from chloroform: mp 123–125°; ir (Nujol) 3.10 (NH) and 6.11 μ (CO).

Anal. Calcd for $C_{11}H_{11}N_3O$: C, 65.67; H, 5.51; N, 20.88. Found: C, 65.66; H, 5.38; N, 20.73.

***N*-(*o*-Pyrrol-1-ylbenzoyl)-*N'*-benzenesulfonyl Hydrazine.**—To a stirred solution of *o*-(pyrrol-1-yl)benzohydrazide (4.0 g, 0.02 mol) dissolved in pyridine (25 ml) and cooled in an ice bath, benzenesulfonyl chloride (5.2 g, 0.03 mol) was added in a dropwise manner. After addition was complete, the stirring of the cooled reaction mixture was continued for 1 hr, and then the reaction mixture was poured onto an ice–hydrochloric acid mixture (100 g of ice and 100 ml of concentrated hydrochloric acid). A yellow solid formed which was removed by filtration and washed with dilute hydrochloric acid. After drying, the yellow product (4.3 g, 63%) was recrystallized from benzene: mp 151.5–153.5°; ir (Nujol) 3.10 (NH), 3.20 (NH), 6.08 (CO), 8.52 (SO_2), and 8.60 μ (SO_2).

Anal. Calcd for $C_{17}H_{15}N_3O_3S$: C, 59.81; H, 4.43; N, 12.31. Found: C, 59.96; H, 4.62; N, 12.63.

***o*-(Pyrrol-1-yl)benzaldehyde (IV).**—*N*-(*o*-Pyrrol-1-ylbenzoyl)-*N'*-benzenesulfonyl hydrazine (68.2 g, 0.2 mol) and ethylene glycol (800 ml) were stirred together while the temperature was slowly raised to 135°, at which time powdered anhydrous potassium carbonate (150 g) was added all at once. The reaction was stirred for 1.5 min and then cooled by the addition of warm water (500 ml). After cooling, the reaction mixture was extracted with ether which in turn was washed with water. The ether extracts were dried and filtered, and the solvent was removed, leaving a dark brown oil. Upon distillation of the oil, 16 g (47% yield) of product was collected at 70–72° (0.05 mm): ir (film) 3.60 (CH aldehyde), 3.70 (CH aldehyde), and 6.00 μ (CO).

Anal. Calcd for $C_{11}H_9NO$: C, 77.17; H, 5.30; N, 8.18. Found: C, 76.95; H, 5.10; N, 8.41.

General Procedure for the Preparation of 9-(*N*,*N*-Disubstituted amino)-9*H*-pyrrolo[1,2-*a*]indole Compounds (Va–c).—To a solution of disubstituted amine hydrochloride (0.05 mol) dissolved in a mixture of ethanol (30 ml) and methanol (20 ml) [for Va, only ethanol (50 ml) was used], compound IV (0.05 mol) was added rapidly and stirred for 3 hr at 25°. The products were precipitated by the addition of ether and separated by filtration: Va, nmr ($CDCl_3$) δ 2.72 (s, 6, CH_3), 5.57 (s, 1, HC-9), 6.44–6.70 (m, 2, HC-1, HC-2), 7.18–7.62 (m, 5, HC-3, HC-5–8), 8.52 (d, 1, HC-1).

9-*N*,*N*-Dimethylamino-9*H*-pyrrolo[1,2-*a*]indole (VII).—Va (1.0 g) was dissolved in water, made basic with a 10% aqueous sodium hydroxide solution, and extracted with ether. The dried ether extracts were concentrated, giving an oil which solidified on standing. The solid was sublimed at 62–68° (0.05 mm): nmr ($CDCl_3$) δ 2.17 (s, 6, CH_3), 4.85 (s, 1, HC-9), 6.12–6.43 (m, 2, HC-1, HC-2).

9-*N*,*N*-Dimethylamino-9*H*-pyrrolo[1,2-*a*]indole Methiodide (VIII).—To a solution of compound VII (3.9 g, 0.02 mol) dissolved in methanol (5 ml), methyl iodide (5 ml) was added. On standing in the cold, crystals were deposited which were separated by filtration: nmr ($CDCl_3$) δ 3.45 (s, 9, CH_3), 6.28–6.70 (m, 3, HC-1, HC-2, HC-9), 7.00–7.92 (m, 5, HC-3, HC-5–8).

