or an acetyl or benzoyl group in the 3-position. On the other hand, the 1-dimethylsulfamoyl and a 3-carbethoxy group were replaced by hydrogen except with compounds VIIe, VIIId and XVII. The indoles XIV

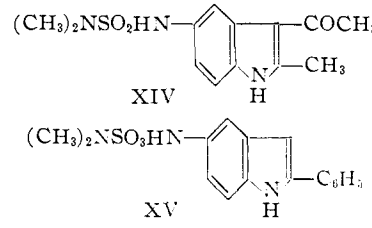


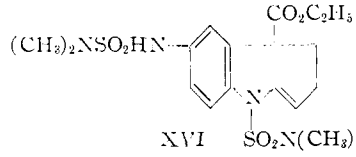
TABLE III

CONVERSION OF ACTIVE METHYLENE ADDUCTS TO INDOLES BY MEANS OF COLD CONCENTRATED SULFURIC ACID

Active methylene adduct	Deriv. of 5-dimethylsulfamamido-indole	Crude yield, %	Pure m.p., °C.	Empirical formula	Analyses, % Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
V	3-Acetyl-2-methyl-[c]	91	240.5–242.5[a]	$C_{13}H_{17}N_3O_3S$	52.86	5.80	14.23	52.94	5.96	14.05
VIIb	3-Benzoyl-2-phenyl-[c]	100	237–239[b]	$C_{23}H_{21}N_3O_3S$	65.85	5.05	10.02	65.82	5.34	9.95
VIId	2-Phenyl-	34.2	204.5–206.5[a]	$C_{16}H_{17}N_3O_2S$	60.93	5.44	13.32	60.85	5.42	13.12
VIIIa	3-Acetyl-6(?)-chloro-2-methyl-[e]	74	240–243[c]	$C_{13}H_{16}ClN_3O_3S$	47.34	4.89	12.74	47.35	4.84	13.06
VIIIc	6(?)-Chloro-2-phenyl-[g]	70	206.5–208.5[d]	$C_{16}H_{16}ClN_3O_2S$	54.93	4.61	12.01	55.04	4.58	12.14
VIIe	Ethyl $\Delta^{3(3a)}$-dehydro-3a,8b-dihydro-7-dimethylsulfamamido-4-dimethylsulfamoylcyclopent[b]-indole-8b-carboxylate[f]	90	187.5–189[a]	$C_{18}H_{26}N_4O_6S_2$	47.15	5.72	12.22	47.46	5.74	12.07
VIIId	Ethyl 6(?)-chloro-$\Delta^{3(3a)}$-dehydro-3a,8b-dihydro-7-dimethylsulfamamido-4-dimethylsulfamoylcyclopent[b]-indole-8b-carboxylate[f]	70	135.5–137.5[a]	$C_{18}H_{25}ClN_4O_6S_2$	43.85	5.11	11.37	43.94	5.11	11.52
XXVa	3-Acetyl-5-dimethylsulfamamido-2-methyl-3-benz[g]-indole[e]	93	234.5–237[a]	$C_{17}H_{19}N_3O_3S$	59.11	5.54	12.17	58.87	5.71	12.18

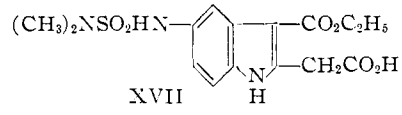
[a] Recrystallized from ethanol. [b] From benzene–ethanol. [c] From benzene–acetone. [d] From benzene–cyclohexane. [e] Infrared spectrum showed a C=O at 1615 to 1633 cm.$^{-1}$. [f] Infrared spectrum showed an unconjugated ester, C=O at 1728 cm.$^{-1}$; C—O at about 1150 cm.$^{-1}$; monosubstituted sulfonamide, NH at about 3270 cm.$^{-1}$, SO_2 at about 1368 and 1160 cm.$^{-1}$; disubstituted sulfonamide, SO_2 at about 1340 and 1145 cm.$^{-1}$. [g] The 5-dimethylsulfamamido group was resistant to hydrolysis with hydrochloric acid.

and XV were formed from adducts V and VIId, respectively. When VIIe was subjected to sulfuric acid treatment, ethyl $\Delta^{3(3a)}$-dehydro-3a,8b-dihydro-7-dimethylsulfamamido-4-dimethylsulfamoylcyclopent[b]indole-8b-carboxylate (XVI) was formed in 90% yield; similarly, VIIId was converted to the 6(?)-chloro derivative of XVI.



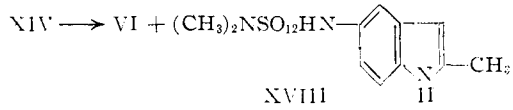
XVI

From the addition of diethyl β-ketoglutarate to the diimide IV only an oil resulted. When this oil was treated with concentrated sulfuric acid it gave 3-carbethoxy-5-dimethylsulfamamidoindole-2-acetic acid (XVII) in 54% yield. The relative positions of the carboxy and carbethoxy groups were determined by comparison of the infrared spectrum with those of known indole derivatives.



