Nitroethylene.—Nitroethylene was prepared by heating 2-nitroethanol with phthalic anhydride under reduced pressure, according to the method of Buckley and Scaife.[8]

3-(2-Nitroethyl)-indole (I). (a) **From Indole and Nitroethylene.**—A solution of nitroethylene (10.0 g., 0.137 mole) in benzene (50 cc.) was added over a period of 50 minutes, with vigorous stirring, to a solution of indole (20.2 g., 0.172 mole) in benzene (50 cc.), maintained at 40–50°. The indole solution became reddish and darkened throughout the addition period. Stirring was continued for 40 minutes at 40–50° and finally the solution was refluxed for one hour. Some brown fumes of nitrogen dioxide were evolved. At the end of the reflux period the odor of nitroethylene was still detectable. A small amount of black precipitate was removed. The filtrate was chromatographed on alumina, using benzene as developer and eluant. A dark brown zone formed at the top of the column. A diffuse, pale yellow band moved down the column quite rapidly. After this yellow band was completely eluted, the column was eluted with 20% chloroform–80% benzene. Nearly all of the dark material remaining on the column was then washed out with 20% ethanol–80% benzene. Evaporation of the first benzene fractions yielded a small amount of indole. The chloroform–benzene fractions were colorless, but upon standing turned yellow, red and finally dark brown. Evaporation of the solvent left tars. Evaporation of the ethanol–benzene fractions also left tars.

Evaporation of the benzene from the yellow band fractions left a yellowish solid. Several recrystallizations from dilute ethanol, with charcoal, yielded 5.3 g. (0.028 mole, 20%) of colorless platelets greatly resembling indole; m.p. 68–68.5° (cor.). ν_{N-H} (cm.$^{-1}$) 3480 in $CHCl_3$, 3450 in CCl_4, Nujol; ν_{NO_2} (cm.$^{-1}$) 1550 in Nujol, 1385 in CCl_4, 1378 in $CHCl_3$.

Anal. Calcd. for $C_{10}H_{10}N_2O_2$ (190.20): C, 63.15; H, 5.30; N, 14.73. Found: C, 63.11; H, 5.01; N, 14.62.

The product obtained by evaporation of the chromatographic solutions usually had a dual melting point when determined on a melting point block. Part of the sample would melt at 54–56° and the remainder at 68–70°. Recrystallization usually yielded the higher melting form, but on one occasion the lower melting form was obtained as colorless platelets, m.p. 56.5–57°.

Anal. Calcd. for $C_{10}H_{10}N_2O_2$ (190.20): C, 63.15; H, 5.30; N, 14.73. Found: C, 63.23; H, 5.42; N, 14.87.

(b) **From Indolemagnesium Iodide and Nitroethylene.**—Indolemagnesium iodide was prepared by the method of Baker[9] from magnesium turnings (1.15 g., 0.047 g. atom), ethyl iodide (7.6 g., 0.049 mole) and indole (5.5 g., 0.047 mole) in absolute ethyl ether (40 cc.). A solution of nitroethylene (3.3 g., 0.045 mole) in absolute ethyl ether (20 cc.) was added slowly, with vigorous stirring, to the ice-cooled solution of indolemagnesium iodide. During the addition, a yellow solid formed in the yellow solution. The mixture was stirred for one hour at room temperature, and finally refluxed for one-half hour. During this time the mixture, which still contained solid, turned brown. The mixture was cooled and stirred into a solution of acetic acid (30 cc.) in water (100 cc.). The ethereal and aqueous layers were separated. The aqueous layer was neutralized with sodium carbonate and the ether layer washed with sodium carbonate solution until the evolution of carbon dioxide was no longer evident. The original neutralized aqueous layer and the sodium carbonate washings were extracted with ether and the ether added to the original washed ether layer. The combined ether solutions were washed with water and dried over anhydrous calcium chloride. Distillation of the ether left a brown, tarry residue, which was chromatographed according to the method of part a. A minute amount of indole was obtained, followed by crude, yellowish 3-(2-nitroethyl)-indole. Two recrystallizations from dilute ethanol yielded 2.4 g. (0.0126 mole) of platelets, m.p. 67–68° (cor.); mixed m.p. with sample from part a, 67–68.5°.

