# Reactions of Lead Tetra-acetate. Part V.[1] The Synthesis of 1-Phenylindazole and Some Derivatives, Pyridylindazoles, and Thienopyrazoles

By W. A. F. Gladstone and R. O. C. Norman

The method for synthesising indazoles from the arylhydrazones of aromatic ketones, by oxidation with lead tetra-acetate followed by cyclisation of the resulting azoacetates with a Lewis acid, has been extended to members of the groups of compounds named in the title.

We report here the concluding results of an exploratory study of our method for synthesising indazoles by the oxidation of aromatic ketone arylhydrazones with lead tetra-acetate followed by treatment of the resulting azoacetates with Lewis acids.[2,3]

[1] Part IV, B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1966, 86.

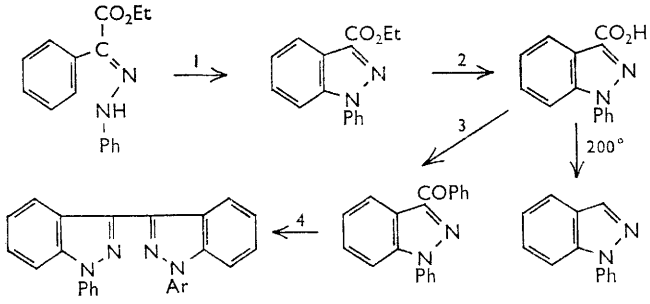
1-*Phenylindazole and Some* 3-*Derivatives*.—The phenylhydrazone of ethyl benzoylformate reacted with lead tetra-acetate to give an azoacetate which was cyclised to

[2] W. A. F. Gladstone and R. O. C. Norman, *J. Chem. Soc.*, 1965, 3048.

[3] W. A. F. Gladstone and R. O. C. Norman, *J. Chem. Soc.*, 1965, 5177.

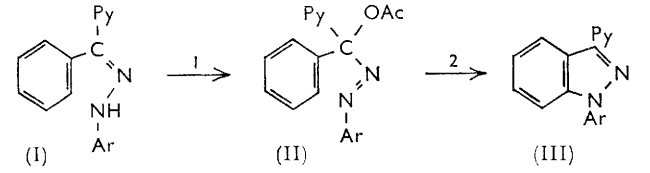
3-ethoxycarbonyl-1-phenylindazole both by boron trifluoride and by aluminium trichloride. Isolation of the azoacetate proved to be unnecessary: treatment of the impure oxidation mixture with boron trifluoride–ether complex gave the indazole in 74% overall yield. The ester could be hydrolysed quantitatively to the carboxylic acid.

This efficient route to 1-phenylindazole-3-carboxylic acid provides a method for synthesising a number of 3-substituted indazoles. The following are examples. (i) Decarboxylation of the acid at 200° gave 1-phenylindazole in 65% yield. (ii) 3-Benzoyl-1-phenylindazole was prepared in 50% yield from the acid by treatment with thionyl chloride followed by aluminium trichloride in benzene. (iii) This product was converted in low yield, *via* its *p*-nitrophenylhydrazone and the corresponding azoacetate, into 1-*p*-nitrophenyl-1′-phenyl-3,3′-biindazolyl.



Reagents: 1, $Pb(OAc)_4$, $BF_3$; 2, $OH^-$; 3, $SOCl_2$,PhH–$AlCl_3$; 4, $ArNH{\cdot}NH_2$, $Pb(OAc)_4$, $BF_3$.

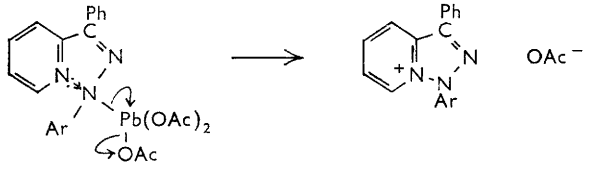
*Pyridylindazoles.*—The phenyl- and *p*-nitrophenylhydrazones of 2- and 3-benzoylpyridine, and the *p*-nitrophenylhydrazone of 4-benzoylpyridine, underwent cyclisation, though with markedly different efficiencies. Our previous studies of the effects of substituents on the direction of ring-closure [2] indicated that cyclisation should occur into the benzene rather than the pyridine ring, and the close similarity of the ultraviolet spectra of the products to those of analogous 1-arylindazoles [2,3] is consistent with the products being indazoles and not pyridinopyrazoles.