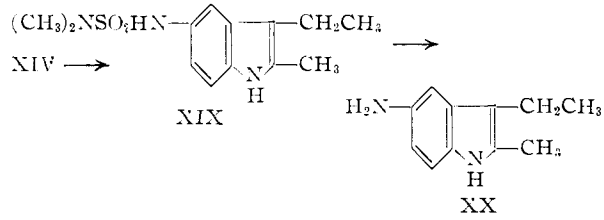
XVII

The structure assigned to XIV was deduced from its reactions. On treatment with 22% hydrochloric acid under reflux it was converted to 5-amino-2-methylindole (VI) and 5-dimethylsulfamamido-2-methylindole (XVIII) in yields of 42.5 and 55%,



XVIII

respectively. On reduction with lithium aluminum hydride in ether XIV was converted to 5-dimethylsulfamamido-3-ethyl-2-methylindole[4] (XIX) which gave 5-amino-3-ethyl-2-methylindole (XX) on hydrolysis with hydrochloric acid. Treatment with hydrochloric acid of the oil obtained from the addition of 3-ethylpentane-2,4-dione to the diimide IV also gave compound XX in 27% yield. This



product has been prepared previously by another route from *p*-nitrophenylhydrazine and methyl *n*-propyl ketone.[5]

5-Amino-2-methyl- and 5-amino-2-phenylindole were characterized through their acetyl derivatives. Ruggli and Grand[6] described 5-acetamido-2(or 3)-phenylindole formed by the reaction of phenacyl bromide with *p*-aminoacetanilide. The observed melting point of the 5-acetamido-2-phenylindole prepared in this investigation was essentially the same as that reported by Ruggli and Grand for their compound, thus establishing their product as probably the 2-phenyl derivative.

(4) E. Leete and L. Marion, *Can. J. Chem.*, **31**, 775 (1953), observed similar results. Indole-3-carboxylic acid, indole-3-aldehyde and ethyl indole-3-carboxylate gave skatole, and 3-acetylindole gave 3-ethylindole when reduced with lithium aluminun hydride in ether under mild conditions.

(5) E. Shaw and D. W. Woolley, THIS JOURNAL, **75**, 1877 (1953).

(6) P. Ruggli and R. Grand, *Helv. Chim. Acta*, **20**, 373 (1937).

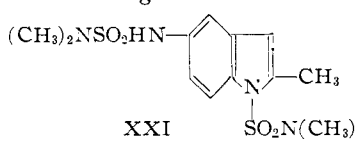
The ultraviolet absorption spectra of many of the indoles which were synthesized are shown in Table IV. The tricyclic system assigned to XI is supported by the similarity of its ultraviolet absorption spectrum to that of 5-dimethylsulfamamido-1-dimethylsulfamoyl-2-methylindole (XXI). In general the structures assigned to the indoles not specifically discussed are based primarily on elemental and infrared analysis.

TABLE IV

ULTRAVIOLET ABSORPTION SPECTRA OF SOME INDOLES IN ABSOLUTE ETHANOL[a]

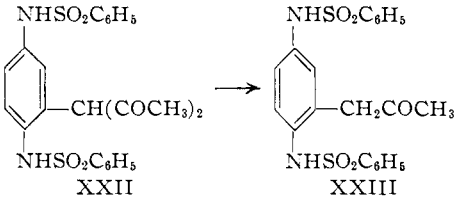
Indole	Maxima mμ	Maxima ε × 10⁻³	Minima mμ	Minima ε × 10⁻³
5-Amino-2-methyl-	214–215	28.2	252–253	6.1
	272–273	7.64		
	310 infl.	3.38		
5-Amino-6(?)-chloro-2-methyl-	212–213	29.3	256–257	3.45
	284–285	7.5		
	314 infl.	4.65		
5-Amino-6,7-dichloro-2-methyl-	226–227	33.6	257–258	3.9
	285–286	8.2		
	316 infl.	4.25		
5-Acetamido-2-methyl-	238–239	28.9		
	263 infl.	8.37		
	305–308 plat.	2.54		
5-Amino-2-phenyl-	230–231	23.8	272–273	7.3
	316–317	22.9		
5-Amino-6,7-dichloro-2-phenyl-	215–216	30.4	230–231	24.3
	236–237	25.5	285–286	6.8
	315–316	26.3		
5-Amino-3-ethyl-2-methyl-[b]	240–241	23.1	264–265	7.65
	276–277	8.54		
3-Acetyl-5-dimethylsulfamamido-2-methyl-	222–223	31.2	236–237	12.3
	246–247	15.3	262-263	10.8
	267–268	11.1	279–281	10.1
	296–297	12.5		
3-Benzoyl-5-dimethylsulfamamido-2-phenyl-	225–226	41.3		
3-Carbethoxy-6(?)-chloro-5-dimethylsulfamamido-1-dimethylsulfamoyl-2-phenyl-	227–228	45.7	257–258	8.7
	276–277	13.4		
3-Carbethoxy-5-dimethylsulfamamidoindole-2-acetic acid	227–228	37.6	262–263	5.14
	285–286	8.82		
5-Dimethylsulfamamido-1-dimethylsulfamoyl-2-methyl-	232–233	31.6	216–217	16.9
	255–262 plat.	10.6		
7-Dimethylsulfamamido-4-dimethylsulfamoylcyclopent[b]indole	234–235	33.3	216–217	12.3
	267–268	10.0	253–254	8.2
Ethyl $\Delta^{3(3a)}$-Dehydro-3a,8b-dihydro-7-dimethylsulfamamido-4-dimethylsulfamoylcyclopent[b]indole-8b-carboxylate	207–208	28.1	230	5.45
	247–248	12.8	273–274	0.62
	302–303	2.36		

