2-ISOTHIOCYANATOBENZYLTRIPHENYLPHOSPHONIUM BROMIDES — NEW TYPE OF FUNCTIONALIZED HETEROCUMULENES SUITABLE FOR SYNTHESIS OF INDOLE DERIVATIVES

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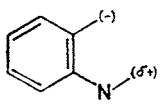
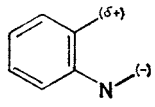
Reaction of 2-bromomethylphenyl isothiocyanates with triphenylphosphine afforded triphenyl-(2-isothiocyanatobenzyl)phosphonium salts. Thier reaction with bases liberated the corresponding carbanions which on intramolecular addition to the N=C=S group gave substituted 3-triphenylphosphoniumindolyl-2-thiolates. These compounds did not react in the Wittig reaction but underwent electrophilic reactions on the sulfur atom or on the indol nitrogen atom. According to a detailed analysis of ^{1}H, ^{13}C, ^{31}P NMR and mass spectra, the indole derivatives exist predominantly in the betaine form. X-Ray diffraction analysis of the unsubstituted betaine, 3-triphenylphosphoniumindolyl-2-thiolate, agrees well with the spectral results.

Syntheses of the indole system are based mostly on formation of the C-2—C-3 bond *via* carbanion of the type *A* or *B*.



A

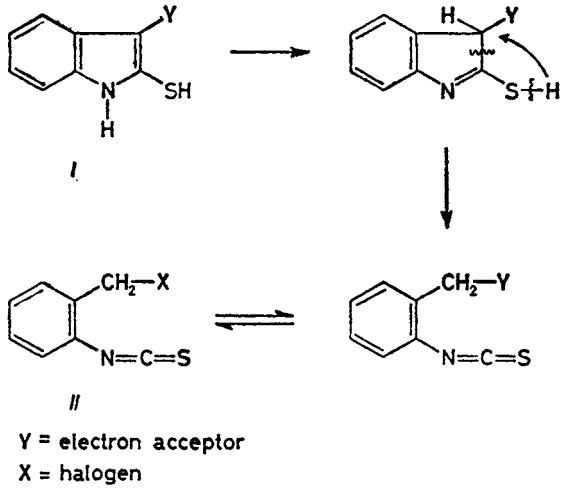


B

The Madelung's synthesis[1] from N-acyl-*o*-toluidines *via* carbanions of the type *A* is the most known example. However, because of low acidity of the methyl protons the reaction requires high temperatures (250°C) and the presence of a strong base ($NaNH_2$) which represents a certain drawback..

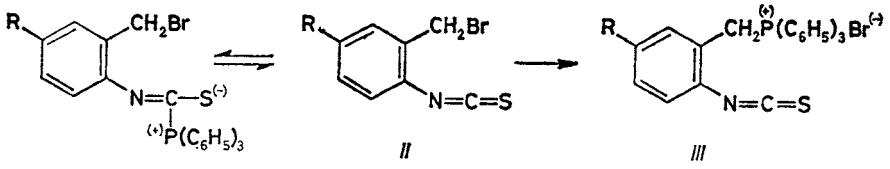
In this work we tried to utilize some 2-bromomethylphenyl isothiocyanates *II* for the synthesis of 2-thiosubstituted indole derivatives *I* according to the retro synthesis depicted in Scheme 1.

2-Bromomethylphenyl isothiocyanates *II* which represent synthetic equivalents of indoles *I* were prepared by radical bromination of *o*-tolyl isothiocyanates with N-bromosuccinimide[2]. These bielectrophilic compounds undergo nucleophilic addition-cyclization reactions, starting by nucleophilic attack at the heterocumulene grouping as the more reactive of both reactive groups (CH_2Br and NCS)[2,3]. We suc-



SCHEME 1

ceeded in substituting the bromine atom in the CH_2Br group by such nucleophiles that do not form stable addition compounds with the NCS group, *e.g.*, triphenylphosphine (Scheme 2).

