formed in granules on the container walls. The aqueous solution was decanted from the polymer, which was found to be soluble in warm dimethylacetamide or in warm 6 *N* hydrochloric acid. Polymer was also formed by prolonged warming of solutions in acetone or isopropyl alcohol.

(b) **1-Methyl-2-vinylimidazole.**—The residue (about 1.0 ml.) from the final distillation of IV was touched with a glass rod which had been dipped in cumene hydroperoxide, and was warmed and stirred. No immediate effect was noted, but on the next day the sample had been converted to a light-brown button of polymer, somewhat tacky at the surface.

A sample of IV which had become light brown and contained an appreciable quantity of low-molecular weight polymer was dissolved in somewhat more than an equal volume of distilled water and placed in a stoppered vessel. The original solution was almost clear; a brown color was present but no insoluble polymer was noted. After standing for about one week, the solution was converted to a thick gel. The gel was not entirely soluble in either hot water or hot dimethylacetamide, but it appeared to dissolve completely, although slowly, in a mixture of equal volumes of the two.

(c) **Copolymers Containing 1-Methyl-2-vinylimidazole.**—Copolymers of (IV) with methyl methacrylate and styrene were prepared by persulfate-catalyzed polymerization in aqueous suspension by conventional procedures. The original charge contained 10% of IV in each case. Analysis of reprecipitated samples showed the presence of 5.2% of IV in the styrene copolymer and 8% of IV in the methyl methacrylate copolymer.

A copolymer of IV with acrylonitrile was prepared similarly in such a way as to give approximately 5% of IV in the product. A film was prepared from the dried copolymer by casting an approximately 15% solution in dimethylacetamide on a glass plate and evaporating the solvent in an oven at 70°. The film so prepared was dyed in a bath containing 2% of Wool-Fast Scarlet G. Supra (a typical acid dye), and 10% each of sulfuric acid and sodium sulfate (based on film weight in each case). After about 20 minutes of heating at 95–100°, the dye-bath was exhausted and the film had been dyed to a deep red shade. Films of pure polyacrylonitrile are only slightly affected under similar conditions.

DECATUR, ALABAMA

[CONTRIBUTION FROM AVERY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

Some Amide Derivatives of Certain Aminomethylpyridines

BY JOHN D. SCULLEY[1] AND CLIFF S. HAMILTON

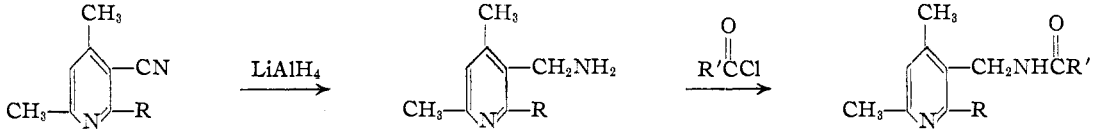
RECEIVED MARCH 23, 1953

Several 3-acylaminomethylpyridines have been synthesized by the reduction of the corresponding 3-cyanopyridine with lithium aluminum hydride and subsequent acylation of the intermediate aminomethyl compound. Some α-aminoacetamidomethylpyridines were prepared when α-chloroacetamidomethylpyridines were warmed with amines. Two ethylenediamine derivatives were synthesized by the reduction of the α-aminoacetamidomethylpyridines with lithium aluminum hydride.

During the course of investigations in this Laboratory leading to possible precursors of 2,7-naphthyridines[2] a number of amide derivatives of some 3-aminomethylpyridines were prepared in which the acyl residue was derived from common acylating agents such as benzoyl chloride and acetic anhydride. The method selected for the synthesis of some of the amides involved the reduction of a 2-substituted 3-cyano-4,6-dimethylpyridine with lithium aluminum hydride followed by the addition of the acid chloride or anhydride directly to the reaction mixture without isolating the intermediate aminomethyl compound. Advantages of this method of preparation have been discussed by Brown.[4]

In view of the known pharmacological applications of certain β-dialkylaminoethyl amides of quinoline and pyridine carboxylic acids, it also seemed of interest to prepare some isomers of amides of this type in which the acyl residue is an α-alkyl or dialkylamino aliphatic carboxylic acid derivative and where the amino residue is an aminomethylpyridine. Aminoacetamides were synthesized by acylating the aminomethylpyridine with chloroacetyl chloride and then warming the substituted chloroacetamide with an excess of the appropriate amine in ethanol solution.