[a] All determinations were made on 10^{-4} to 10^{-5} *M* solutions using a model 11 Cary recording spectrophotometer. [b] Ref. 5, maxima at 231–232 mμ (ε × 10^{-3} 24.7) and 284–286 mμ (ε × 10^{-3} 6.84), minimum at 260 mμ (ε × 10^{-3}, 3.74).



XXI

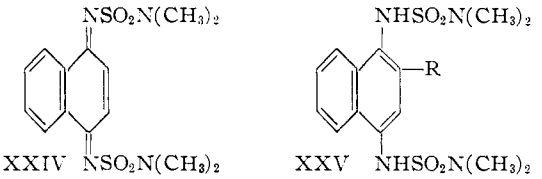
It is noteworthy that compound V also may be converted to an indole in the presence of alkali. Treatment of V with hot 5% aqueous sodium hydroxide led to the formation of XXI. The subsequent hydrolysis of XXI with hydrochloric acid gave 5-amino-2-methylindole (VI) in 89% yield. On the other hand, the corresponding acetylacetone adduct of *p*-quinonedibenzenesulfonimide (XXII) merely hydrolyzed under similar conditions to the acetone derivative XXIII.[3c]



XXII XXIII

The stability to hot hydrochloric acid of compounds XII and XIII was noted previously. Likewise 6(?)-chloro-5-dimethylsulfamamido-2-phenylindole was unaffected by this reagent since an attempt to convert it to the 5-amino derivative failed.

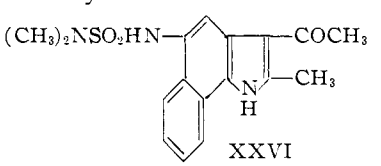
Active methylene compounds also have been added to 1,4-naphthoquinonebis-(dimethysulfamimide) (XXIV) which was prepared by the lead tetraacetate oxidation of the corresponding diamide.[7] Acetylacetone and the ethyl esters of acetoacetic and benzoylacetic acids added to XXIV to give XXVa, b and c, respectively. Attempted addition of 2-carbethoxycyclohexanone to XXIV merely caused reduction of the diimide.



XXIV XXV

R =
a, —CH(COCH3)2
b, —CH(COCH3)CO2C2H5
c, —CH(COC6H5)CO2C2H5

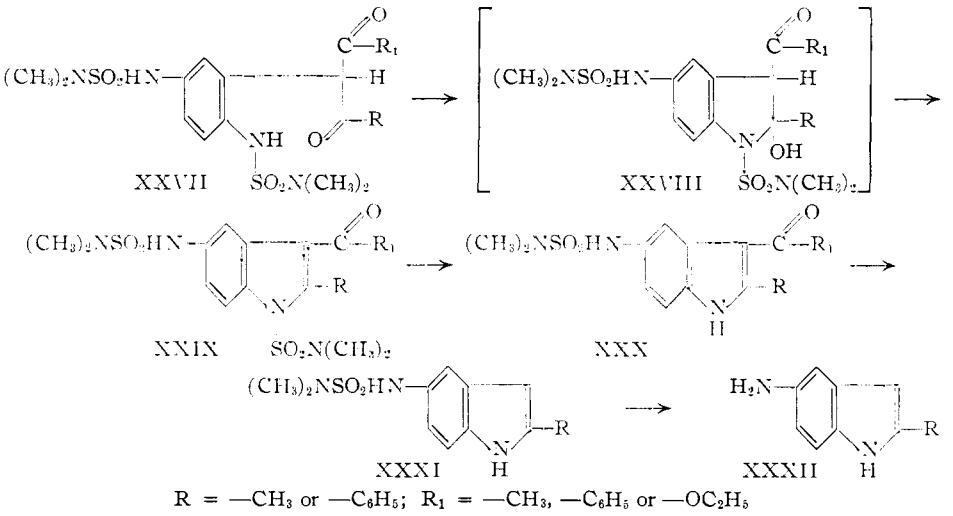
Several attempts to convert XXVa with hydrochloric acid to 5-amino-2-methyl-3-benz[g]indole were unsuccessful. Only an insoluble, high melting dark purple solid was obtained when treated under reflux; at steam-bath temperature the original product was recovered unchanged. Cold concentrated sulfuric acid, however, converted it to 3-acetyl-5-dimethylsulfamamido-2-methyl-3-benz[g]indole (XXVI). Adduct XXVc was resistant to the action of hydrochloric acid.