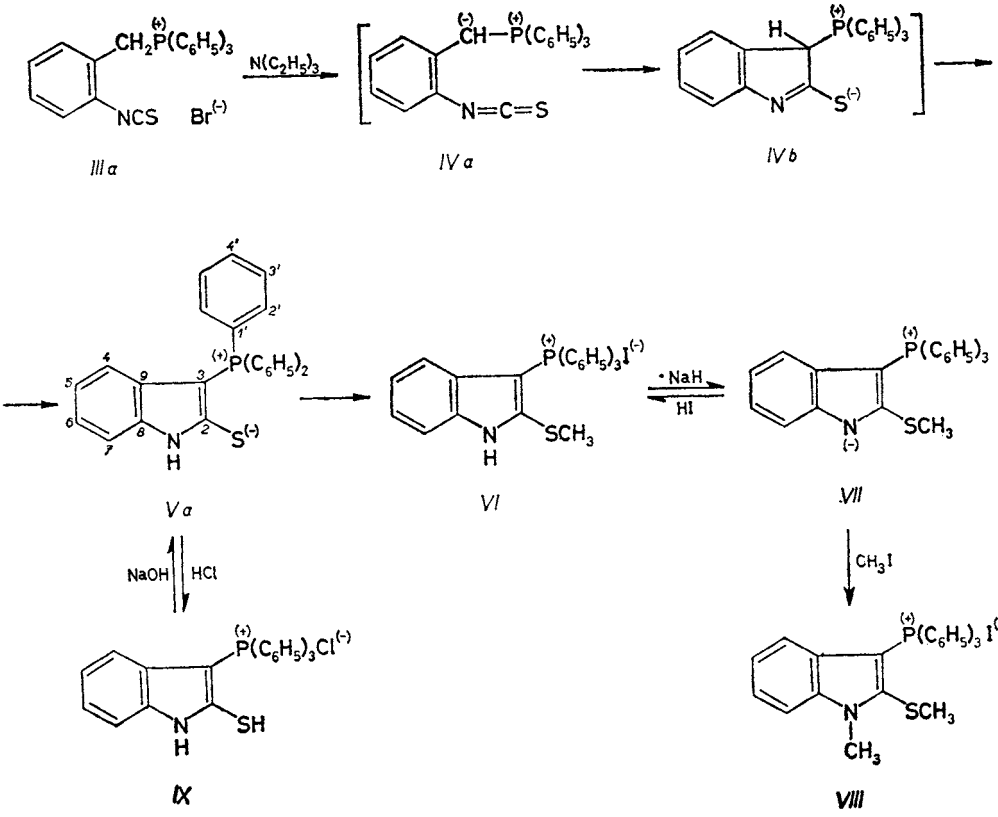


SCHEME 2

The synthesized 2-isothiocyanatobenzyltriphenylphosphonium bromides *III* represent a new type of functionalized heterocumulenes suitable for synthesis of indole derivatives. Because of the electron acceptor character of the triphenylphosphonium group, the CH_2 group in these isothiocyanates behaves as a CH-acid capable of forming the corresponding carbanion when treated with bases. Thus, the mentioned reaction sequence leads to reactivity inversion of one of the two electrophilic centers (CH_2Br group) in compounds *II*. This situation gave impetus to a study of the intramolecular cyclization.

On treatment with bases (*e.g.* triethylamine), the CH_2 group in 2-isothiocyanatobenzyltriphenylphosphonium bromides *III* loses proton under formation of carba-

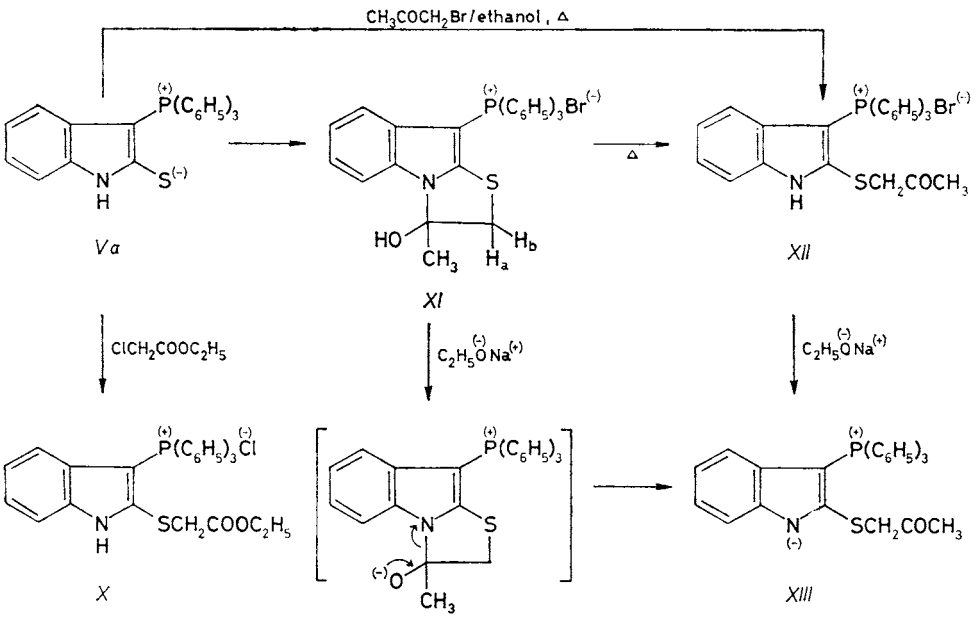
nion *IVa*. Intramolecular nucleophilic addition (Ad_{Ni}) to the NCS group and subsequent stabilization of the cyclic intermediate *IVb* by proton transfer from the C-3 carbon atom to the indole nitrogen atom (aromatization) affords 3-triphenylphosphoniumindolyl-2-thiolates *V* (Scheme 3). This process can be regarded as an intramolecular reaction of isothiocyanate with the phosphorus ylide. We have found that, thanks to the suitable position of both reaction centers, the intramolecular cyclization is much preferred over the intermolecular Wittig reaction of the intermediate *IVa*. Thus, for example, when triethylamine was added to solutions of isothiocyanates *III* in aqueous methanol, containing a several hundredfold excess of formaldehyde, compounds *V* were again obtained as the sole products; no *o*-styryl isothiocyanates were formed. Similarly, deprotonation of isothiocyanate *IIIa* with triethylamine in the presence of large excess of methyl iodide afforded 2-methylthioindolyl-3-triphenylphosphonium iodide (*VI*) (Scheme 3). This compound arose in quantitative yield by reaction of compound *Va* with methyl iodide. On treatment with sodium hydride in dimethyl sulfoxide, compound *VI* was converted to 2-methyl-