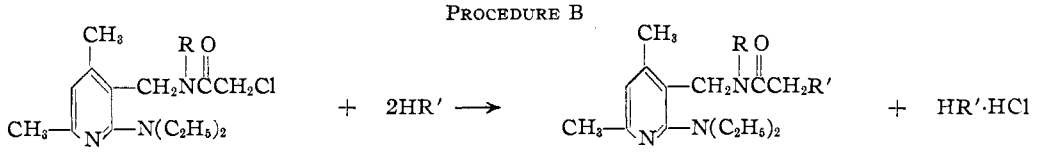
PROCEDURE A



I, R = OCH_3; R′ = C_6H_5
II, R = OCH_3; R′ = CH_2Cl
III, R = $N(C_2H_5)_2$; R′ = CH_3[3]

IV, R = $N(C_2H_5)_2$; R′ = C_6H_5
V, R = $N(C_2H_5)_2$; R′ = CH_2Cl
VI, R = Cl; R′ = CH_3[3]

PROCEDURE B



VIII, R = H; R′ = diethylamino
IX, R = H; R′ = cyclohexylamino

X, R = H; R′ = morpholino
XI, R = benzyl; R′ = dimethylamino

(1) Parke, Davis and Company Fellow 1951–1952.
(2) C. F. H. Allen, *Chem. Revs.*, **47**, 275 (1950).
(3) Acetic anhydride used as the acylating agent.
(4) W. G. Brown in R. Adams, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 488.

TABLE I

Compound	Procedure	Yield, %	M.p.,[b] °C.	Formula	Analyses,[a] % Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
I	A	75	128–129.5[c]	$C_{16}H_{18}N_2O_2$	71.09	6.71	10.36	70.98	6.82	10.57
II	A	73	126.5–127.5[d]	$C_{11}H_{15}N_2O_2Cl$	54.43	6.23	11.54	54.17	6.33	11.60
III	A	75	126.5–127[e]	$C_{14}H_{23}N_3O$	67.43	9.30	16.85	67.68	9.49	17.04
IV	A	77.6	134.5–135.5[c]	$C_{19}H_{25}N_3O$	73.28	8.09	13.50	73.32	8.03	13.65
V	A	70	110–112[g]	$C_{14}H_{22}N_3OCl$	59.25	7.81	14.81	59.05	8.03	14.98
VI	A	20	136.5–138[f]	$C_{10}H_{13}N_2OCl$	56.47	6.16	13.17	56.39	6.26	13.38
VII	A[g]	89	62–64[h]	$C_{21}H_{28}N_3OCl$	67.45	7.55	11.24	67.51	7.74	11.19
VIII	B	91.6	B.p. 191–193 at 0.5 mm.	$C_{30}H_{38}N_{10}O_{15}$[i]	46.27	4.92	17.99	46.28	4.71	18.15
IX	B	85	76–78[h]	$C_{26}H_{34}N_4O$	69.33	9.89	16.17	69.07	10.11	15.94
X	B	91	73–75[h]	$C_{18}H_{30}N_4O_2$	64.64	9.04	16.75	64.60	9.13	16.61
XI	B[g]	73	B.p. 201–205 at 0.5 mm.	$C_{35}H_{40}N_{10}O_{15}$[j]	50.00	4.80	16.66	50.13	4.93	16.81

[a] Analyses by John D. Sculley. [b] All melting points uncorrected. [c] Recrystallized from 1:1 benzene–petroleum ether (b.p. 30–60°). [d] Recrystallized from ethanol. [e] Recrystallized from petroleum ether (b.p. 60–69°). [f] Recrystallized from 50% aqueous ethanol. [g] For modified procedure see experimental section. [h] Recrystallized from petroleum ether (b.p. 30–60°). [i] Formula and analyses for the dipicrate, m.p. 147–149° after recrystallization from ethanol. [j] Formula and analyses for the dipicrate, m.p. 168–169.5° (dec.) after recrystallization from ethanol.

Reduction of two of the α-dialkylaminoacetamides with lithium aluminum hydride was carried out to give substituted ethylenediamines for pharmacological screening.