Reagents: 1, $Pb(OAc)_4$; 2, Lewis acid

a: Ar = $C_6H_5$, Py = 2-pyridyl; b: Ar = *p*-$C_6H_4NO_2$, Py = 2-pyridyl; c: Ar = $C_6H_5$, Py = 3-pyridyl; d: Ar = *p*-$C_6H_4NO_2$, Py = 3-pyridyl; e: Ar = *p*-$C_6H_4NO_2$, Py = 4-pyridyl.

Various methods [2,3] were investigated for these conversions. The azoacetate (IIc) was not cyclised by boron trifluoride but treatment of the corresponding phenylhydrazone (Ic) with lead tetra-acetate followed by aluminium trichloride gave the indazole (IIIc) in 59% yield. The *p*-nitrophenylhydrazones (Id) and (Ie) were cyclised in 79 and 91% overall yield, respectively, by lead tetra-acetate followed by boron trifluoride in benzene. The 2-pyridyl compounds gave much lower yields: the phenylhydrazone (Ia) was cyclised in only 1·5% yield by the method which gave 59% for the 3-pyridyl analogue (Ic) and the *p*-nitrophenylhydrazone (Ib) gave only 3% of the corresponding indazole (IIIb) when treated by the method used successfully for the 3- and 4-pyridyl analogues. The latter yield was raised to 22% when a mixture of lead tetra-acetate and the boron trifluoride–ether complex in benzene was used. The lower yields from the 2- compared with the 3- and 4-pyridyl compounds may be due to the fact that the azoacetate is formed *via* an organo-lead intermediate which, in the case of the 2-pyridyl compound, undergoes an intramolecular reaction, as shown, to give a water-soluble product which is ultimately lost in the work-up procedure. In accord with this, when an attempt was made to isolate the azoacetate (IIb) the organic residue accounted for only a small fraction of the reactant. Other examples of such intramolecular displacements during oxidations by lead tetra-acetate are discussed in a later Paper.[4]

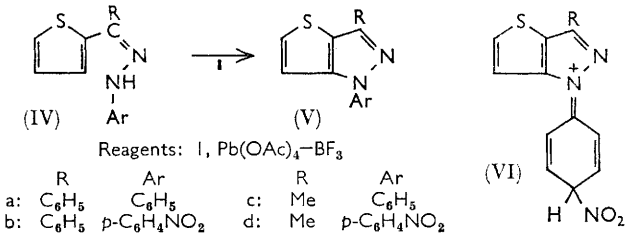


*Thienopyrazoles.*—Arylhydrazones of both 2-benzoyl- and 2-acetylthiophen were cyclised to give the thieno[3,2-*c*]pyrazole ring system, which has not previously been obtained. That cyclisation of the 2-benzoyl compounds should occur onto the thiophen ring rather than onto the benzene ring was expected from the known greater reactivity towards electrophiles of thiophen at the 3-position than of benzene at any one position,[5] together with our previous observations of substituent effects on cyclisation.[2] This expected orientation was verified by examination of the proton magnetic resonance (p.m.r.) spectrum of the product from the *p*-nitrophenylhydrazone (IVb): this had an AB quartet ($J$ = 5·7 c./sec.) due to two adjacent protons on the thiophen ring, consistent only with the structure (Vb). The structure of the product from the phenylhydrazone (IVa) could not be elucidated from its p.m.r. spectrum, but verification of the expected structure (Va) was obtained from the finding that nitration of the product gave the thienopyrazole (Vb).

