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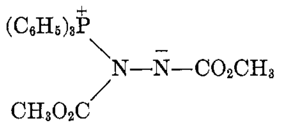
[1] D. C. Morrison, *J. Org. Chem.*, **23**, 1072 (1958).

[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).

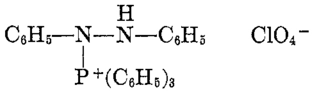
the esters rather than the azo linkage. Azobenzene was reported to be unreactive toward the phosphite esters. Triphenylphosphine reacted with diethyl azodicarboxylate in ether with Dry Ice cooling to give a red solid which formed a "sticky mass" at room temperature and was not characterized.[2]

The adduct which formed between triphenylphosphine and dimethyl azodicarboxylate was produced in solution and found to undergo a variety of cycloaddition reactions with a number of reagents.[3] Apparently the adduct was not isolated. A quasi-1,3-dipole structure was suggested for the adduct as shown in **1**. The triphenylphosphine–diethyl azodicarboxylate adduct was found to catalyze the reaction between the azo ester and several mercaptans to yield disulfides and diethyl hydrazodicarboxylate.[4] The phosphine was recovered unchanged. Formation of the phosphine–azo ester adduct was observed by the decrease in absorption of the azo group at 405 nm.



1

We have found that azobenzene reacts readily with triphenylphosphine at room temperature in aqueous ethanol or methanol containing perchloric acid to form a 1:1:1 adduct of the azo compound, phosphine, and perchloric acid. The reaction can be followed in dilute solution by observing the decrease in absorption of the azo group at 320 nm or the decrease in the polarographic reduction wave for the azo linkage, $E_{1/2} = -0.05$ V *vs.* sce, in perchloric acid solution. In higher concentrations the adduct precipitates in high yield (80–85%) after 5–10 min. The adduct is believed to have the following structure **2**. It appears to be stable, melts to a red-brown liquid at 169–171°, and is very soluble in acetonitrile, dimethylformamide, and dimethyl sulfoxide and does not appear to dissolve in ethanol or water. The infrared spectrum of the compound has numerous peaks characteristic of the phenyl group and an absorption peak at 3200 cm^{-1} which is believed to be due to the N–H stretching mode. The nmr spectrum shows one signal with several peaks at δ 6.7–7.5, a second multipeak signal at δ 7.5–8.4, and a single peak at δ 9.4. These signals have relative areas, in the order given, of 10:14.6:1.3. The nmr spectrum is in agreement with the suggested structure. The uv spectrum has a maximum at 270 nm (ε 8000) and end absorption increasing from 240 nm.



$$\mathrm{C_6H_5{-}\underset{\displaystyle \overset{|}{P}{}^{+}(C_6H_5)_3}{N}{-}\overset{H}{N}{-}C_6H_5 \qquad ClO_4^-}$$

2

The adduct was successfully titrated with KOH in acetonitrile, dimethylformamide, dimethyl sulfoxide, and pyridine. Glass and calomel electrodes were used and a reasonably large (250 mV) break in the potentiometric curve was found. The solutions turned yellow on reacting with base, presumably indicating the regeneration of azobenzene. The equivalent weight was found to be 530, as compared to the calculated value of 545. Other aromatic azo compounds, 4,4′-azodianiline and 4,4′-azodiphenetole, were found to react slowly with triphenylphosphine under the same conditions, but no products were isolated. No reaction was observed between azobenzene and tributylphosphine.

This reaction would appear to be similar to those involving the addition of tertiary phosphines to activated carbon–carbon double bonds.[5] Triphenylphosphine adds to the carbon–carbon double bond of benzalmalononitrile to form an adduct which then adds HCl to give a phosphonium chloride.[6]

Experimental Section

Materials.—Azobenzene and triphenylphosphine were Eastman Reagent chemicals. All other chemicals and solvents were the best available reagent grade materials.

Methods.—Infrared spectra were recorded with a Beckman IR-20 spectrophotometer. A Beckman DK-2A instrument was used to measure uv absorption. The nmr spectra were obtained with a Varian A-60A spectrometer.

Potentiometric titrations were done with a Corning Model 111 digital pH meter equipped with glass and calomel electrodes. A Hewlett-Packard Model 185 CHN analyzer was used for the C, H, and N analyses. The phosphorus analysis was by the Galbraith Laboratories, Knoxville, Tenn.

Preparation of the Adduct.—A solution of azobenzene (1.82 g, 10 mmol) and triphenylphosphine (2.62 g, 10 mmol) was prepared in 100 ml of 95% ethanol; 2 ml of 72% $HClO_4$ (23 mmol) was added to this solution. Precipitation of the adduct began within 5 min. The crystals were filtered after 1 hr and washed with ethanol. A yield of 4.63 g (85%) was obtained. The compound melts with decomposition to a red-brown liquid at 169–171°. The adduct was also prepared using aqueous methanol (10% H_2O) as solvent with about the same yield.

Anal. Calcd for $C_{30}H_{26}ClN_2O_4P$: C, 66.1; H, 4.82; N, 5.13; P, 5.69. Found: C, 65.8; H, 4.68; N, 5.28; P, 5.63.

Potentiometric Titrations.—Weighed amounts (0.05–0.2 mmol) of the adduct were titrated with standard solutions of KOH (0.02–0.04 *M*) in ethanol. Reaction was rapid and reasonably stable readings were obtained in dimethyl sulfoxide. The equivalent weight found was 530, compared with a calculated value of 545.

Registry No.—**2**, 32120-81-3; azobenzene, 103-33-3; triphenylphosphine, 603-35-0.

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A Novel Two-Step Synthesis of 10*H*-Benz[*b*]indeno[2,1-*d*]thiophene. Heterocyclopentadienes. III

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A particularly successful method for the synthesis of monoheterocyclopentadienes (**1**) is the addition of

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