Still other amide and phthalimide derivatives were prepared by treatment of the previously isolated aminomethyl compound with the appropriate reagents.

Attempts at both acid- and base-catalyzed ring closures involving the elimination of water between the carbonyl group of the amide linkage and the methyl group in the 4-position on the pyridine ring were unsuccessful. Under drastic conditions only tarry decomposition products were obtained and when milder conditions were employed the starting material was recovered unchanged. In one case 3-benzamidomethyl-4,6-dimethyl-2-pyridone was obtained in 53% yield by heating 3-benzamidomethyl-4,6-dimethyl-2-methoxypyridine with zinc chloride at 180°.

Experimental[5]

3-Cyano-4,6-dimethyl-2-pyridone.—This pyridone was prepared by the method of van Wagtendonk and Wibaut[6] in 91% yield.

2-Chloro-3-cyano-4,6-dimethylpyridine.—This substance was prepared (91% yield) by a modification[7] of the method of Mariella and Leech. The product crystallized from benzene as colorless rods (m.p. 98–100°). Mariella and Leech[8] reported the m.p. as 94.5–95° from aqueous ethanol.

3-Cyano-4,6-dimethyl-2-methoxypyridine.—This nitrile was prepared in 93% yield by the method of Mariella and Leech.[8] The product melted at 93.5–95° after recrystallization from 1:1 benzene–petroleum ether (b.p. 30–60°). Mariella and Leech reported the m.p. as 93.5–94° after purification by sublimation.

3-Cyano-2-diethylamino-4,6-dimethylpyridine.—A mixture of 2-chloro-3-cyano-4,6-dimethylpyridine (50 g., 0.3 mole) and diethylamine (73.14 g., 1 mole) was heated at 170° with shaking for 18 hours in a steel bomb. After cooling, the mixture was removed and the bomb was rinsed with two 50-ml. portions of benzene. The crystalline diethylamine hydrochloride was separated by filtration and the filtrate was evaporated. The dark residual oil was distilled to give 51.2 g. (90.2%) of a colorless to pale yellow oil of sweetish odor and exhibiting a bluish fluorescence, b.p. 125.5–129° (1.5 mm.).

(5) All melting points uncorrected.

(6) H. M. van Wagtendonk and J. P. Wibaut, *Rec. trav. chim.*, **61**, 728 (1942).

(7) P. J. Vanderhorst and C. S. Hamilton, THIS JOURNAL, **75**, 656 (1953).

(8) R. P. Mariella and J. L. Leech, *ibid.*, **71**, 331 (1949).

The monopicrate was prepared for analysis. Yellow crystals (m.p. 94.5–96.5°) were obtained after recrystallization from ethanol.

Anal. Calcd. for $C_{18}H_{20}N_6O_7$: C, 50.00; H, 4.66; N, 19.44. Found: C, 50.16; H, 4.95; N, 19.48.

3-Aminomethyl-4,6-dimethyl-2-methoxypyridine.—A saturated ether solution of 37.95 g. (0.234 mole) of 3-cyano-4,6-dimethyl-2-methoxypyridine was added to a slurry of 17.76 g. (0.468 mole) of lithium aluminum hydride in 150 ml. of dry ether. After the addition of the nitrile the mixture was stirred at room temperature for 1 hour. The excess hydride was decomposed by the careful dropwise addition of the minimum amount of water. The insoluble solids were removed by filtration and were extracted by trituration with three 75-ml. portions of hot benzene which were added to the filtrate. The solvent was evaporated and the resulting orange residual oil was distilled under reduced pressure to give 32.28 g. (83%) of a colorless oil, b.p. 88–92° (0.5 mm.).

The monopicrate was prepared for analysis. Fine yellow needles (m.p. 231° dec.) were obtained after recrystallization from 75% aqueous ethanol.

Anal. Calcd. for $C_{15}H_{17}N_5O_8$: C, 45.57; H, 4.33; N, 17.72. Found: C, 45.31; H, 4.35; N, 17.43.