Tryptamine (3-(2-Aminoethyl)-indole) (II).—3-(2-Nitroethyl)-indole (7.8 g., 0.041 mole) in 95% ethanol (150 cc.) and platinic oxide (0.45 g.) were treated with hydrogen at 41 p.s.i. in a Parr low pressure hydrogenation apparatus until no further pressure drop was observed. The catalyst was filtered off and the ethanol distilled at reduced pressure. The light brown residue, which crystallized upon cooling in an ice-bath, was dissolved in ether and the solution filtered. Glacial acetic acid was added to the filtrate until precipitation was complete. The precipitated tryptamine acetate was dissolved in water and basified with 2 *N* sodium hydroxide solution. The precipitated tryptamine was filtered off, washed with water, dissolved in benzene and the solution dried over sodium sulfate. Part of the benzene was distilled in a nitrogen atmosphere. Cooling the concentrated solution caused the formation of tan, granular crystals (5.1 g., 0.032 mole, 78%), m.p. 115–117° (cor.) (reported m.p. 116–117°[3a]). An aqueous solution of Eastman Kodak Co. white label tryptamine hydrochloride was basified with 5% sodium hydroxide solution to yield tryptamine, m.p. 113–114.5°; mixed m.p. with sample obtained above, m.p. 113–116.5°. The infrared spectra of the two samples were identical.

β-(3-Indolemethyl)-β-nitrostyrene (III).—The procedure for the preparation of β-nitrostyrenes developed by Knoevenagel and Walter[10] and Hass, Susie and Heider[11] was used in this preparation. A solution of 3-(2-nitroethyl)-indole (2.01 g., 0.0106 mole), benzaldehyde (1.13 g., 0.0106 mole), *n*-amylamine (2 drops) and absolute ethanol (2 cc.) was refluxed in a test-tube on the steam-bath for 11 hours. Crystals formed slowly over a period of 48 hours when the dark brown solution was kept at −20°. Two recrystallizations from absolute ethanol yielded 0.93 g. (0.0033 mole, 31%) of glistening orange flakes, m.p. 151–152° (cor.); ν_{N-H} (cm.$^{-1}$) 3490 in $CHCl_3$, 3480 in CS_2, 3410 in Nujol; ν_{NO_2} (cm.$^{-1}$) 1524 in Nujol, 1329 in Nujol, $CHCl_3$, 1325 in CS_2. (Compare with β-methyl-β-nitrostyrene ν_{NO_2} 1534, 1330 cm.$^{-1}$ in Nujol.)

Anal. Calcd. for $C_{17}H_{14}N_2O_2$ (278.30): C, 73.36; H, 5.07; N, 10.07. Found: C, 73.34; H, 5.25; N, 10.05.

---

[8] G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1471 (1947).

[9] J. W. Baker, *ibid.*, 461 (1946).

[10] E. Knoevenagel and L. Walter, *Ber.*, **37**, 4502 (1904).

[11] H. B. Hass, A. G. Susie and R. L. Heider, *J. Org. Chem.*, **15**, 8 (1950).

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS 14, MINN.

Compounds Derived from the Addition of Amines to 2,4-Pentadienenitrile

BY JOHN M. STEWART

RECEIVED DECEMBER 3, 1953

In recent years several reports have appeared dealing briefly with the addition reactions of amines and 2,4-pentadienenitrile.[1–4] At the time of the appearance of these articles a more comprehensive study of these reactions was in progress in this Laboratory and the results of this work are reported herewith.