IIIa *IVa* *IVb* *Va* *VI* *VII* *IX* *VIII*

SCHEME 3

-thio-3-triphenylphosphoniumindolate (*VII*) which was easily further alkylated with methyl iodide to give 1-methyl-2-methylthioindolyl-3-triphenylphosphonium iodide (*VIII*) (Scheme 3). Compound *V* and *VII* reacted with hydrogen halides under formation of the corresponding phosphonium salts *IX* and *VI* which liberated the starting compounds on treatment with bases. Compounds *V* reacted even with less reactive halogeno derivatives: For example, alkylation with ethyl chloroacetate afforded 2-ethoxycarbonylmethylthioindolyl-3-triphenylphosphonium chloride (*X*) (Scheme 4). Reaction of *Va* with bromoacetone was more complex. At temperatures

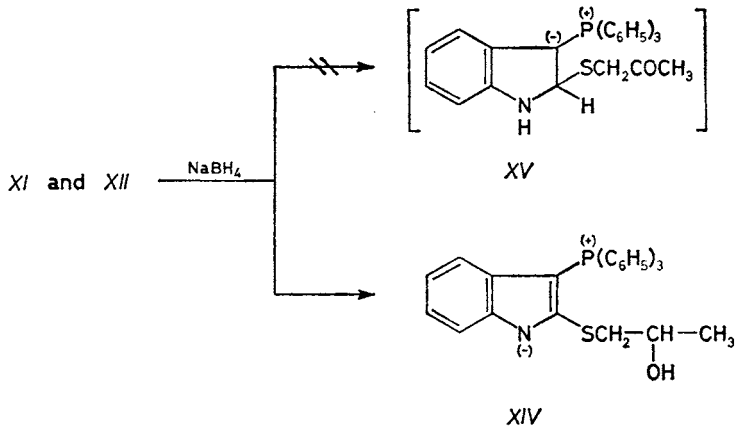


SCHEME 4

above 15°C we obtained the corresponding thiazolo[1,2-*b*]indole *XI* which on heating in ethanol gave the originally expected 2-(2-oxopropylthio)indolyl-3-triphenylphosphonium bromide (*XII*). The surprising irreversibility of the reaction *XI* → *XII* indicates that the nucleophilic replacement of bromine by sulfur takes place either after, or simultaneously with, the nucleophilic addition of the indole NH group to the bromoacetone carbonyl. The formation of *XI* is not exceptional. This type of compounds can be prepared by reaction of thioamides, or heterocyclic compounds with an —NH—CS— grouping, with α-haloketones[4–7].

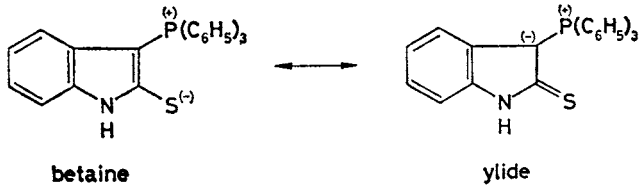
Reaction of *XII* with sodium ethoxide afforded 2-(2-oxopropylthio)-3-triphenylphosphoniumindolate (*XIII*). Compounds *XI* and *XII* were reduced with sodium borohydride in ethanol to 2-(2-hydroxypropylthio)-3-triphenylphosphoniumindolate

(*XIV*) (Scheme 5). Thus, the carbonyl group rather than the indole C-2—C-3 double bond was reduced because reduction of the latter should give the intermediate *XV* suitable for intramolecular Wittig reaction.



SCHEME 5

Compounds *V* do not react in the Wittig reaction with aldehydes even under drastic conditions. Also introduction of the carbonyl component directly into the molecule (compound *XIII*) did not lead to the desired result. Characteristic for these compounds are alkylations at the sulfur atom; formation of alkylation products at the C-3 atom was not observed. On the basis of these data we can assume that the compounds *V* are betaines. The ylide mesomeric structure contributes little and can be considered only in connection with some spectral data (Scheme 6).



SCHEME 6

The reaction isothiocyanate *III* → betaine *V* is accompanied by an $sp^3 \rightarrow sp^2$ hybridization change of the CH_2 carbon atom that has its characteristic manifestation in the ^1H NMR and ^{13}C NMR spectra. Whereas in isothiocyanates *III* the triphenylphosphonium group influences chemical shifts of the benzene protons only by the strong I-effect, in compounds *V* also a mesomeric interaction with π-electrons

of the aromatic system can exist. Therefore, chemical shifts of the H-4—H-7 protons are within the interval $\delta = 1{\cdot}91$ (Table I).