3-Aminomethyl-2-diethylamino-4,6-dimethylpyridine.—A solution of 63.09 g. (0.333 mole) of 3-cyano-2-diethylamino-4,6-dimethylpyridine in 150 ml. of ether was added to a slurry of 25.27 g. (0.666 mole) of lithium aluminum hydride in 200 ml. of dry ether. The remainder of the procedure was identical to that used in the preparation of 3-aminomethyl-4,6-dimethyl-2-methoxypyridine. A 53 g. (88%) yield of a colorless to pale yellow oil (b.p. 123–124.5° (4.5 mm.)) was obtained.

The dipicrate was prepared for analysis. Yellow crystals (m.p. 160–161° dec.) were obtained after recrystallization from ethanol.

Anal. Calcd. for $C_{24}H_{27}N_9O_{14}$: C, 43.31; H, 4.09; N, 18.94. Found: C, 43.26; H, 4.23; N, 19.08.

1-(2-Diethylamino-4,6-dimethyl-3-picolyl)-3-phenylurea.—Phenyl isocyanate (1.19 g., 0.01 mole) and 3-aminomethyl-2-diethylamino-4,6-dimethylpyridine (2.07 g., 0.01 mole) were each dissolved in 50 ml. of dry ether. The ether solution containing the phenyl isocyanate was poured rapidly with stirring into the ether solution of the amine. A pure white solid formed almost immediately and the mixture was permitted to stand at room temperature for one hour. The product was collected by filtration and was washed with 25 ml. of ether. The yield of analytically pure product (m.p. 205.5–207°) was 3.02 g. (92.6%).

Anal. Calcd. for $C_{19}H_{26}N_4O$: C, 69.90; H, 8.03; N, 17.17. Found: C, 70.02; H, 7.97; N, 17.19.

N-(2-Diethylamino-4,6-dimethyl-3-picolyl)-phthalimide.—To a mixture of 6.22 g. (0.03 mole) of 3-aminomethyl-2-diethylamino-4,6-dimethylpyridine and 30 ml. of benzene was added 4.44 g. (0.03 mole) of finely ground phthalic anhydride, and the mixture was heated under gentle reflux for 5 hours. Evaporation of the solvent gave 9.05 g. (89%)

of dense yellow crystals (m.p. 68–75°). White needles (m.p. 73–75°) were obtained by recrystallization from petroleum ether (b.p. 30–60°).

Anal. Calcd. for $C_{20}H_{23}N_3O_2$: C, 71.19; H, 6.87; N, 12.45. Found: C, 71.33; H, 6.58; N, 12.53.

N-(2-Diethylamino-4,6-dimethyl-3-picolyl)-3-nitrophthalimide.—The nitrophthalimide derivative was prepared from 3-nitrophthalic anhydride and the aminomethyl compound in 80% yield in a similar manner. Orange prisms (m.p. 134.5–136°) were obtained by recrystallization from petroleum ether (b.p. 60–69°).

Anal. Calcd. for $C_{20}H_{22}N_4O_4$: C, 62.81; H, 5.80; N, 14.65. Found: C, 62.75; H, 6.02; N, 14.78.

Procedure A for the Preparation of 3-Acylaminomethylpyridines (I, II, III, IV, V, VI).—Table I summarizes the data for these reactions.

To a slurry of 13.28 g. (0.35 mole) of lithium aluminum hydride in 150 ml. of dry ether was added, dropwise with stirring, 0.175 mole of the appropriate nitrile dissolved in the minimum amount of ether necessary to effect complete solution. (In the case of 3-cyano-2-diethylamino-4,6-dimethylpyridine 150 ml. of ether was used.) After the nitrile had been added the mixture was stirred for 2 hours at room temperature and was then heated under reflux with stirring for 2 additional hours.

The excess hydride was decomposed by the careful addition of the minimum amount of 20% aqueous sodium hydroxide solution. To this mixture 0.525 mole of the acylating agent (acetic anhydride, benzoyl chloride, or chloroacetyl chloride) was slowly added. (When benzoyl chloride was used, 200 ml. of pyridine was added to the mixture before the addition of the acid chloride.) The mixture was then stirred for 3 hours at room temperature and then was transferred to a large beaker where it was made basic with a saturated aqueous sodium carbonate solution. The insoluble solids were removed by filtration and were extracted by triturating with three 100-ml. portions of hot benzene, the benzene extracts being added to the filtrate. The layers were separated and the aqueous layer was extracted with benzene. The organic solutions were combined and were dried over anhydrous magnesium sulfate. Evaporation of the solvent gave the solid amide which was recrystallized from an appropriate solvent.