9-Cyano-3*H*-pyrrolo[1,2-*a*]indole (IX).—To a stirred mixture of compound VIII (17.0 g, 0.05 mol) and water (100 ml), potassium cyanide (13.0 g, 0.2 mol) dissolved in water (100 ml) was rapidly added, followed by refluxing for 2 hr. A dark solid, filtered from the cooled reaction mixture, was extracted using hot ethanol which was next passed through a charcoal column. The ethanol (3.0 l.) was removed on a rotary evaporator and the residue was recrystallized: nmr ($CDCl_3$) δ 3.82 (s, 2, H_2C-3), 6.10–6.30 (m, 1, HC-2), 6.95 (d, 1, HC-1), 7.08–7.90 (m, 4, HC-5–8).

Reduction of 9-Dimethylamino-9*H*-pyrrolo[1,2-*a*]indole Hydrochloride (Va) and 9-Dimethylamino-9*H*-pyrrolo[1,2-*a*)indole (VII).—Compounds Va (0.01 mol) and VII (0.01 mol) were reduced in a Parr hydrogenator at 50 lb/in.^{2} over a 2-hr period utilizing ethanol (150 ml) as solvent and Pd-C (10%) as catalyst. The reduction of compound Va resulted in the uptake of 2 equiv of hydrogen while that of VII was slightly over 1 equiv. Prior to evaporation of the solvent in the case of compound Va, the catalyst was removed by filtration and dimethylamine hydrochloride (0.5 g) was precipitated by the addition of ether. With compound VII, after removal of catalyst, the solvent and dimethylamine, whose presence was shown by the strong amine odor, were removed on a rotary evaporator. The solid residues were recrystallized from ethanol. The reduction of hydrochloride salt Va gave a 65% yield while the free base, VII, gave 30% yield of product: mp 77–80° (lit.[5] 79–80°); uv max (ethanol) 281.9 mμ (lit.[5] 280 mμ).

Anal. Calcd for $C_{11}H_{11}N$: C, 84.04; H, 7.05; N, 8.91. Found: C, 84.21; H, 7.02; N, 8.77.

TABLE I

EXPERIMENTAL DATA[a]

No.	Yield, %	Mp, °C[b]	Recrystn solvent[c]	Uv spectra,[d] λ_{max}, mu (ε)	Ir spectra,[e] μ
Va	53	185	A–C	253 (12,000)	4.02 (NH$^+$)
				265 (10,000)	4.32 (NH$^+$)
Vb	44	210	A–C	252 (11,500)	3.92 (NH$^+$)
				266 (10,100)	4.13 (NH$^+$)
Vc	56	180	A–C	253 (11,300)	4.00 (NH$^+$)
				265 (10,000)	4.21 (NH$^+$)
VII		54–56		263 (10,900)	
VIII	98	130	B–C	255 (12,900)	
				270 (7,200)	
IX	50	106–108.5	A	260 (14,200)	4.58 (CN)
				271 (14,200)	
				275 (14,200)	
				282 (13,600)	
				292 (12,100)	
				95% EtOH	

[a] Satisfactory analytical data (±0.3% for C, H, N, and, when present, Cl) were reported for all compounds in table: Ed. [b] Decomposes. [c] A = ethanol, B = methanol, C = ether. [d] Va–c (methanol), VII–IX (95% ethanol). [e] Nujol.

Registry No.—IV, 31739-56-7; Va, 31739-57-8; Vb, 31739-58-9; Vc, 31739-59-0; VII, 31739-60-3; VIII, 31739-61-4; IX, 31739-62-5; *o*-(pyrrol-1-yl)-benzohydrazide, 31739-63-6; *N*-(*o*-pyrrol-1-ylbenzoyl)-*N'*-benzenesulfonyl hydrazine, 31739-64-7.