As follows from the ^{13}C NMR spectra of indole and its derivatives, chemical shifts of carbon atoms C-8 and C-9 are only little affected by 1,2-substitution. In all the derivatives synthesized, the shifts of their signals agree relatively well with those for carbon atoms in unsubstituted indoles (Table II). Chemical shifts of the C-2 and C-3 atoms differ extremely from each other and considerably from those of indole. The downfield shift of the C-2 signal (δ 173·2; $\Delta\delta$ 49·2) for *Va* and upfield shift of the C-3 signal (δ 75·0; $\Delta\delta$ 27·0) as compared with indole is caused by strong polarization of the $^{(+)}P(C_6H_5)_3—C=C—S^{(-)}$ system. The same changes in chemical shifts of the double bond carbon atom signals relative to those in unsubstituted ethylene were observed with vinyltriphenylphosphonium salts[8]. If the β-carbon atom of such double bond bears a substituent with lone electron pair, the chemical shift changes for the C-α and C-β signals are still more pronounced[9,10] and agree qualitatively with the observed shifts of the C-2 and C-3 signals in the compounds synthesized. Comparison of C-2 and C-3 chemical shifts in the "methylated" derivatives *VI*, *VIII* (in which the double bond is "fixed" between C-2 and C-3) and betaines *V*, together with the simple fact that chemical shifts of carbon atom signals depend on their hybridization, indicates indirectly that also the "ylide" resonance structure contributes to the actual structure of these compounds (Scheme 6).

TABLE I

Chemical shifts in ^1H NMR spectra of the synthesized compounds

Compound	H-4(d)	H-5(dd)	H-6(dd)	H-7(d)	$P(C_6H_5)_3$ H(m)	Other protons
Va	7·24	6·95	5·59	5·33	7·68—8·2	11·4 s (NH)
Vb	[a]	—	[a]	5·45	7·40—8·25	11·5 s (NH)
Vc	[a]	—	[a]	5·51	7·44—8·15	11·1 s (NH)
VI	8·24	7·09	6·78	6·06	7·51—7·95	12·45 s (NH); 2·75 s (CH_3)
VII	[a]	6·95	6·61	5·98	7·40—7·88	2·55 s (CH_3)
VIII	[b]	7·34	6·93	6·05	7·55—7·83	1·88 s (CH_3S); 4·1 s (CH_3N)
IX	[a]	7·10	6·80	6·20	7·50—7·83	3·43 s (SH)
XII	[a]	6·98	6·64	6·08	7·50—7·88	2·19 s (CH_3); 4·08 s (CH_2)
XIII	[a]	6·93	6·6	5·95	7·48—7·83	1·18 d (CH_3); 2·93 d (CH*a*); 4·05 m (CH)
X	7·95	7·1	6·78	6·08	7·55—7·80	1·1 t (CH_3); 3·98 q (CH_2) 4·35 s (CH_2)

[a] Overlap with the H-$P(C_6H_5)_3$ signal.

As the result of ^{13}C–^{31}P spin–spin coupling, ^{13}C NMR signals of the carbon atoms C-2, C-3, C-8, and C-9 (and also of carbon atoms in the $P(C_6H_5)_3$ group) appear as doublets. On the basis of the coupling constants $^{x}J(^{13}C, ^{31}P)$ (Table II) which depend on hybridization of the carbon atom and its distance from the phosphorus atom, the C-2, C-3, C-8, and C-9 carbon atoms of the indole system were unequivocally identified. It is known[8,11] that the magnitude of $^{1}J(C, P)$ constants increases in the order $sp^3 < sp^2 < sp$. The high values of the ^{1}J(C-3, P) coupling constants found in the synthesized compounds show that the $P(C_6H_5)_3$ group is bonded to an unsaturated carbon atom with a hetero atom attached to the other carbon atom of the double bond, *e.g.* $^{(+)}P(C_6H_5)_3$—C=C—$O^{(-)}$ (J(C, P) = 117–135 Hz; ref.[12]).