XXVI

The probable order of the individual reactions during the conversion of these adducts to amino indoles is shown in the scheme below (XXVII to XXXII). The evidence for this sequence is based on several of the cyclization and hydrolytic reactions which were observed. The intermediate XXVIII is similar to that usually postulated in the Fischer indole synthesis. Type XXIX is illustrated by compounds XII and XIII formed by the hydrochloric acid treatment of adducts VIIIb and VIIId, respectively; type XXX is illustrated by compound XIV, obtained from the sulfuric acid treatment of V, and

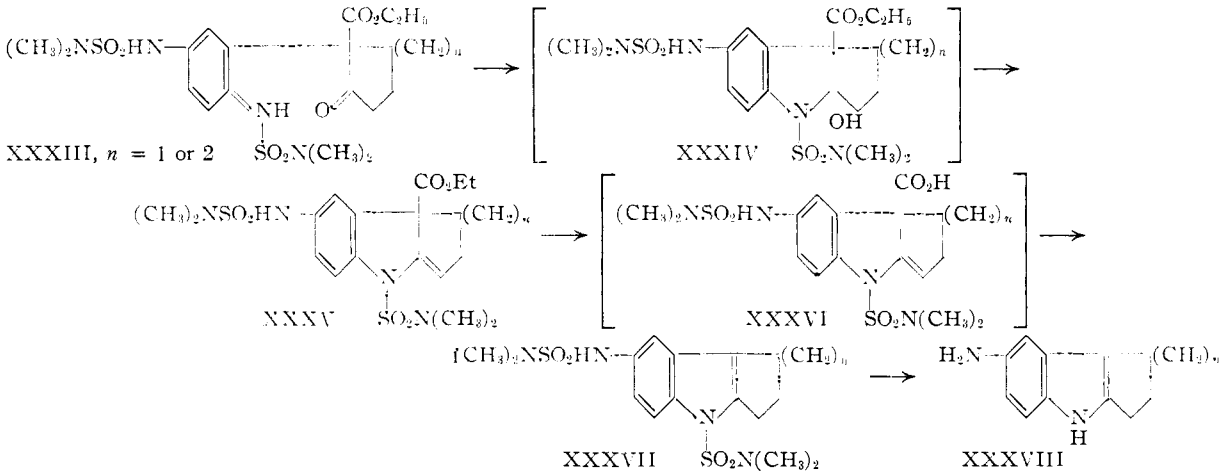
(7) R. Adams and J. Dunbar, unpublished work.



R = —CH_3 or —C_6H_5; R_1 = —CH_3, —C_6H_5 or —OC_2H_5

by compound XVII; type XXXI is illustrated by compound XVIII obtained from the hydrolysis of XIV with hydrochloric acid.

The cyclization and hydrolysis of adducts having no α-hydrogen atom, such as those of α-carbethoxycycloalkanones, may proceed by a somewhat modified route. The succession of reactions by which they may be converted to indoles is shown in the scheme below (XXXIII to XXXVIII). Type XXXV (n — 1) is illustrated by compound XVI formed by sulfuric acid treatment of VIIe; type XXXVII is illustrated by compound XI formed by the hydrochloric acid treatment of VIIe.



Acknowledgment.—The authors are indebted to Mr. Joseph Nemeth, Mrs. Lucy Chang and Mrs. Esther Fett for the microanalyses, to Mr. James Brader, Mrs. Louise Griffin and Miss Helen Miklas for the determination of the infrared absorption spectra, and to Miss Gerardine Meerman for the determination of the ultraviolet absorption spectra.

Experimental

All melting points are corrected. The infrared spectra were run in Nujol mulls using a Perkin–Elmer model 21 double beam spectrophotometer.

Addition of Active Methylene Compounds to *p*-Quinone Diimides. A. General Procedure.[8]—To a solution of 1.0 g. of the quinone diimide in the minimum quantity of anhydrous dioxane at room temperature was added 1.1 mole equivalents of re-distilled active methylene compound and about 40 mg. of sodium methoxide. After the orange color was discharged 6 drops of glacial acetic acid was added. The adducts formed by the addition of β-diketones were isolated most conveniently by pouring the reaction mixture with stirring into 300 ml. of water which causes the products to separate as white powders. The adducts formed by the addition of β-ketoesters were isolated by concentrating the reaction mixture to about 15 ml. in a stream of dry air followed by the addition of 100 ml. of petroleum ether (b.p. 30–60°). In most instances the product separated initially as an oil which crystallized after intermittent scratching. If the oil did not crystallize, the solvents were decanted and the oil recrystallized from the appropriate solvent. The constants of the products are shown in Table I.

The attempted addition of diethyl malonate, diethyl methylmalonate, ethyl n-butylacetoacetate, ethyl α-chloroacetoacetate, benzoylacetonitrile, diethyl succinosuccinate, methone, desoxybenzoin, cyclopentadiene, acetylene, ethyl 2-ketonipecotate, sodioformylacetone and 3-carbethoxy-1-methyl-4-piperidone to *p*-quinonebis-(dimethylsulfamimide) (IV), and 2-carbethoxycyclohexanone to 1,4-naphthoquinonebis-(dimethylsulfamimide) (XXIV) under the same experimental conditions resulted only in the isolation of *p*-phenylenebis-(dimethylsulfamamide), dark red oils and amorphous solids. The addition of acetylacetone to the 2,5-dichloro derivative of IV gave a red oil which could not be recrystallized. In these additions, the orange diimide solution became dark very gradually or faded to a pale orange.