These transformations required careful handling owing to the instability of the intermediate azoacetates. Treatment of the phenylhydrazone (IVa) with lead tetra-acetate in methylene dichloride led to the immediate formation of a black tar from which no pure materials could be isolated, but when boron trifluoride–

[4] W. A. F. Gladstone and R. O. C. Norman, *J. Chem. Soc.* (*C*), 1966, 1536.
[5] F. B. Deans and C. Eaborn, *J. Chem. Soc.*, 1959, 2303.

ether complex and benzene were included in the reaction mixture which was cooled and shaken for only 1 min. before being poured into water, the thienopyrazole (Va) was obtained in 74% yield. The same method gave the thienopyrazoles (Vb—d) in 60, 14, and 12% yields,




| | R | Ar | | R | Ar |
|---|---|---|---|---|---|
| a: | $C_6H_5$ | $C_6H_5$ | c: | Me | $C_6H_5$ |
| b: | $C_6H_5$ | $p$-$C_6H_4NO_2$ | d: | Me | $p$-$C_6H_4NO_2$ |

respectively; the lower yields from acetyl compared with those from benzoyl compounds have been noted before.[2,3]

Nitration of the thienopyrazoles (Va) and (Vc) gave the nitro-derivatives (Vb) and (Vd), respectively, with no trace of compounds containing a nitro-group in the thiophen ring. This result is consistent with the current view of electrophilic aromatic substitution. The unshared electron-pair at N–1 is able to aid delocalisation of the positive charge in the transition state for nitration of the benzenoid ring, as represented by the contribution of the structure (VI), but not for nitration at the 4- or 5-positions of the thiophen ring. This potential is evidently more significant than that of the sulphur atom which activates the unsubstituted positions in the thiophen ring.

## EXPERIMENTAL

Lead tetra-acetate was from Hopkin and Williams (guaranteed 85% purity). Chromatography was on alumina (Spence type "H"). Proton magnetic resonance spectra were measured in solution in deuterochloroform (unless stated otherwise) on a Perkin-Elmer 60 Mc. spectrometer; those of *p*-nitrophenyl fragments had the characteristics previously described.[3] Other materials were as described previously.[2]

Arylhydrazones were prepared by standard methods. 3-*Benzoylpyridine* p-*nitrophenylhydrazone* had m. p. 200—201° (from methanol) (Found: C, 67·9; H, 4·1; N, 16·7. $C_{18}H_{14}N_4O_2$ requires C, 67·9; H, 4·4; N, 17·6%). 2-*Benzoylthiophen phenylhydrazone* had m. p. 91—92° (from ethanol) (Found: C, 73·3; H, 5·1; N, 9·8; S, 11·15. $C_{17}H_{14}N_2S$ requires C, 73·3; H, 5·1; N, 10·1; S, 11·5%). 2-*Benzoylthiophen* p-*nitrophenylhydrazone* had m. p. 145—162° (mainly at 145—147 and 161—162°, from either ethanol or light petroleum-chloroform; 157—161° after resolidification. The two geometrical isomers may be present) (Found: C, 63·0; H, 3·9; N, 13·4; S, 10·2. $C_{17}H_{13}N_3O_2S$ requires C, 63·1; H, 4·0; N, 13·0; S, 9·9%).