The mixture of *cis* and *trans* forms of 2,4-pentadienenitrile obtained by the pyrolysis of the benzoate of crotonaldehyde cyanohydrin, according to the method of Snyder, Stewart and Myers,[5] was used throughout this investigation. It has been reported previously[1,4] that no apparent difference in reactivities was noted when the *cis* and *trans* isomers were carefully separated and used individually with the same amines, and the products obtained were identical.

Aliphatic primary and secondary amines added readily to 2,4-pentadienenitrile at room tempera-

---

[1] M. Frankel, H. S. Mosher and F. C. Whitmore, THIS JOURNAL, **72**, 81 (1950).

[2] S. J. Allen and J. G. Drewitt, U. S. Patent 2,527,510 (Oct. 31, 1950).

[3] P. Kurtz, *Ann.*, **572**, 23 (1951).

[4] Ph.D. Thesis of K. H. Takemura, Univ. of Illinois, 1950 (private communication from Prof. H. R. Snyder).

[5] H. R. Snyder, J. M. Stewart and R. L. Myers, THIS JOURNAL, **71**, 1055 (1949).

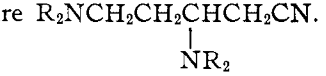
TABLE I

Cpd., 3-Pentenenitriles	Yield, %	B.p. °C.	Mm.	Ref. index, n_D	°C.	Neut. equiv., Calcd.	Neut. equiv., Found	Hydrochloride M.p., °C.	Hydrochloride Analyses, % Calcd.	Hydrochloride Analyses, % Found
5-Ethylamino-	47–56[a]	61–63	2	1.4666	20	124.2	125.0	117–119	Cl, 22.06	21.75
5-Isopropylamino-	69–80	61–62	1	1.4610	20	138.2	138.6	158–159	Cl. 20.36	19.95
5-*n*-Butylamino-	46–50[b]	77–79	1.5	1.4615	25	152.2	153.4	196–197	Cl, 18.79	18.62
5-*s*-Butylamino-	73.7	74–76	1.5	1.4622	20			152–153	Cl, 18.79	18.70
5-Cyclohexylamino-	26.3[c,d]	110–112	1	1.4942	20					
5-Ethylenimino-[e]	90.0	93–96	10	1.4722	20					
5-Dimethylamino-	80.0[f]	65–67	3	1.4543	20	124.1	123.8	161–162	Cl, 22.06	21.88
5-Di-*n*-butylamino-	30.0[g]	111–112	1	1.4570	25			Oil		
5-Piperazino-	17.2[h]	122–123	1	1.5130	26					
Pentanenitriles										
5-Ethylamino-		68–69	3	1.4420	20	126.2	127.0	138–140	Cl, 21.79	21.75
		107–108	15						N, 17.24	17.57
5-Isopropylamino-		73–74	2	1.4397	20	140.2	140.0	152–153.5	Cl, 20.07	20.02
5-*n*-Butylamino-		82–84	2	1.4445	20	154.25	155.2	222–224	Cl, 18.59	18.51
5-*s*-Butylamino-		77–78	1.5	1.4425	20			164–166	Cl, 18.59	18.43
5-Cyclohexylamino-		110–111	1	1.4756	20			228–229.5	Cl, 16.36	16.22
5-Dimethylamino-		67–68	3	1.4335	20			138–140	Cl, 21.80	21.66
									C, 51.68	51.86
									H, 9.29	9.43
5-Di-*n*-butylamino-		107–109	1	1.4465	20	210.36	208.2	Oil		
5-Piperazino-		111–112	1	1.4946	20			222–223	Cl, 29.52	29.12
		175–180[j]	1	1.4942	20			224	Cl, 22.27	22.07
1-Aminopentanes										
5-Ethylamino-		78–79	10	1.4512	20			214–216[k]	Cl, 34.91	34.61
5-Isopropylamino-		85–87	10	1.4483	20			224–226	Cl, 32.65	32.56
		46–47	1	1.4460	25				N, 12.90	12.70
5-*n*-Butylamino-		65–67	1	1.4541	20			295–296	Cl, 30.67	30.46
5-*s*-Butylamino-		93–95	7	1.4510	20			225–227	Cl, 30.67	30.33
5-Cyclohexylamino-		98–99	1	1.4805	20	92.16	94.2	246–248	Cl, 27.57	27.28
5-Ethylenimino-		74–77	8	1.4560	25	64.11	65.0	211–213	Cl, 44.77[l]	45.35
5-Dimethylamino-		53–54[m]	2	1.4424	20	65.11	65.82	159–161	Cl, 34.91	34.52
5-Di-*n*-butylamino-		99–100	1	1.4517	20	107.2	108.1	Oil		