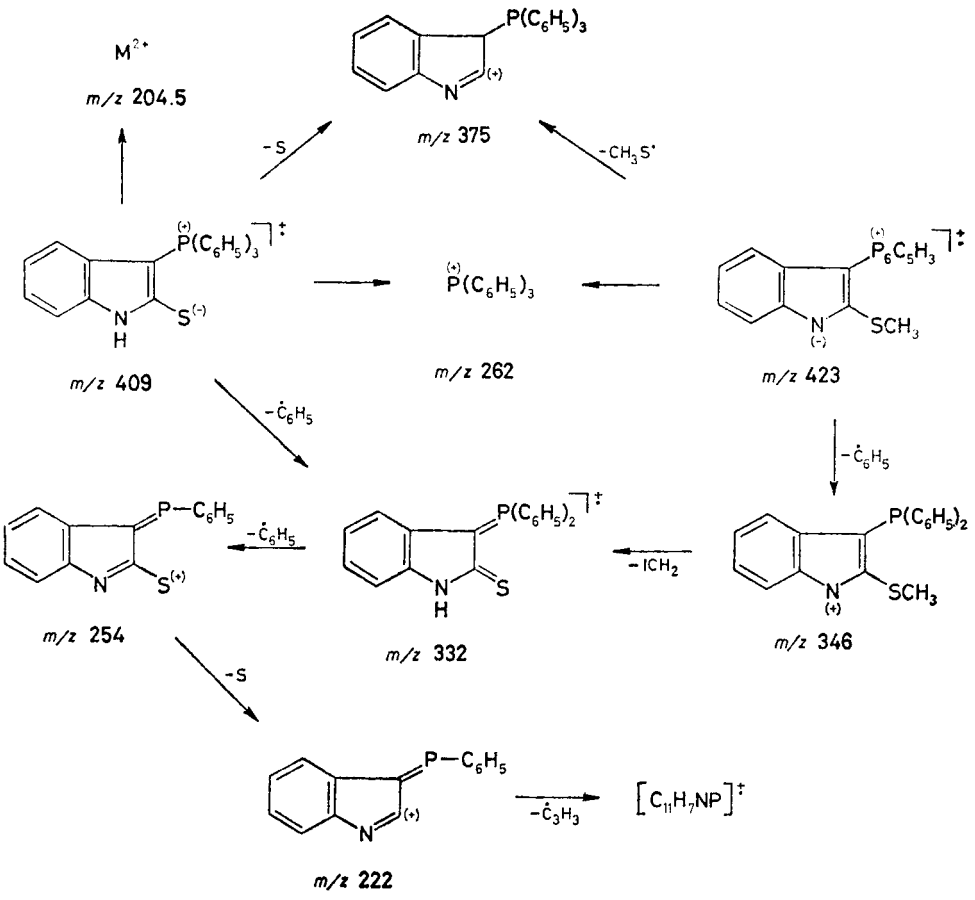
TABLE II

Chemical shifts and coupling constants in ^{13}C NMR spectra of the synthesized compounds

C-atom x_J(C, P), Hz	*Va*	*VI*	*VII*	*VIII*
1′	122·9	120·0	120·8	119·8
($x = 1$)	(93·9)	(90·6)	(90·5)	(92·0)
2′	133·6	134·2	133·4	133·8
($x = 2$)	(9·4)	(11·3)	(11·3)	(11·3)
3′	128·4	130·3	129·7	129·9
($x = 3$)	(13·2)	(13·2)	(13·2)	(13·2)
4′	132·3	135·0	134·1	134·4
($x = 4$)	(3·8)	(1·8)	(3·3)	(2·1)
2	173·2	148·5	159·8	144·2
($x = 2$)	(16·9)	(18·8)	(17·5)	(16·9)
3	75·0	81·7	65·3	90·0
($x = 1$)	(137·1)	(124·5)	(123·2)	(122·7)
9	131·6	129·8	132·4	128·0
($x = 2$)	(16·9)	(11·7)	(13·5)	(11·3)
8	138·8	138·7	148·4	139·0
($x = 3$)	(15·0)	(13·1)	(17·9)	(13·1)
4	108·1	114·0	114·5	112·6
5	113·0	117·5	115·4	117·9
6	118·4	123·1	116·1	123·8
7	118·5	122·4	117·6	122·5
S-CH_3	—	19·1	18·5	18·0
N-CH_3	—	—	—	31·6

The sp^3 to sp^2 change of the phosphorus-bound carbon is indicated by the shift of the phosphorus signal from δ + 21·77 for isothiocyanate *IIIa* to δ + 8·84 for betaine *Va* and δ + 10·54 for *VI*. The mentioned chemical shifts of phosphorus atom with coordination number 4 are in the region typical for triphenylphosphonium salts (δ + 5 to +40; refs[13-15]).

Mass spectra of selected derivatives also confirm the discussed structures. The presence of the same fragment ions of *m/z* 376, 332, 262, 254, 222, and 183 in the mass spectra of *Va* and *VI* indicates similar fragmentation pattern with different relative intensities (Scheme 7).



SCHEME 7

The above speculations were unequivocally confirmed by X-ray diffraction analysis[16] of compound *Va* (Fig. 1) showing that the C-2—C-3 bond length (140·9 pm) is typical of a double bond, whereas the C-2—S bond length (171·4 pm) is near to

values for simple C—S bonds. Thus, of the two mesomeric structures of compound *V* the betain one is preferred.

EXPERIMENTAL

Infrared spectra of the synthesized compounds were measured on a double beam IR-75 spectrometer (Zeiss, Jena) in chloroform or in KBr pellets in the region 800—4 000 cm^{-1}. ^1H NMR and ^{13}C NMR spectra were taken on Tesla BS 497 (80 MHz; CW) and Tesla BS 567 (25·12 MHz; FT) instruments in deuteriochloroform and hexadeuteriodimethyl sulfoxide, respectively, using tetramethylsilane as internal standard. Signals in the ^{13}C NMR spectra were assigned by the selective proton decoupling technique. Mass spectra were measured on an MS 902 S (AEI, Manchester) spectrometer (direct inlet, 70 eV). The ^{31}P NMR spectra were taken in chloroform on a JEOL FX 100 instrument in the FT mode, using 85% H_3PO_4 as external standard. 2-Bromomethylphenyl isothiocyanate (*IIa*) and 2-bromomethyl-4-bromophenyl isothiocyanate (*IIb*) were prepared by bromination of the corresponding *o*-tolyl isothiocyanates with N-bromosuccinimide[2,3].