Azoacetates, where isolated, were prepared by the method of Iffland *et al.*[6] except that the products were purified by chromatography. In other cases the solution of the azoacetate was freed from lead salts and acetic acid by treatment, successively, with a very dilute hydrazine solution and aqueous sodium hydrogen carbonate. α-(3′-*Pyridyl*)-α-p-*nitrophenylazobenyzl acetate* (33%) had m. p. 114—115° (from light petroleum–chloroform) (Found: C, 63·6; H, 4·4; N, 15·0. $C_{20}H_{16}N_4O_4$ requires C, 63·8; H, 4·3; N, 14·9%). α-(2′-*Thienyl*)-α-p-*nitrophenylazobenzyl acetate* (51%) was an orange solid, m. p. 118—119° (from light petroleum-chloroform), which decomposed on standing in air (Found: C, 60·1; H, 4·4; N, 10·65; S, 8·1. $C_{19}H_{15}N_3O_4S$ requires C, 59·8; H, 4·0; N, 11·0; S, 8·4%). α-Ethoxycarbonyl-α-phenylazobenzyl acetate was a yellow oil which was not further purified after chromatography (p.m.r. spectrum: multiplet (10H), *ca.* τ 2·5; quartet (2H), centred at τ 5·76 ($J$ = 7·2 c./sec.); singlet (3H), τ 7·74; triplet (3H), centred at τ 8·75 ($J$ = 7·2 c./sec.). α-(3′-Pyridyl)-α-phenylazobenzyl acetate was an orange oil (carbonyl absorption at 1750 cm.$^{-1}$) which was not further purified after chromatography. α-(2′-Thienyl)-α-phenylazoethyl acetate was a dark oil (carbonyl absorption at 1735 cm.$^{-1}$) which rapidly decomposed. An attempt to prepare α-(2′-thienyl)-α-phenylazobenzyl acetate gave only a black tar together with starting material.

*Products from Ethyl Benzoylformate.*—Boron trifluoride–ether complex (50 ml.) was added to a solution of α-ethoxycarbonyl-α-phenylazobenzyl acetate (8·5 g.) in ether (20 ml.) at 0°, and the red solution was heated on the water-bath for 20 min. and poured into water. The resulting yellow solid was washed with dilute aqueous sodium hydroxide and crystallised from ethanol to give 3-*ethoxycarbonyl*-1-*phenylindazole* (5 g.; 73%), m. p. 114—115°, $\lambda_{max.}$ (in ether) 250, 265, 276, and 305 mμ (Found: C, 72·3; H, 5·6; N, 10·4. $C_{16}H_{14}N_2O_2$ requires C, 72·2; H, 5·3; N, 10·5%).

A solution of another portion of the azoacetate (13·5 g.) in benzene (250 ml.) was heated under reflux for 1 hr. over aluminium trichloride (20 g.). Hydrolysis followed by removal of the benzene and crystallisation from ethanol gave 3-ethoxycarbonyl-1-phenylindazole (5·5 g.; 50%).

In a third experiment, ethyl benzoylformate phenylhydrazone (23·5 g.) was treated with lead tetra-acetate and the resulting oil, without attempted purification, was treated with boron trifluoride–ether complex as above. 3-Ethoxycarbonyl-1-phenylindazole was obtained in 74% overall yield from the phenylhydrazone.

A suspension of 3-ethoxycarbonyl-1-phenylindazole (4·20 g.) in aqueous N-sodium hydroxide (110 ml.) was heated under reflux until solution was complete (4 hr.). The cooled solution was diluted with water (200 ml.), washed with ether (50 ml.), and acidified, giving 1-*phenylindazole*-3-*carboxylic acid* (3·75 g.; 99·7%), m. p. 180° (decomp.) (from aqueous ethanol); $\lambda_{max.}$ as for the ethyl ester (Found: C, 70·8; H, 4·2; N, 11·5. $C_{14}H_{10}N_2O_2$ requires C, 70·6; H, 4·2; N, 11·8%). When a small portion of this compound was heated, it effervesced on melting to give a product which was insoluble in aqueous sodium hydroxide.

A solution of 3-ethoxycarbonyl-1-phenylindazole (6·5 g.) in ethanol (100 ml.) and water (20 ml.) containing sodium hydroxide (5 g.) was heated under reflux for 30 min. The ethanol was distilled and the cooled mixture was acidified and extracted with ether. The ether was distilled and the residue was heated slowly until effervescence ceased. An ethereal solution of this product was washed with aqueous sodium hydroxide and water, dried ($MgSO_4$), and the ether

[6] D. C. Iffland, L. Salisbury, and W. R. Schafer, *J. Amer. Chem. Soc.*, 1961, **83**, 747.