[a] Kurtz[3] reports a yield of 62%, b.p. 120–124° (12 mm.). [b] When the crude adduct was hydrogenated to 5-*n*-butylaminopentanenitrile before distillation, the two-step yield was 58–64%. [c] Takemura[4] reports a yield of 22%, b.p. 99–101° (0.4 mm.), n^{20}_D 1.4944. [d] When the crude adduct was hydrogenated to 5-cyclohexylaminopentanenitrile before distillation, the two-step yield was 78.4%. [e] *Anal.* Calcd. for $C_7H_{10}N_2$: C, 68.83; H, 8.25. Found: C, 69.52; H, 8.13. [f] Kurtz[3] reports a 43% yield of dimethylamine adduct, b.p. 86–96° (15 mm.). [g] When the crude adduct was directly hydrogenated at low pressure to 5-di-*n*-butylaminopentanenitrile before distillation, the two-step yield was 51.3%. [h] This represents a conversion to a one to one adduct, based on piperazine. The dipicrate (unrecrystallized) had no definite melting point. [i] E. Ochiai, K. Tsuda and J. Yokoyama, *Ber.*, **68B**, 2294 (1935), report b.p. 125° (9 mm.); hydrochloride, m.p. 211° (from ethyl acetate). [j] Hydrogenated secondary addition product derived from two moles of 2,4-pentadienenitrile and one mole of piperazine. [k] J. von Braun and W. Pinkernelle, *Ber.*, 70B, 1240 (1937), report m.p. 210°. [l] For $ClCH_2CH_2N(CH_2)_5NH_2 \cdot 2HCl$. [m] Kurtz[3] reports 5-dimethylamino-1-aminopentane, b.p. 73–75° (14 mm.).

ture without addition of a catalyst. Conversion of these adducts to known compounds in a variety of cases has shown this addition to take place at carbon atoms 2 and 5. The actual position of the double bond in the amine–cyanobutadiene adducts has not been proven, but it would seem most likely that this double bond is situated between carbon atoms 3 and 4, for example, $R_2NCH_2CH{=}CHCH_2CN$. This has been shown to be the case for the adducts of 2,4-pentadienenitrile with nitroparaffins,[6] acetoacetic ester[7] and thiophenol.[4] The adducts of 2,4-pentadienenitrile are listed then in Table I as 5-substituted-amino-3-pentenenitriles. Ammonia and aniline failed to add under a variety of conditions, including the addition of acidic and basic catalysts. However, Kurtz[3] has reported that hydrogenation of a mixture of 2,4-pentadienenitrile and ammonia in tetrahydrofuran gave poor yields of 5-aminopentanenitrile.

In experiments in which a large excess of amine was used, addition of a second molecule of amine took place. This type of secondary addition reportedly[1,6,8] is base catalyzed and proceeds through an initial shift of the double bond to a position between carbon atoms 2 and 3, followed by an addition to this conjugated system to give the type structure $R_2NCH_2CH_2CHCH_2CN$.



$$R_2NCH_2CH_2\underset{\displaystyle NR_2}{\underset{|}{C}}HCH_2CN$$

The primary addition compounds of amines and 2,4-pentadienenitrile were found to revert to the starting materials if too high a temperature was reached during vacuum distillation. Addition products derived from primary amines were more sensitive to heat than those derived from secondary amines. This resulted in low yields for some of the higher boiling adducts. Direct low pressure hydrogenation of the crude reaction mixtures in these cases, followed by vacuum distillation, gave two-

---

(6) J. L. Charlish, W. H. Davies and J. D. Rose, *J. Chem. Soc.*, 227 (1948).