2-Bromomethyl-4-chlorophenyl Isothiocyanate (*IIc*)

Prepared analogously as *IIa* (ref.[2]) in 47% yield; m.p. 59—60°C, for $C_8H_5BrClNS$ (262·6) calculated: 36·59% C, 1·92% H, 5·33% N; found: 36·54% C, 1·96% H, 5·37% N. IR spectrum

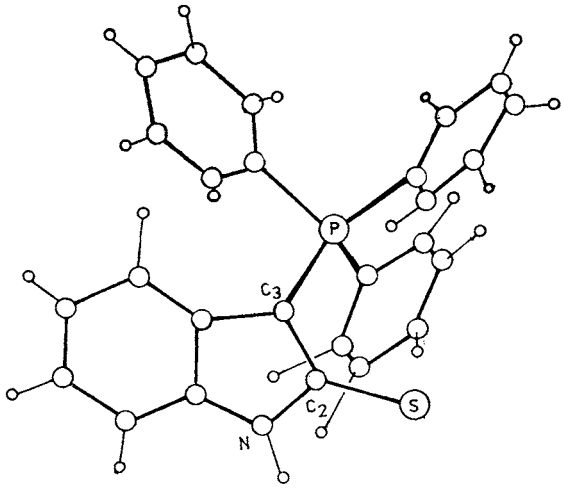


FIG. 1

Molecular structure of *Va* as determined by X-ray diffraction. Crystallographic data: $C_{26}H_{20}$·.NPS, $M = 409{\cdot}48$; $a = 945{\cdot}1$ (1), $b = 2\,559{\cdot}0$ (2), $c = 1\,850{\cdot}0$ (1) pm, $\beta = 104{\cdot}7°$. $V = 43{\cdot}398$ (5) . 10^4 pm, $D_{obs} = 1{\cdot}25$ (1), $D_{calc} = 1{\cdot}2508$ g cm^{-3}, $Z = 16$. Space symmetry group *C2/c* with two molecules in the unit cell. $R = 0{\cdot}04$. Selected bond lengths (pm) and angles (°): C2—S 171·4 (4), C_2—N 136·2 (2), C_2—C_3 140·9 (6), C_3—P 171·1 (5), N—C_2—S 121·4 (3), S—C_2—C_3 131·0 (4), N—C_2—C_3 107·6 (4), C_2—C_3—P 113·0 (2)

($CHCl_3$) ν, cm^{-1}: 2 047 (NCS). ^1H NMR spectrum (C^2HCl_3): 4·44 s, 2 H (CH_2), 7·26—7·34 m, 3 H (H-Ar).

2-Isothiocyanatobenzyltriphenylphosphonium Bromide (*IIIa*)

A solution of freshly crystallized triphenylphosphine (11·5 g; 44 mmol) in dry ether (100 ml) was added to 2-bromomethylphenyl isothiocyanate (10 g; 44 mmol) in dry ether (50 ml). After refluxing for 1 h, ether was carefully distilled off and the cold solid residue was triturated several times with ether. The crude product (92%) melted at 208—214°C and was crystallized from isopropyl alcohol–ether, m.p. 219°C; yield 84%. For $C_{26}H_{21}BrPS$ (490·4) calculated: 63·68% C, 4·32% H, 2·86% N; found: 63·59% C, 4·38% H, 2·81% N. IR spectrum ($CHCl_3$) ν, cm^{-1}: 2 090 (NCS). ^1H NMR spectrum (C^2HCl_3): 5·41 d, 2 H (CH_2, J(H, P) = 15·4 Hz), 7·00—7·37 m, 4 H (H-Ar), 7·55—7·95 m, 15 H (H-$(C_6H_5)_3$P). ^{13}C NMR spectrum (C^2HCl_3): 123·44 (C-1, J(C-1, P) = 9·44 Hz), 132·9 (C-2, J(C, P) = 5·6 Hz), 128·1 (C-3, J(C, P) = 1·9 Hz), 128·0 (C-4, J(C, P) = 2·6 Hz), 127·4 (C-5, J(C-5, P) = 3·8 Hz), 132·1 (C-6, J(C-6, P) = 5·4 Hz), 138·2 (C-7), 116·9 (C-1′, P) = 86·6 Hz), 134·0 (C-2′, J(C-2′, P) = 9·4 Hz), 130·35 (C-3′, J(C-3′, P) = = 11·3 Hz), 135·42 (C-4′, J(C-4′, P) = 3·8 Hz). ^{31}P NMR spectrum (C^2HCl_3): +21·74 ($P(C_6H_5)_3$).

5-Bromo-2-isothiocyanatobenzyltriphenylphosphonium Bromide (*IIIb*)

Prepared as described for *IIIa* in 81% yield; m.p. 197—199°C. For $C_{26}H_{20}Br_2NPS$ (569·3) calculated: 54·85% C, 3·54% H, 2·46% N; found: 54·81% C, 3·52% H, 2·51% N. IR spectrum ($CHCl_3$) ν, cm^{-1}: 2 095 (NCS). ^1H NMR spectrum (C^2HCl_3): 5·40 d, 2 H (CH_2, ^1J(P, H) = = 15·5 Hz), 7·10—7·95 m, 18 H (H-Ar, H-P$(C_6H_5)_3$).