[7] J. P. Burnett and C. Ainsworth, *J. Org. Chem.*, 1958, **23**, 1382.

distilled to give 1-phenylindazole (3·0 g.; 65%), m. p. 80—81·5° (from light petroleum), identical (m. p., mixed m. p., and infrared spectrum) with authentic material[7] (Found: C, 80·5; H, 5·3; N, 14·2. Calc. for $C_{13}H_{10}N_2$: C, 80·4; H, 5·2; N, 14·4%).

Treatment of 1-phenylindazole-3-carboxylic acid with thionyl chloride, followed by aluminium trichloride in benzene under reflux (1 hr.), gave *3-benzoyl-1-phenylindazole* (50%), m. p. 146—147° (from light petroleum); $\lambda_{max.}$ (in ether) 246 and 322 mμ (Found: C, 80·7; H, 4·8; N, 9·6. $C_{20}H_{14}N_2O$ requires C, 80·5; H, 4·7; N, 9·4%).

3-Benzoyl-1-phenylindazole (2 g.) in acetic acid (100 ml.) was heated under reflux with *p*-nitrophenylhydrazine (1·5 g.). Concentration of the acetic acid gave the p-*nitrophenylhydrazone* (1·8 g.), m. p. 202—204° (from acetic acid) (Found: C, 71·6; H, 4·2; N, 15·9. $C_{26}H_{19}N_5O_2$ requires C, 72·0; H, 4·4; N, 16·2%). The crude material (1·6 g.) in methylene dichloride (100 ml.) was treated with lead tetra-acetate (3 g.) in methylene dichloride (100 ml.). After removal of lead compounds and distillation of the methylene dichloride, the residue was chromatographed in light petroleum–ether (4 : 1, v/v) to give, successively, 3-benzoyl-1-phenylindazole (0·5 g.) and a viscous yellow oil which was heated for 10 min. at 100° with boron trifluoride–ether complex (30 ml.). After hydrolysis, the olive-green solid was extracted into chloroform and chromatographed to give, with light petroleum–ether (4 : 1, v/v), 3-benzoyl-1-phenylindazole (0·2 g.) and, with light petroleum–ether (3 : 7, v/v), *1-phenyl-1′-p-nitrophenyl-3,3′-bi-indazolyl* (0·07 g.), m. p. 233—235° (from n-butanol); $\lambda_{max.}$ (in ethanol) 225, 260sh, 319sh, 332, and 371 mμ (Found: C, 72·0; H, 4·0; N, 16·3. $C_{26}H_{17}N_5O_2$ requires C, 72·4; H, 4·0; N, 61·2%).

*Products from 3-Benzoylpyridine*.—A suspension of lead tetra-acetate (35 g.) in acetic acid (100 ml.) was added to 3-benzoylpyridine phenylhydrazone (18 g.) suspended in benzene (600 ml.). After 3 hr. the mixture was washed with water, aqueous sodium hydrogen sulphite, aqueous sodium carbonate, and water, and dried ($CaCl_2$). The solution was heated under reflux for 30 min. over aluminium trichloride (25 g.) and poured, cold, into water (2 l.) containing sodium hydroxide (100 g.). The organic layer was dried ($MgSO_4$) and the residue in light petroleum–chloroform (9 : 1, v/v) was filtered through alumina to give *1-phenyl-3-(3′-pyridyl)indazole* (10·5 g.; 58·8%), m. p. 94—96° (from light petroleum); $\lambda_{max.}$ (in ether) 244, 262, and 316 mμ (Found C, 79·1; H, 4·8; N, 16·1. $C_{18}H_{13}N_3$ requires C, 79·7; H, 4·8; N, 15·5%).

Lead tetra-acetate (15 g.) was added to a suspension of 3-benzoylpyridine *p*-nitrophenylhydrazone (7 g.) in benzene (300 ml.) and acetic acid (50 ml.). When the hydrazone had all dissolved (20 min.), lead compounds and acetic acid were removed (see above) and the benzene solution of the azoacetate was heated to 60° with boron trifluoride–ether complex (50 ml.). Water (500 ml.) was added and the mixture was distilled until the benzene had been removed, leaving 1-p-*nitrophenyl-3-(3′-pyridyl)indazole* (5·5 g.; 79%), m. p. 253° (from n-butanol); $\lambda_{max.}$ (in ethanol) 228, 269sh, 303, and 348 mμ (Found: C, 67·7; H, 3·9; N, 17·4. $C_{18}H_{12}N_4O_2$ requires C, 68·3; H, 3·8; N, 17·7%).