(7) J. L. Charlish, W. H. Davies and J. D. Rose, *ibid.*, 232 (1948).

(8) D. D. Coffman, THIS JOURNAL, **57**, 1981 (1935).

TABLE II

Cpd., Pentanoic acids	Yield, %[a]	Acid·HCl M.p., °C.	Acid·HCl Cl Anal., % Calcd.	Acid·HCl Cl Anal., % Found	Ethyl ester·HCl M.p., °C.	Ethyl ester·HCl Cl Anal., % Calcd.	Ethyl ester·HCl Cl Anal., % Found
5-Ethylamino-	72				129–132	16.91	16.86
5-Isopropylamino-	76	129–133	18.12	17.84	119–122	15.85	15.72[b]
5-*n*-Butylamino-		124.5–126[c]	16.91	16.85			
5-*s*-Butylamino-		121–122	16.91	16.87			
5-Cyclohexylamino-	71	190–192	14.98	14.98	163–166	13.44	13.47
5-Dimethylamino-	84	160–163.5	19.52	20.00			
5-Diethylamino-	70	198–201	16.91	16.74[d]			
5-Piperidino-	72	204–207[e]	15.99	15.88			

[a] As the hydrochloride of the acid. [b] Calcd. for $C_{13}H_{22}ClO_2N$: C, 53.68; H, 9.91. Found: C, 53.74; H, 9.65. [c] E. Ochiai, K. Tsuda and J. Yokoyama, *Ber.*, **68B**, 2296 (1935), report the hydrochloride, m.p. 124.5° (from acetone–ether). [d] Calcd. for $C_9H_{20}ClNO_2$: C, 51.54; H, 9.61. Found: C, 51.97; H, 9.63. [e] Recrystallized from acetone; m.p. 202–204° from ethanol–ether. W. B. Thomas and S. M. McElvain, THIS JOURNAL, **56**, 1809 (1934), report the hydrochloride of the acid, m.p. 198–200°.

step yields of 5-substituted-aminopentanenitriles much improved over the yields obtained when direct distillation of the 5-substituted-amino-3-pentenenitriles was followed by low pressure hydrogenation.

The unsaturated addition products were hydrogenated at low pressure to 5-substituted-aminopentanenitriles. These compounds in turn were hydrogenated at high pressure in the presence of ammonia. In the high pressure hydrogenations if the amine grouping was tertiary, high yields of only 5-dialkylamino-1-aminopentanes were obtained. However, when the amine grouping was secondary, an intramolecular reductive alkylation took place to a large extent to give N-substituted piperidines in addition to 5-alkylamino-1-aminopentanes. Thus, from the 5-ethylamino-, 5-isopropylamino-, 5-*n*-butylamino-, 5-*s*-butylamino- and 5-cyclohexylaminopentanenitriles were obtained the N-ethyl-, N-isopropyl-, N-*n*-butyl-, N-*s*-butyl- and N-cyclohexylpiperidines. A similar reductive cyclization has been reported recently by Boekelheide, *et al.*,[9] in the reduction of 4-(2-pyridyl)-butanenitriles.

The 5-substituted-aminopentanenitriles were also hydrolyzed to 5-substituted-aminopentanoic acids, which were isolated as their hydrochloride salts. The ethyl esters of these acids usually formed rather easily on heating the acid hydrochlorides in absolute ethanol.

Experimental

Carbon, hydrogen and nitrogen analyses reported were performed by the Clark Microanalytical Laboratory, Urbana, Illinois.

Melting points are uncorrected.