Addition of Ethyl Benzoylacetate to 1,4-Naphthoquinonebis-(dimethylsulfamimide).—One drop of triethylamine was added to a solution of 0.1 g. of the diimide and 0.1 g. of

(8) Special conditions were used for addition of ethyl benzoylacetate to 1,4-naphthoquinonebis-(dimethylsulfamimide).

ethyl benzoylacetate in 15 ml. of anhydrous benzene. After standing for 48 hours the solution was colorless and white crystals had separated.

2-Azido-*p*-phenylenebis-(dimethylsulfamamide).—To a suspension of 0.5 g. of *p*-quinonebis-(dimethylsulfamimide) in 25 ml. of glacial acetic acid was added 0.51 g. of sodium azide dissolved in 2 ml. of water. The mixture was allowed to stand for 36 hours with intermittent shaking. At the end of this time the light brown solution was reduced to a volume of 10 ml. in a stream of dry air and diluted with 100 ml. of water. The light tan crystals that separated were collected by filtration and dried; 0.41 g. (72.7%). The product was recrystallized from chloroform–petroleum ether (b.p. 90–110°); light tan crystals, m.p. 152–153° dec.

Anal. Calcd. for $C_{10}H_{17}N_7O_4S_2$: C, 33.05; H, 4.71; N, 26.98. Found: C, 33.15; H, 4.94; N, 27.11.

The compounds containing the azido group are unstable to daylight; exposed samples decompose to dark colored crystals.

2-Azido-*p*-quinonebis-(dimethylsulfamimide).—To a suspension of 0.095 g. of the 2-azido diamide in 2 ml. of glacial acetic acid, 0.12 g. of lead tetraacetate was added. The solution immediately became red. After standing for 30 minutes 0.5 ml. of ethylene glycol was added. The reaction mixture was then cooled in an ice-bath and diluted with 6 ml. of water. After filtering and drying there was obtained 0.09 g. (95%) of orange solid which was purified by recrystallization from ethyl acetate–cyclohexane; m.p. 120–122° dec.

Anal. Calcd. for $C_{10}H_{15}N_7O_4S_2$: C, 33.23; H, 4.18; N, 27.13. Found: C, 33.47; H, 4.36; N, 26.86.

2-Benzenesulfonyl-*p*-quinonebis-(dimethylsulfamimide).—To a suspension of 0.81 g. of the 2-benzenesulfonyl diamide[3] in 5 ml. of glacial acetic acid was added 0.8 g. of lead tetraacetate. The solution immediately became orange and the color deepened as the oxidation proceeded. After standing for 2 hours the mixture was cooled in an ice-bath and the product isolated by filtration and washed with two 5-ml. portions of ice-cold 60% aqueous acetic acid. There was obtained 0.78 g. (96.5%) of orange powder which was recrystallized from benzene–cyclohexane; m.p. 175–177° dec.

Anal. Calcd. for $C_{16}H_{20}N_4O_6S_3$: C, 41.73; H, 4.37; N, 12.17. Found: C, 42.10; H, 4.36; N, 12.09.

2,3-Dichloro-*p*-quinonebis-(dimethylsulfamimide).—To a suspension of 0.5 g. of the 2,3-dichloro diamide[3] in 10 ml. of glacial acetic acid was added 0.57 g. of lead tetraacetate. The mixture was heated on the steam-bath for 5 minutes and then allowed to cool; crystals of the diimide separated. After cooling in an ice-bath the mixture was diluted with 4 ml. of water and filtered. The product was washed with two 5-ml. portions of ice-cold 60% aqueous acetic acid and dried. There was obtained 0.49 g. (100%) of diimide which was recrystallized from chloroform–carbon tetrachloride; orange crystals, m.p. 182.5–184.5° dec.

Anal. Calcd. for $C_{10}H_{14}Cl_2N_4O_4S_2$: C, 30.85; H, 3.63; N, 14.39. Found: C, 30.78; H, 3.64; N, 14.53.

2,5-Dichloro-*p*-quinonebis-(dimethylsulfamimide).—This product was prepared in 98% yield in a similar manner from the 2,5-dichloro diamide.[3] Red crystals from chloroform–carbon tetrachloride, m.p. 189.5–191.5° dec.

Anal. Calcd. for $C_{10}H_{14}Cl_2N_4O_4S_2$: C, 30.85; H, 3.63; N, 14.39. Found: C, 30.87; H, 3.74; N, 14.23.

The infrared spectra of the 2,3-dichloro and 2,5-dichloro diimides differ principally in the region from 700–825 cm.$^{-1}$.