Pyrrole Studies. XVII.[1] Alkylation of Pyrrylthallium(I)

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Whereas alkylation of pyrrylmagnesium bromide with alkyl halides yields the isomeric 2- and 3-alkylpyrroles as the major products, alkylation of alkali metal salts of pyrrole gives, with few exceptions, the 1-substituted compounds as the predominant products with only small amounts of the C-alkylated compounds. The position of electrophilic attack on the pyrryl anion appears, however, to be determined largely by the ionic radius of the alkali metal ion and the polarity of the solvent and significant variations in the isomer ratios have also been observed with different alkyl halides.[2]

The similarity in the ionic radius of K^+ and Tl^+ (1.33 and 1.47 Å, respectively) prompted a study of pyrrylthallium(I) and its reaction with alkyl halides. More-

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(1) Part XVI: C. F. Candy and R. A. Jones, *J. Chem. Soc. C*, 1405 (1971).

(2) For a summary of references, see K. Schofield, "Heteroaromatic Nitrogen Compounds: Pyrroles and Pyridines," Butterworth, London, 1967; R. A. Jones, *Advan. Heterocycl. Chem.*, **11**, 383 (1970).

over, previous studies[3,4] have already shown that acylation of pyrrylthallium(I) with acyl chlorides occurs very readily to give the 1-acylpyrroles in considerably better yields than from the procedure using pyrrylpotassium.

Pyrrylthallium(I) was readily isolated from the reaction of thallium ethoxide with pyrrole[3,4] and, compared with pyrrylpotassium, it is a relatively stable solid, only slightly light sensitive and almost completely inert to atmospheric water. It is insoluble in organic solvents and is not decomposed in cold water. Dilute aqueous acids, however, regenerate pyrrole. The precise structure of pyrrylthalluim(I) is unknown, but the similarity of its ^{1}H nmr spectrum measured in diethyl ether (triplets at τ 3.15 and 3.74, $J = 2$ Hz) with those of pyrrylsodium[5] and pyrrylmagnesium bromide[5,6] suggests an ionic or ion-pair structure.

With the exception of the reactions with ethyl iodide and *tert*-butyl iodide, pyrrylthallium(I) reacted with alkyl iodides to give the corresponding 1-alkylpyrroles in high yield to the exclusion of C-alkylated products (Table I). No attempts were made to optimize the yields by varying the reactions conditions, but the experimental simplicity of the method, compared with that using pyrrylpotassium, recommends it as a superior method for the N-alkylation of pyrroles. The low yields of 1-ethyl- and 1-*tert*-butylpyrrole, with the concomitant formation of pyrrole, are most probably due to the preferential β elimination of hydrogen iodide, induced by the pyrryl anion, from the alkyl iodides.

TABLE I

ALKYLATION OF PYRRYLTHALLIUM(I)

Alkylating agent	Reaction time, hr	Reaction temp, °C	Yield of purified 1-alkylpyrrole,[a] %
Methyl iodide	14	20	98 (99)
Ethyl iodide	24	60	51[b]
Propyl iodide	24	60	68 (98)
Isopropyl iodide	24	60	95 (98)
n-Butyl iodide	32	60	82 (97)
tert-Butyl iodide	15	60	15[c]
Trimethylsilyl chloride	1	20	93 (97)
Benzyl bromide	20	20	82 (96)

[a] Yields, based on pyrrylthallium(I) consumed, of products isolated by distillation. Figures given in parentheses give the purity of the product before distillation. All products were identified by nmr spectroscopy (Table II). [b] Pyrrole (38%) and unidentified product (11%) detected. [1,2-Diethylpyrrole was not detected. *Cf.* reaction of ethyl iodide with pyrrylpotassium: G. Ciamician and C. M. Zannetti, *Ber.*, **22,** 659 (1889).] [c] Pyrrole (84%) recovered.

1-Methyl- and 1-ethylpyrrole were also isolated in 57 and 62% yield, respectively, from the reaction of the corresponding alkyl tosylate and pyrrylthallium(I) at 60° over 20 hr, but alkyl chlorides and bromides were found to react less readily. Preliminary investigations also suggest that thallium salts may be used with equal success in the N-alkylation of substituted pyrroles; *e.g.*, the thallium(I) salt of 2-formylpyrrole with methyl iodide gave an almost quantitative yield of 1-methyl-2-formylpyrrole.