N-Benzyl-N-(2-diethylamino-4,6-dimethyl-3-picolyl)-α-chloroacetamide (VII).—3-Benzamidomethyl-2-diethylamino-4,6-dimethylpyridine (12.46 g., 0.04 mole) was placed in the thimble of a Soxhlet extractor attached to a flask containing dry ether (300 ml.) and lithium aluminum hydride (4.55 g., 0.12 mole). After heating under reflux for 22 hours with stirring all of the amide was removed from the thimble. The Soxhlet extractor was replaced with a reflux condenser and 250 ml. of dry benzene was added to the mixture. Heating under reflux was continued for 4 hours. The excess hydride was decomposed with the minimum amount of water and the solid material was removed by filtration. To the filtrate was added 15 g. of solid sodium bicarbonate and 5.65 g. (0.05 mole) of chloroacetyl chloride and the mixture was permitted to stand overnight. The solids were removed by filtration and the filtrate was evaporated to give 13.32 g. (89%) of slightly colored product melting at 58–62°. After recrystallizing twice from petroleum ether (b.p. 30–60°) clusters of white needles (m.p. 62–64°) were obtained.

Anal. Calcd. for $C_{21}H_{28}N_3OCl$: C, 67.45; H, 7.55; N, 11.24. Found: C, 67.51; H, 7.74; N, 11.19.

3-Acetamidomethyl-2-diethylamino-4,6-dimethyl-5-nitropyridine.—A nitrating mixture was prepared by adding 12 ml. of fuming nitric acid (sp. gr. 1.51) to a mixture of 12 ml. of acetic anhydride and 12 ml. of glacial acetic acid. The temperature was maintained below −5° during the entire addition.

The nitrating mixture was then added to 12.5 g. (0.05 mole) of 3-acetamido-2-diethylamino-4,6-dimethylpyridine (III) suspended in 300 ml. of acetic anhydride. During the addition the temperature was kept between 10 and 15°. When all of the nitrating mixture had been added the ice-bath was removed and the mixture was permitted to stand at room temperature for 2 hours. The mixture was poured onto ice and was made basic with sodium carbonate. The yellow product was collected and dried. The yield was 6.01 g. (40.8%). After recrystallization from isopropyl alcohol the product melted at 144–146.5°. Two additional recrystallizations from petroleum ether (b.p. 60–69°) raised the melting point to 148–148.5°.

Anal. Calcd. for $C_{14}H_{22}N_4O_3$: C, 57.21; H, 7.53; N, 19.04. Found: C, 57.42; H, 7.69; N, 19.05.

3-Benzamidomethyl-4,6-dimethyl-2-pyridone.—A 10-g. (0.037 mole) quantity of 3-benzamidomethyl-4,6-dimethyl-2-methoxypyridine (I), 10 g. (0.073 mole) of freshly fused zinc chloride and 100 ml. of dry ether were heated in a bomb for 8 hours at 180° with continuous shaking. The bomb was cooled and the ether solution was poured out. A glassy residue which remained in the bomb was removed with hot methanol. The ether solution was evaporated to dryness and the residual gum was dissolved in methanol. The methanol solutions were combined and were concentrated to about 50 ml., and a 250-ml. quantity of concentrated aqueous ammonium hydroxide was added to the methanol solution. After standing overnight in the refrigerator a white amorphous solid which had precipitated was collected by filtration. After recrystallization from isopropyl alcohol 5.02 g. (53%) of white needles (m.p. 210–211°) was obtained.

Anal. Calcd. for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N, 10.93. Found: C, 70.15; H, 6.30; N, 10.79.

Procedure B for the Preparation of 3-(α-Aminoacetamidomethyl)-2-diethylamino-4,6-dimethylpyridines (VIII, IX, X).—Table I gives the data for these reactions.

A mixture of 0.01 mole of the α-chloroacetamido compound, 0.04 mole of the amine and 20 ml. of ethanol was heated under gentle reflux for two hours. The alcohol and excess amine were removed under reduced pressure and 30 ml. of ether was added to the residue. The insoluble amine hydrochloride was separated by filtration and the ether solution was evaporated under reduced pressure to give the crude product which was recrystallized from petroleum ether (b.p. 30–60°). When the product was an oil purification was accomplished by distillation.