*Product from 4-Benzoylpyridine*.—When treated in the same way as its 3-isomer, 4-benzoylpyridine *p*-nitrophenylhydrazone (4·4 g.) gave, after chromatography, 1-p-*nitrophenyl-3-(4′-pyridyl)indazole* (4·0 g.; 91%), m. p. 218—220° (from benzene, followed by sublimation *in vacuo*); $\lambda_{max.}$ (in methanol) 226, 258sh, 276, 308, and 352 mμ (Found: C, 68·9; H, 3·8; N, 17·7. $C_{18}H_{12}N_4O_2$ requires C, 68·3; H, 3·8; N, 17·7%).

*Products from 2-Benzoylpyridine*.—When treated in the same way as its 3-isomer, 2-benzoylpyridine phenylhydrazone (27 g.) gave *1-phenyl-3-(2′-pyridyl)indazole* (0·4 g.; 1·5%), m. p. 58—60° (from light petroleum); $\lambda_{max.}$ (in ether) 243, 270sh, and 322 mμ (Found: C, 79·1; H, 4·7; N, 15·7. $C_{18}H_{13}N_3$ requires C, 79·7; H, 4·8; N, 15·5%).

A solution of 2-benzoylpyridine *p*-nitrophenylhydrazone (0·3 g.) in benzene (150 ml.) was treated with a mixture of lead tetra-acetate (2 g.), benzene (40 ml.), and boron trifluoride–ether complex (20 ml.). After 5 min. on the water-bath, the solution was poured into aqueous 2N-sodium hydroxide and filtered. The residue was washed with chloroform (20 ml.) and the washings, together with the organic layer of the filtrate, were evaporated. Chromatography of the residue in light petroleum–ether (17 : 3, v/v) gave 1-p-*nitrophenyl-3-(2′-pyridyl)indazole* (0·065 g.; 22%), m. p. 210° (from n-butanol); $\lambda_{max.}$ (in ethanol) 229, 282sh, 304, and 354 mμ (Found: C, 68·1; H, 3·9; N, 17·0. $C_{18}H_{12}N_4O_2$ requires C, 68·3; H, 3·8; N, 17·7%). This indazole (3·5%) was also formed by treating 2-benzoylpyridine *p*-nitrophenylhydrazone in the same way as its 3-isomer.

*Products from 2-Benzoylthiophen*.—A cooled mixture of lead tetra-acetate (45 g.), boron trifluoride–ether complex (200 ml.), methylene dichloride (200 ml.), and benzene (400 ml.) was added to 2-benzoylthiophen phenylhydrazone (17·2 g.) in benzene (600 ml.). After 1 min. (shaking) the mixture was poured into water and the benzene layer was washed with aqueous sodium hydroxide, dried ($MgSO_4$), and distilled. The residue, after chromatography in light petroleum–ether (4 : 1, v/v), gave *1,3-diphenylthieno[3,2-c]pyrazole* as a pale brown solid (12·5 g.; 73%), m. p. 138—139° (from ethanol). The m. p. was not raised by elution of a portion in light petroleum from alumina, although the resulting material was colourless; $\lambda_{max.}$ (in ethanol) 226 (ε 24,800), 255 (ε 20,700), 312 mμ (ε 29,800) (Found: C, 73·8; H, 4·4, N, 10·1; S, 11·8. $C_{17}H_{12}N_2S$ requires C, 73·9; H, 4·4; N, 10·1; S, 11·6%).