Treatment of Active Methylene Adducts with Hydrochloric Acid.—A suspension of 0.5 to 1.0 g. of the active methylene adduct in 40 ml. of 22% hydrochloric acid was heated under reflux for the periods noted in Table II. The colored reaction mixtures were then filtered hot through a sintered glass funnel. The filtrate was cooled in an ice-bath, made alkaline with 15% aqueous sodium hydroxide, and extracted with two 100-ml. portions of ether. The combined ethereal extracts were dried over anhydrous magnesium sulfate and the ether removed in a stream of dry nitrogen. The crude amino indoles which resulted were purified most easily by sublimation. Purification could be effected, if necessary, by recrystallization from benzene. The amino indoles prepared in this manner were stable over long periods of time if protected from exposure to daylight. See Table II for constants.

5-Acetamido-2-methylindole.—A solution of 0.5 g. of 5-amino-2-methylindole in 50 ml. of anhydrous benzene and 2 ml. of acetic anhydride was heated to boiling for 15 minutes during which time the volume of the solution was permitted to decrease to about 10 ml. Upon cooling in an ice-bath a white solid separated which weighed 0.59 g. (94%). It was recrystallized from ethanol–benzene; white crystals, m.p. 159–160.5°.

Anal. Calcd. for $C_{11}H_{12}N_2O$: C, 70.19; H, 6.43; N, 14.90. Found: C, 70.07; H, 6.23; N, 14.86.

5-Acetamido-2-phenylindole.—The 5-amino-2-phenylindole was prepared as described for the 2-methyl derivative. After cooling the reaction mixture to room temperature sufficient ethanol was added to dissolve the crystals and the solution was then concentrated to the cloud point. After cooling in an ice-bath, 0.13 g. (90%) of off-white crystals resulted which were purified for analysis by crystallization from benzene–ethanol; m.p. 214.5–215.5°.[9]

Anal. Calcd. for $C_{16}H_{14}N_2O$: C, 76.77; H, 5.64; N, 11.20. Found: C, 76.73; H, 5.49; N, 11.35.

The infrared spectrum showed a monosubstituted amide, NH at 3250 cm.$^{-1}$, C=O at 1648 cm.$^{-1}$, indole, NH at 3430 cm.$^{-1}$, C–N at 1413 and 1247 cm.$^{-1}$.

3-Benzoyl-6(?)-chloro-5-dimethylsulfamamido-1-dimethylsulfamoyl-2-phenylindole (XII).—A suspension of 0.7 g. of 2-[4(?)-chloro-2,5-bis-(dimethylsulfamamido)-phenyl]-1,3-diphenylpropane-1,3-dione (VIIIb) in 40 ml. of 22% hydrochloric acid was heated under reflux for 24 hours. At the end of this time the green reaction mixture was cooled and filtered. There was obtained 0.6 g. (88%) of solid which was recrystallized from benzene–cyclohexane; white needles, m.p. 174–177°.

Anal. Calcd. for $C_{25}H_{26}ClN_4O_5S_2$: C, 53.42; H, 4.66; N, 9.97. Found: C, 53.34; H, 4.52; N, 10.0.

The infrared spectrum of the compound showed a C=O at 1633 cm.$^{-1}$ and a mono- and disubstituted sulfonamide.

Ethyl 6(?)-Chloro-5-dimethylsulfamamido-1-dimethylsulfamoyl-2-phenylindole-3-carboxylate (XIII).—A suspension of 1.5 g. of ethyl α-[4(?)-chloro-2,5-bis-(dimethylsulfamamido)-phenyl]-benzoylacetate (VIIIc) in 40 ml. of 22% hydrochloric acid was refluxed for 17 hours. At the end of this time the purple mixture was cooled in an ice-bath and filtered. There was obtained 1.2 g. (84%) of pale green solid, which was recrystallized from ethanol (Darco); white crystals, m.p. 160–162°.

Anal. Calcd. for $C_{21}H_{25}ClN_4O_6S_2$: C, 47.67; H, 4.76; N, 10.59. Found: C, 47.82; H, 4.46; N, 10.31.

The infrared spectrum showed an ester, C=O at 1718 cm.$^{-1}$, C–O at 1275 and 1178 cm.$^{-1}$; monosubstituted sulfonamide, NH at 3295 cm.$^{-1}$, SO_2 at 1398 and 1156 cm.$^{-1}$; disubstituted sulfonamide, SO_2 at 1340 and 1147 cm.$^{-1}$; indole, C–N at 1423 and 1250 cm.$^{-1}$.

7-Dimethylsulfamamido-4-dimethylsulfamoylcyclopent-[b]indole (XI).—A suspension of 1.0 g. of 2-[2,5-bis-(dimethylsulfamamido)-phenyl]-2-carbethoxycyclopentanone (VIIe) in 40 ml. of 22% hydrochloric acid was refluxed for 24 hours. At the end of this time the reaction mixture was cooled and filtered. There was obtained 0.51 g. (63%) of tan crystals which became white after several recrystallizations from ethanol (Darco); m.p. 160–163°.

Anal. Calcd. for $C_{15}H_{22}N_4O_4S_2$: C, 46.61; H, 5.73; N, 14.50. Found: C, 46.67; H, 5.90; N, 14.72.