N-Benzyl-N-(2-diethylamino-4,6-dimethyl-3-picolyl)-α-dimethylaminoacetamide (XI).—N-Benzyl-N-(2-diethylamino-4,6-dimethyl-3-picolyl)-α-chloroacetamide (VII) (11.22 g., 0.03 mole) was dissolved in 150 ml. of ether and the mixture was cooled to −10°. A chilled solution of dimethylamine (5.41 g., 0.12 mole) in 50 ml. of ethanol was added rapidly to the ether solution and the mixture was allowed to warm gradually to room temperature. After standing at room temperature for 1 hour the mixture was heated under gentle reflux for 1 hour. An additional 5.41-g. (0.12 mole) quantity of dimethylamine in 50 ml. of ethanol was then added and the mixture was held at a temperature of 40–45° for 10 hours. The ether was then slowly distilled from the mixture, while the temperature of the solution increased to about 60°. The ethanol was evaporated under reduced pressure leaving a red oil to which 30 ml. of ether was added. The precipitated dimethylamine hydrochloride was separated and the oily product was distilled after evaporation of the ether. The yield was 8.49 g. (73%) of a pale yellow oil (b.p. 201–205° (0.5 mm.)).

The dipicrate was prepared for analysis. Yellow crystals (m.p. 168–169.5° dec.) were obtained after recrystallization from ethanol.

Anal. Calcd. for $C_{35}H_{40}N_{10}O_{15}$: C, 50.00; H, 4.80; N, 16.66. Found: C, 50.13; H, 4.93; N, 16.81.

N-(2-Diethylamino-4,6-dimethyl-3-picolyl)-N′,N′-diethylethylenediamine.—A 10.25-g. (0.032 mole) quantity of VIII dissolved in 25 ml. of dry ether was added to a slurry of 3.64 g. (0.096 mole) of lithium aluminum hydride in 50 ml. of dry ether and the mixture was stirred at room temperature for 2 hours. After decomposition of the excess hydride with the minimum amount of water, the solid material was removed by filtration and was extracted with two 25-ml. portions of benzene which were added to the filtrate. Evaporation of the ether–benzene solution gave a yellow residual oil which was distilled under reduced pressure. The yield of pale yellow oil boiling at 147–150° (0.38 mm.) was 7.72 g. (78.7%). The dipicrate was prepared for analysis. Yellow crystals (m.p. 168–170° dec.) were obtained after recrystallization from ethanol.

Anal. Calcd. for $C_{30}H_{40}N_{10}O_{14}$: C, 47.12; H, 5.27; N, 18.32. Found: C, 46.83; H, 5.30; N, 18.23.

N-Benzyl-N-(2-diethylamino-4,6-dimethyl-3-picolyl)-N′,N′-dimethylethylenediamine.—This compound was prepared from XI by a procedure identical to that used for the preparation of the immediately preceding ethylenediamine

derivative. A 92.8% yield of the pale yellow oily product (b.p. 175–178° (0.45 mm.)) was obtained. The solid tetrapicrate (m.p. 152–154°) was obtained after recrystallization from methanol and was used for analysis.

Anal. Calcd. for $C_{47}H_{48}N_{16}O_{28}$: C, 43.93; H, 3.77; N, 17.44. Found: C, 43.64; H, 3.81; N, 17.55.

LINCOLN 8, NEBRASKA

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

Quinone Imides. XXVIII. Addition of Active Methylene Compounds to *p*-Quinonedibenzenesulfonimide and its Derivatives

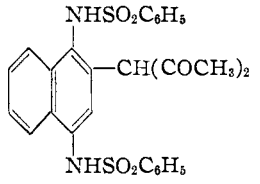
BY ROGER ADAMS AND DALE C. BLOMSTROM[1]

RECEIVED APRIL 11, 1953

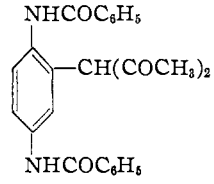
p-Quinonedibenzenesulfonimide undergoes the Michael reaction with several active methylene compounds to give monosubstituted *p*-phenylenedibenzenesulfonamides. The corresponding 2-chloro and 2-methyl diimide derivatives also give substituted diamides, which probably have the 2,5-orientation.