2,4-Pentadienenitrile and Amine Addition Reactions. (5-Substituted-amino-3-pentenenitriles).—The 2,4-pentadienenitrile[5] was added to a slight molar excess of amine in a pressure bottle, and the bottle was flushed out with argon before sealing. If no immediate exothermic reaction ensued, the mixture was warmed at 50° for one-half hour and then allowed to stand at room temperature for 18 hours. Unreacted starting materials were stripped under vacuum and the crude product was either purified by vacuum distillation or directly hydrogenated at low pressure.

Yields, physical constants and analyses of the 5-substituted amino-3-pentenenitriles are listed in Table I. In addition to the compounds listed in Table I, the adducts of piperidine and diethylamine also were prepared and converted to the various types of derivatives described below. These compounds have been well characterized by Frankel, *et al.*[1]

5-Substituted-aminopentanenitriles.—Low pressure hydrogenation of the 5-substituted amino-3-pentenenitriles in ether solution over 7% palladium-on-charcoal catalyst resulted in quantitative conversions to 5-substituted-aminopentanenitriles. Table I lists physical constants and analyses for these compounds.

High Pressure Hydrogenation of 5-Substituted-aminopentanenitriles.—These hydrogenations were carried out in ethanol solution saturated with ammonia over Raney nickel catalyst at initial pressures of 800–1400 p.s.i. and temperatures of 90–100°. The products were separated by vacuum distillation.

Table I lists the physical constants and analyses for the 5-substituted-amino-1-aminopentanes.

Hydrolyses of 5-Substituted-aminopentanenitriles (5-Substituted-aminopentanoic Acids).—Hydrolyses were carried out in concd. hydrochloric acid—heating the mixtures on a steam-bath for 2–3 hours. The resulting solution was then carefully evaporated to dryness, and the solid residue was extracted twice with hot acetone or with cold absolute ethanol. Acetone proved more satisfactory, since it did not dissolve the by-product ammonium chloride as readily as did the ethanol. In addition, in some cases in which ethanol was used and the mixtures were warmed, the acids were at least partly converted to their ethyl esters. The hydrochlorides of the 5-substituted-aminopentanoic acids were precipitated by addition of ether to the acetone or ethanol solutions and could be recrystallized from either acetone or ethanol–ether mixtures. Acetone recrystallization appeared to give crystals of somewhat higher melting point. Table II lists the physical constants and analyses for these compounds.

TABLE III

ADDITION PRODUCTS OF 2,4-PENTADIENENITRILE WITH TWO MOLES OF AMINE

Cpd. pentanenitriles	B.p. °C.	B.p. Mm.	Ref. index, n_D	Ref. index, °C.	Neut. equiv., Calcd.	Neut. equiv., Found
3,5-Di-(ethylamino)-	82–85	1	1.4635	20	81.61	83.9
3,5-Di-(*n*-butylamino)-	142–143	3	1.4612	20	112.7	114.0
3,5-Di-(dimethylamino)-	105–115[a]	5	1.4549	25		

[a] P. Kurtz[3] reports a b.p. 120–122° (10 mm.).

DEPARTMENT OF CHEMISTRY
MONTANA STATE UNIVERSITY
MISSOULA, MONTANA

---

[9] V. Boekelheide, W. J. Linn, P. O. Grady and M. Lamborg, THIS JOURNAL, **75**, 3243 (1953).

Diels–Alder Reactions with Arylethenesulfonyl Fluorides

BY WILLIAM E. TRUCE AND FRED D. HOERGER[1]

RECEIVED FEBRUARY 4, 1954

Although several aromatic and saturated aliphatic sulfonyl fluorides have been prepared by treating the corresponding sulfonyl chlorides with boiling potassium fluoride solution,[2] no unsaturated aliphatic sulfonyl fluorides are reported. 2-Phenyl-

---

[1] This work is taken from Mr. Hoerger's M.S. thesis.

[2] W. Davies and J. H. Dick, *J. Chem. Soc.*, 2104 (1931).