The infrared spectrum of the compound showed a monosubstituted sulfonamide, NH at 3240 cm.$^{-1}$, SO_2 at 1329 and 1168 cm.$^{-1}$; and a disubstituted sulfonamide, SO_2 at 1315 and 1143 cm.$^{-1}$.

Treatment of Active Methylene Adducts with Cold Concentrated Sulfuric Acid.—A mixture of 15.0 ml. of sulfuric acid (sp. gr., 1.84) and 1.0 g. of the active methylene adduct was subjected to intermittent shaking for 15 minutes. After standing at room temperature for 24 hours the reaction mixture was poured with stirring into 200 ml. of ice-water. The solid that separated was collected by filtration, washed with water, and dried. The constants for the products are found in Table III.

The reaction product from ethyl α-[2,5-bis-(dimethylsulfamamido)-phenyl]-benzoylacetate (VIId) was isolated by extraction of the aqueous acidic solution with two 100-ml. portions of ether. The combined ether extracts were dried

(9) Ref. 6, 5-acetamido-2(or 3)-phenylindole, m.p. 217°.

over anhydrous magnesium sulfate and evaporated to dryness.

3-Carbethoxy-5-dimethylsulfamamidoindole-2-acetic Acid (XVII).—To 1 g. of *p*-quinonebis-(dimethylsulfamimide) and 0.64 g. of redistilled diethyl β-ketoglutarate in 80 ml. of anhydrous dioxane 40 mg. of sodium methoxide was added. The orange color was discharged in 4 minutes. Six drops of glacial acetic acid was added and the dioxane removed in a stream of dry air. The residual oil was dissolved in 15 ml. of concentrated sulfuric acid and the reaction mixture allowed to stand 24 hours. At the end of this time the dark brown solution was poured with stirring into 200 ml. of ice-water and the solid that separated was collected by filtration, washed with water, and dried. There was obtained 0.62 g. (54%) of tan solid which became white after recrystallization from acetone–benzene (Darco); m.p. 194.5–197°.

Anal. Calcd. for $C_{15}H_{19}N_3O_6S$: C, 48.77; H, 5.18; N, 11.38. Found: C, 48.52; H, 5.05; N, 11.32.

The infrared spectrum of the compound showed a carboxylic acid C=O at 1715 cm.$^{-1}$, OH at 2600 cm.$^{-1}$; ester, C=O at 1662 cm.$^{-1}$, C—O at 1215 cm.$^{-1}$; and a monosubstituted sulfonamide.[10]

Hydrolysis of 3-Acetyl-5-dimethylsulfamamido-2-methylindole (XIV) with Hydrochloric Acid: 5-Amino-2-methyl- (VI) and 5-Dimethylsulfamamido-2-methylindole (XVIII).—A suspension of 0.38 g. of 3-acetyl-5-dimethylsulfamamido-2-methylindole in 30 ml. of 22% hydrochloric acid was heated under reflux for 35 minutes. At the end of this time the clear orange solution was cooled in an ice-bath, made alkaline with 15% aqueous sodium hydroxide, and extracted with two 100-ml. portions of ether. The combined ethereal extracts were dried over anhydrous sodium sulfate and the ether removed to give 0.08 g. (42.5%) of light tan crystals. After sublimation at 160° and 10 mm. pressure white crystals, m.p. 157–159°, were obtained. A melting point of a mixture with authentic 5-amino-2-methylindole was not depressed.

Reacidification of the aqueous layer with concentrated hydrochloric acid caused the precipitation of a white solid. After filtering and drying there was obtained 0.18 g. (55%) of pale tan solid which became white after two recrystallizations from benzene–cyclohexane (Darco); m.p. 176–178.5°. It proved to be 5-dimethylsulfamamido-2-methylindole. Higher yields of this product probably could be obtained by employing a shorter period of heating under reflux.

Anal. Calcd. for $C_{11}H_{15}N_3O_2S$: C, 52.15; H, 5.97; N, 16.59. Found: C, 52.39; H, 6.04; N, 16.43.

5-Dimethylsulfamamido-3-ethyl-2-methylindole (XIX).—In a 100-ml. one-necked flask equipped with a reflux condenser and drying tube a mixture of 0.5 g. of 3-acetyl-5-dimethylsulfamamido-2-methylindole, 0.2 g. of lithium aluminum hydride and 50 ml. of anhydrous ether was heated under reflux for 15 minutes and then the excess lithium aluminum hydride was decomposed by the addition of wet ether. The reaction mixture was evaporated to dryness in a stream of dry air, 50 ml. of water was added to the solid residue and the mixture acidified with sulfuric acid. After filtering and drying there was obtained 0.46 g. (97%) of white powder which was purified by recrystallization from benzene–cyclohexane; white crystals, m.p. 152–153°.

Anal. Calcd. for $C_{13}H_{19}N_3O_2S$: C, 55.49; H, 6.81; N, 14.93. Found: C, 55.51; H, 6.64; N, 15.00.

The infrared spectrum showed a monosubstituted sulfonamide, NH at 3260 cm.$^{-1}$; SO_2 at 1335 and 1152 cm.$^{-1}$, and an indole, NH at 3410 cm.$^{-1}$.