5-Chloro-2-isothiocyanatobenzyltriphenylphosphonium Bromide (*IIIc*)

Prepared as described for *IIIa* in 87% yield, m.p. 221—222°C. For $C_{26}H_{20}BrClNPS$ (524·9) calculated: 59·49% C, 3·84% H, 2·67% N; found: 59·51% C, 3·87% H, 2·63% N. IR spectrum ($CHCl_3$) ν, cm^{-1}: 2 094 (NCS). ^1H NMR spectrum (C^2HCl_3): 5·41 d, 2 H (CH_2, ^1J(P, H) = = 15·5 Hz), 7·11—7·94 m, 18 H (H-Ar, H-P$(C_6H_5)_3$).

3-Triphenylphosphoniumindolyl-2-thiolate (*Va*)

A solution of triethylamine (0·56 g; 5·5 mmol) in acetonitrile (20 ml) was added to a solution of 2-isothiocyanatobenzyltriphenylphosphonium bromide (*IIIa*), (2·45 g; 5 mmol) in acetonitrile (100 ml). After standing for 1 h, the crystals were filtered, washed successively with water, methanol, and ether and dried; m.p. 305—319°C (decomposition); yield 94%. For $C_{26}H_{20}NPS$ (409·4 calculated: 76·28% C, 4·92% H, 3·42% N; found 76·33% C, 4·89% H, 3·40% N. IR spectrum (KBr) ν, cm^{-1}: 1 430 ($NHCS^{(-)}$). ^{31}P NMR spectrum (C^2HCl_3): +8·84 ($P(C_6H_5)_3$). ,Mass spectrum, m/z (rel. intensity, %): 409 (100), 408 (68·8), 376 (11·7), 332 (2·6), 298 (8·8), 262 (6·1), 254 (18·1), 222 (34·4), 204 (5·5), 183 (24·9).

5-Bromo-3-triphenylphosphoniumindolyl-2-thiolate (*Vb*)

Prepared as described for *Va* in 91% yield; m.p. 300—318°C (decomposition). For $C_{26}H_{19}BrNPS$ (498·3) calculated: 63·82% C, 3·91% H, 2·86% N; found: 63·78% C, 3·94% H, 2·83% N. IR spectrum (KBr) ν, cm^{-1}: 1 435 (NHCS).

5-Chloro-3-triphenylphosphoniumindolyl-2-thiolate (*Vc*)

Prepared as described for *Va* in 91% yield; m.p. 303–320°C (decomposition). For $C_{26}H_{19}ClNPS$ (444·9) calculated: 70·16% C, 4·30% H, 3·15% N; found: 70·19% C, 4·33% H, 3·18% N. IR spectrum (KBr) ν, cm^{-1}: 1 431 (NHCS).

2-Methylthioindolyl-3-triphenylphosphonium Iodide (*VI*)

Methyl iodide (1·42 g; 10 mmol) was added to a suspension of *Va* (2·05 g; 5 mmol) in ethanol (25 ml) and the mixture was stirred at 50°C until it became homogeneous (about 0·5 h). After cooling to −18°C, the product *VI* was collected; yield 89%, m.p. 197°C. For $C_{27}H_{23}INPS$ (551·3) calculated: 58·82% C, 4·20% H, 2·54% N; found: 58·76% C, 4·27% H, 2·51% N. IR spectrum ($CHCl_3$) ν, cm^{-1}: 3 130; 3 090 (NH), 2 956 (CH_3). ^{31}P NMR spectrum ($CHCl_3$): +10·54 ($P(C_6H_5)_3$).

2-Methylthio-3-triphenylphosphonium-1-indolate (*VII*)

A solution of sodium ethoxide (from 0·12 g; 5 mmol of sodium in 5 ml of ethanol) was added to a solution of *VI* (2·76 g; 5 mmol) in hot ethanol (9 ml). After cooling, the crystals were collected, crystallized from benzene and dried *in vacuo* for 24 h; m.p. 156°C; yield 74%. For $C_{27}H_{22}NPS$ (423·5) calculated: 76·57% C, 5·24% H, 3·31% N; found: 76·49% C, 5·26% H, 3·38% N. IR spectrum ($CHCl_3$) ν, cm^{-1}: 2 922 (CH_3).

1-Methyl-2-methylthioindolyl-3-triphenylphosphonium Iodide (*VIII*)

Compound *VII* (2·12 g; 5 mmol) was dissolved in warm ethanol (30 ml) and stirred with methyl iodide (0·71 g; 5 mmol) for 10 min. Ether (10 ml) was added and the mixture was set aside overnight at −18°C. The crystals were filtered off, washed with ether and dried. The analytical sample was obtained by crystallization from ethanol–ether, m.p. 218°C; yield 92%. For $C_{28}H_{25}INPS$ (564·6) calculated: 59·57% C, 4·46% H, 2·48% N; found: 59·46% C, 4·43% H, 2·43% N. IR spectrum ($CHCl_3$) ν, cm^{-1}: 2 940 (CH_3).