Early workers on the reactions of *p*-benzoquinones and naphthoquinones with active methylene compounds obtained highly colored products which were not purified or characterized. More recently Wood, *et al.*,[2] demonstrated that in the presence of ethanolic ammonia, ethyl cyanoacetate, malonitrile and cyanoacetamide add to *p*-benzoquinone to give 2,5-disubstituted hydroquinones in low yields. Smith and co-workers[3] observed that *p*-benzoquinones bearing three substituents add active methylene compounds readily in the vacant position in good yields, and that tetrasubstituted benzoquinones containing methyl groups react by an attack on a methyl group with formation of coumarins.

The succession of reactions which so often occurs when benzoquinones add various reagents is not usually encountered with the quinone diimides. Thus 1,4-naphthoquinonedibenzenesulfonimide in presence of triethylamine as catalyst adds diethyl malonate, ethyl benzoylacetate, acetylacetone and nitroethane to form the monosubstituted diamides as exemplified by the acetylacetone adduct (I).[4] *p*-Quinonedibenzimide also forms similar monoadducts (II).[5]

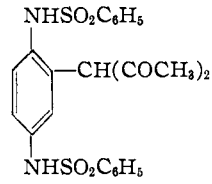


I

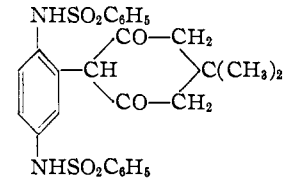


II

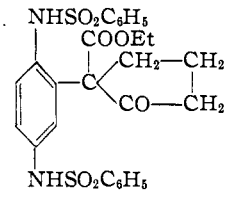
This Michael reaction has now been extended to the *p*-quinonedibenzenesulfonimides. *p*-Quinonedibenzenesulfonimide reacted with acetylacetone (III), methone (IV) and the ethyl esters of acetoacetic acid, benzoylacetic acid, malonic acid and cyclopentanone-2-carboxylic acid (V) to form the monosubstituted diamides in good yields.



III



IV



V

2-Chloro- and 2-methyl-*p*-quinonedibenzenesulfonimide likewise reacted with acetylacetone, ethyl acetoacetate and diethyl malonate to give monoadducts with the substitution probably in the 5-position by analogy to other additions to these diimides. Ethyl cyanoacetate, malononitrile, nitromethane, nitroethane and 2-nitropropane failed to give isolable products with any of the three diimides. Tar formation and reduction of the diimides were the primary reactions.

The additions were carried out in dioxane solution with a catalytic amount of sodium methoxide. The use of triethylamine as catalyst, so successful in the naphthalene series, led only to the formation of tars, amorphous solids, and *p*-phenylenedibenzenesulfonamide. The successful reactions were rapid; complete decolorization of the diimide solution usually occurred within one minute, in some cases within ten seconds. Products from solutions in which only partial decolorization occurred were contaminated with colored impurities. No purifiable adduct was obtained from reaction mixtures which did not fade but turned red-brown instead. No product could be isolated from the addition of diethyl malonate to *p*-quinonedibenzenesulfonimide at room temperature, but a moderate yield was obtained when the reaction was carried out in dilute solution at 70° with a large excess of diethyl malonate.

3-(2,5-Dibenzenesulfonamidophenyl)-2,4-pentanedione (III) was hydrolyzed to the corresponding acetone derivative (VI). When subjected to

(1) An abstract of a thesis submitted by Dale C. Blomstrom to the Graduate College of the University of Illinois, 1953, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy; Cincinnati Chemical Company Fellow, 1950–1951; Standard Oil Company of Indiana Fellow, 1951–1952.

(2) J. H. Wood, *et al.*, THIS JOURNAL, **66**, 1540 (1944).

(3) L. I. Smith and W. J. Dale, *J. Org. Chem.*, **15**, 832 (1950), and many previous papers.

(4) R. Adams and W. Moje, THIS JOURNAL, **74**, 5557 (1952).

(5) R. Adams and D. S. Acker, *ibid.*, **74**, 5872 (1952).