5-Amino-3-ethyl-2-methylindole (XX). Method A.—A suspension of 0.5 g. of 5-dimethylsulfamamido-3-ethyl-2-methylindole in 35 ml. of 22% hydrochloric acid was heated under reflux for 2 hours. The resulting red solution was cooled in an ice-bath, made alkaline with 15% aqueous sodium hydroxide, and extracted with two 100-ml. portions of ether. From the combined ethereal extracts was obtained 0.3 g. (97%) of light tan crystals. Two sublimations at 150° and 8 mm. pressure gave white crystals, m.p. 146–148° (lit.[8] m.p. 148–149°).

Anal. Calcd. for $C_{11}H_{14}N_2$: C, 75.84; H, 8.10; N, 16.08. Found: C, 75.73; H, 7.98; N, 16.22.

Method B.—To a solution of 1.0 g. of *p*-quinonebis-(dimethylsulfamimide) and 0.4 g. of 3-ethylpentane-2,4-dione in 80 ml. of anhydrous dioxane, 40 mg. of sodium methoxide was added; there was a slight discharge of the orange color. After standing for 16 hours 6 drops of glacial acetic acid was added to the pale orange solution and the dioxane was removed in a stream of dry air. The residual oil could not be crystallized. It was suspended in 40 ml. of 22% hydrochloric acid and heated under reflux for 16 hours. At the end of this time the dark red solution was cooled in an ice-bath, made alkaline with 15% aqueous sodium hydroxide, and extracted with two 100-ml. portions of ether. The dark brown gummy solid from the ether solution was sublimed at 160° and 5 mm. pressure to yield 0.2 g. of yellow solid. Resublimation gave 0.15 g. (27.6%) of white crystals m.p. 145–148°. A melting point of a mixture with authentic 5-amino-3-ethyl-2-methylindole was not depressed.

5-Dimethylsulfamamido-1-dimethylsulfamoyl-2-methylindole (XXI).—To 50 ml. of 5% aqueous sodium hydroxide heated to 100°, 0.5 g. of 3-[2,5-bis-(dimethylsulfamamido)-phenyl]-pentane-2,4-dione was added. The clear yellow solution was heated at 90–100° for 20 minutes, cooled in an ice-bath, and acidified by the slow addition of concentrated hydrochloric acid. The oil that formed was extracted with two 75-ml. portions of ether and the combined ethereal extracts dried over magnesium sulfate. The ether was removed in a stream of dry air and the residue recrystallized from ethyl acetate–cyclohexane. There was obtained 0.25 g. (58%) which was recrystallized from ethyl acetate–cyclohexane to give white needles, m.p. 95.5–97.5°.

Anal. Calcd. for $C_{13}H_{20}N_4O_4S_2$: C, 43.32; H, 5.59; N, 15.55. Found: C, 43.60; H, 5.88; N, 15.53.

The infrared spectrum showed a monosubstituted sulfonamide, NH at 3270 cm.$^{-1}$; SO_2 at 1387 and 1159 cm.$^{-1}$; disubstituted sulfonamide, SO_2 at 1352 and 1145 cm.$^{-1}$.

Hydrolysis of 5-Dimethylsulfamamido-1-dimethylsulfamoyl-2-methylindole (XXI) with Hydrochloric Acid.—A suspension of 0.72 g. of 5-dimethylsulfamamido-1-dimethylsulfamoyl-2-methylindole in 40 ml. of 22% hydrochloric acid was heated under reflux for 11 hours. The resulting clear red solution was cooled in an ice-bath, made alkaline with 15% aqueous sodium hydroxide and extracted with two 100-ml. portions of ether. The combined ethereal extracts were dried over anhydrous magnesium sulfate and evaporated to dryness. There was obtained 0.26 g. (89%) of light tan crystals. Sublimation at 160° and 10 mm. pressure gave white crystals, m.p. 157–159°. A melting point of a mixture with authentic 5-amino-2-methylindole was not depressed.

1,4-Naphthoquinonebis-(dimethylsulfamimide) (XXIV).—A suspension of 1.5 g. of the diamide[7] and 1.82 g. of lead tetraacetate in 15 ml. of glacial acetic acid was heated on the steam-bath for 20 minutes and then allowed to cool to room temperature and to stand for 15 minutes. At the end of this time the mixture was cooled in an ice-bath and diluted with 8 ml. of water. The diimide was isolated by filtration and washed with two 10-ml. portions of ice-cold 60% aqueous acetic acid. There was obtained 1.37 g. (91.5%) of product which was purified by recrystallization from chloroform–carbon tetrachloride; yellow crystals, m.p. 205–206° dec.

Anal. Calcd. for $C_{14}H_{18}N_4O_4S_2$: C, 45.39; H, 4.90; N, 15.13. Found: C, 45.32; H, 4.81; N, 15.03.

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(10) An acetyl or carbethoxy group in the 3-position of the indole nucleus was observed to absorb about 50 cm.$^{-1}$ below the value expected for an α,β-unsaturated ketone or ester.