TABLE II

^{1}H NMR DATA FOR 1-SUBSTITUTED PYRROLES[a]

1 substituent	Registry no.	Pyrrole ring protons[b] α	Pyrrole ring protons[b] β	Substituent protons[b]
Me[c,d]	96-54-8	3.67	3.97	6.84 (CH_3)
Et[c,d]	617-92-5	3.51	3.90	6.40 (CH_2), 8.87 (CH_3)
n-Pr	5145-64-2	3.47	3.91	6.42 (NCH_2), 8.42 (CH_2), 9.16 (CH_3)
i-Pr[d]	7057-97-8	3.45	3.90	6.19 (CH), 8.85 ($C(CH_3)_2$)
n-Bu	589-33-3	3.45	3.99	6.25 (NCH_2), 7.85–8.60 (CH_2CH_2), 9.15, (CH_3)
tert-Bu[d]	24764-40-7	3.35	4.00	8.64 ($C(CH_3)_3$)
$Si(CH_3)_3$	18276-53-4	3.37	3.84	9.79 ($Si(CH_3)_3$)
CH_2Ph[c,d]	2051-97-0	3.52	3.77	2.85–3.25 (C_6H_5), 5.46 (CH_2)

[a] Solvent $CDCl_3$. [b] Chemical shifts (τ) in parts per million (ppm). [c] *Cf.* R. A. Jones, T. McL. Spotswood, and P. Cheuychit, *Tetrahedron*, **23**, 4469 (1967). [d] Data identical with that for the compound prepared from 2,5-diethoxytetrahydrofuran and the appropriate amine.[4]

Experimental Section

Alkylation of Pyrrylthallium(I).—Pyrrylthallium(I) (0.04 mol) was stirred with the appropriate alkyl halide (0.1 mol) in the absence of a solvent in a flask from which the light was excluded and under the conditions given in Table I. The thallium(I) halide was filtered off and washed with dry ether, and the combined filtrates were analyzed by glpc on a Perkin-Elmer 452 gas chromatograph using a 1 m × 0.25 in. (o.d.) polypropylene glycol on Celite (20:80 w/w) column at 100° with a nitrogen inlet pressure of 15 psig.

1-Methyl-2-formylpyrrole.—The thallium(I) salt of 2-formylpyrrole (0.003 mol), prepared from 2-formylpyrrole and thallium(I) ethoxide, was stirred in the absence of a solvent with methyl iodide (0.01 mol) at room temperature for 5 hr. After removal of the thallium(I) iodide, distillation of the filtrate gave 1-methyl-2-formylpyrrole (91%) which was identical in all respects with a sample prepared by the formylation of 1-methylpyrrole.[4]

Registry No.—Pyrrylthallium(I), 31981-10-9.

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[3] M. J. Zalesko, Ph.D. Thesis, Princeton University, 1970.

[4] C. F. Candy, R. A. Jones, and P. H. Wright, *J. Chem. Soc. C*, 2563 (1970).

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[6] A. J. Castro, J. F. Deck, N. C. Ling, J. P. Marsh, and G. E. Means, *J. Org. Chem.*, **30**, 344 (1965).

Reaction of Azobenzene with Triphenylphosphine

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Diethyl azodicarboxylate reacts vigorously with triethyl phosphite in ether solution to form a 1:1 adduct, described as a colorless, mobile oil.[1] Triphenylphosphine was also reported to react with the azo ester to form a yellowish-white precipitate which became resinous. This material was not characterized but did yield triphenylphosphine oxide on shaking with water.[1]

A number of esters of azodicarboxylic acid, phenyl diazosulfone, and 2,2′,4,4′,6,6′-hexanitroazobenzene were reported to react readily with triethyl and triphenyl phosphite to form adducts.[2] However, the phosphite was believed to add to the carbonyl group of

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[1] D. C. Morrison, *J. Org. Chem.*, **23**, 1072 (1958).

[2] V. A. Ginsburg, M. N. Vasil'eva, S. S. Dubov, and A. Ya. Yakubovich, *Zh. Obshch. Khim.*, **30**, 2854 (1960); *Chem. Abstr.*, **55**, 17477 (1961).