A finely divided suspension of this compound (3·1 g.) in acetic anhydride (100 ml.) at 0° was treated dropwise with nitric acid (*d* 1·5) (0·75 ml.). The mixture was allowed to warm to room temperature, giving a yellow precipitate. The whole was poured into warm water and the yellow solid was washed with hot water and, when dry, was chromatographed in light petroleum–ether (4 : 1, v/v) to give 1-p-*nitrophenyl-3-phenylthieno[3,2-c]pyrazole* (2·7 g.), m. p. 177—179° (from ethanol–acetone); $\lambda_{max.}$ (in ethanol) 245 (ε 19,800), 280sh, and 360 mμ (ε 32,100); p.m.r. spectrum (in dioxan): $A_2B_2$ quartet, centred at τ 1·63 and 1·91 ($J_{AB}$ = 9·3 c./sec.), AB quartet, centred at τ 2·22 and 2·46 ($J$ = 5·7 c./sec.), both superimposed on unresolved resonances (Found: C, 63·3; H, 3·5; N, 13·1; S, 10·1. $C_{17}H_{11}N_3O_2S$ requires C, 63·5; H, 3·5; N, 13·1; S, 10·0%).

This compound was also obtained (60%) by treating the *p*-nitrophenylhydrazone of 2-benzoylthiophen as for the phenylhydrazone.

*Products from 2-Acetylthiophen*.— 2-Acetylthiophen phenylhydrazone (12·5 g.) was treated in the same way as the 2-benzoyl analogue. Chromatography of the resulting oil in light petroleum gave, successively, biphenyl (0·25 g.) and a pale yellow oil which was crystallised from light petroleum (b. p. 30—40°) at −50° to give *1-phenyl-3-*

*methylthieno*[3,2-c]*pyrazole* (0·5 g.), m. p. 46—47°; $\lambda_{max.}$ (in ethanol) 243 (ε 11,600) and 293 mμ (ε 16,700); p.m.r. spectrum: AB quartet, centred at τ 2·59 and 2·83 ($J$ = 5·4 c./sec.), superimposed on a multiplet (total 7H), singlet (3H), τ 7·40 (Found: C, 67·0; H, 4·5; N, 13·1; S, 15·0. $C_{12}H_{10}N_2S$ requires C, 67·3; H, 4·7; N, 13·1; S, 15·0%). A further chromatographic fraction consisted of this pyrazole and a little 2-acetylthiophen. It was mixed with the mother-liquors from the crystallisation and treated with 2,4-dinitrophenylhydrazine as described previously,[3] giving a further quantity of the pyrazole (1·3 g.). This was nitrated, as described above, to give 1-p-*nitrophenyl*-3-*methylthieno*[3,2-c]*pyrazole* (0·96 g.), m. p. 155—156° (from n-butanol); $\lambda_{max.}$ (in ethanol) 237 (ε 13,100), 272sh, and 347 mμ (ε 24,000); p.m.r. spectrum: $A_2B_2$ quartet (4H), centred at τ 1·69 and 2·13 ($J_{AB}$ = 9·3 c./sec.), AB quartet (2H), centred at τ 2·43 and 2·71 ($J$ = 5·4 c./sec.), singlet (3H), τ 7·50 (Found: C, 55·5; H, 3·55; N, 16·35; S, 12·3. $C_{12}H_9N_3O_2S$ requires C, 55·6; H, 3·5; N, 16·2; S, 12·4%).

This compound was also obtained (12%) by treating the *p*-nitrophenylhydrazone of 2-acetylthiophen (7 g.) as for the phenylhydrazone. 4-Nitrobiphenyl (20 mg.) was also isolated, together with an unidentified solid (50 mg.) which had strong absorption at 2130 cm.$^{-1}$

*Added in proof.*—It has recently come to our notice that R. Kuhn and W. Münzing (*Chem. Ber.*, 1952, **85**, 29) isolated 1,3-diphenyl-8-azaindazolium chloride in 44% yield by treating the *syn*-isomer of 2-benzoylpyridine phenylhydrazone with lead tetra-acetate followed by hydrogen chloride. This is in accord with our suggested explanation for the low yields of indazoles from 2-benzoylpyridine arylhydrazones.

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