2-Mercaptoindolyl-3-triphenylphosphonium Chloride (*IX*)

Gaseous hydrogen chloride was introduced into a suspension of *Va* (2·05 g; 5 mmol) in ethanol (10 ml) until the mixture became homogeneous. The solvent was removed under reduced pressure and the product was crystallized twice from chloroform–ether; yield 96%; m.p. 186–188°C. For $C_{26}H_{21}ClNPS$ (445·8) calculated: 70·04% C, 4·75% H, 3·14% N; found: 70·9% C, 4·83% H, 3·18% N. IR spectrum ($CHCl_3$) ν, cm^{-1}: 3 125, 3 092 (NH).

2-(2-Oxopropyl-1-thio)indolyl-3-triphenylphosphonium Bromide (*XII*)

A) A mixture of *Va* (2·05 g; 5 mmol), bromoacetone (0·69 g; 5 mmol), and ethanol (30 ml) was refluxed for 15 min. After cooling to −18°C, the product was collected and crystallized from chloroform–ether, m.p. 164°C; yield 95%. For $C_{29}H_{25}BrNOPS$ (546·4) calculated: 63·75% C, 4·61% H, 2·56% N; found: 62·66% C, 4·68% H, 2·48% N. IR spectrum ($CHCl_3$) ν, cm^{-1}: 3 160 (NH), 2 936 (aliphatic CH), 1 672 (C=O).

B) Compound *XI* (5 mmol) in ethanol (20 ml) was refluxed for 0·5 h. The solvent was evaporated under diminished pressure and the solid residue was crystallized from chloroform–ether. Yield quantitative.

3-Hydroxy-3-methylthiazolo[1,2-*b*]indol-9-yltriphenylphosphonium Bromide (*XI*)

A mixture of *Va* (2·05 g; 5 mmol), bromoacetone (0·69 g; 5 mmol), and anhydrous ethanol (50 ml) was stirred at 15°C for 4 h. After addition of ether (25 ml) and standing in a refrigerator overnight, the crystalline product was collected on filter, washed with ether and dried, m.p. 228°C; yield 97%. For $C_{29}H_{25}BrNOPS$ (546·4) calculated: 63·75% C, 4·61% H, 2·56% N; found: 63·72% C, 4·63% H, 2·51% N. IR spectrum $(CHCl)_3$ ν, cm^{-1}: 2 949 (aliphatic CH), 3 260 (OH), 1 107 (CO). ^1H NMR spectrum (C^2HCl_3): 1·93 s, 3 H (CH_3), 3·51 d, 1 H (H_a, J_{gem} = 11·3 Hz), 4·12 d, 1 H (H_b, J_{gem} = 11·3 Hz), 7·68–8·30 m, 15 H (H-$(C_6H_5)_3P$), 5·40 d, 6·58 dd, 6·94 dd, and 7·59 d, all 1 H (indole H).

2-(Ethoxycarbonylmethylthio)indolyl-3-triphenylphosphonium Chloride (*X*)

The title compound was prepared as described for *XII* and crystallized from chloroform–hexane; m.p. 199–201°C; yield 94%. IR spectrum ($CHCl_3$) ν, cm^{-1}: 1 680 (CO), 3 180 (NH). For $C_{30}H_{27}ClNO_2PS$ (532·0) calculated: 67·72% C, 5·12% H, 2·63% N; found: 67·68% C, 5·08% H, 2·71% N.

2-(2-Oxopropyl-1-thio)-3-triphenylphosphonium-1-indolate (*XIII*)

A solution of sodium ethoxide (from 0·01 mol of sodium in 30 ml of ethanol) was added to a suspension of *XI* or *XII* (0·01 mol) in anhydrous ethanol (15 ml). After stirring for 15 min, the reaction mixture was poured into ice-cold water (100 ml). The solid product was filtered, dried and crystallized from chlorofom–hexane; m.p. 123–125°C; yield 75%. IR spectrum ($CHCl_3$) ν, cm^{-1}: 1 703 (CO). For $C_{29}H_{24}NOPS$ (465·5) calculated: 74·82% C, 5·19% H, 3·00% N; found: 74·79% C, 5·21% H, 2·93% N.

2-(2-Hydroxypropyl-1-thio)-3-triphenylphosphoniumindolate (*XIV*)

Solid sodium borohydride (0·015 mol) was added to a suspension of *XII* or *XIII* (0·01 mol) in ethanol (30 ml) during 10 min. The mixture was stirred until it became homogeneous, set aside overnight and the product was filtered and crystallized from chloroform–ethyl acetate; m.p. 86–89°C; yield 53%. IR spectrum ($CHCl_3$) ν, cm^{-1}: 3 535 (OH). For $C_{29}H_{26}NOPS$ (467·6) calculated: 74·49% C, 5·60% H, 2·99% N; found: 74·53% C, 5·51% H, 3·01% N.

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