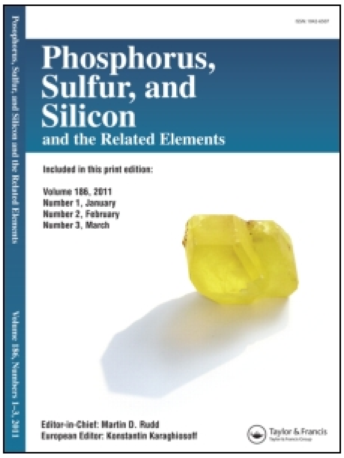

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Studies on Phosphonium Ylides, XXIV: Reactions of Phosphorus Ylides with 1,2,3,4-Tetrahydro1-Naphthylidene-Malononitrile

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Studies on Phosphonium Ylides, XXIV: Reactions of Phosphorus Ylides with 1,2,3,4-Tetrahydro-1-Naphthylidene-Malononitrile

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*1,2,3,4-tetrahydro-1-naphthylidene-malononitrile (**1**) reacts with carbethoxymethylene and carbmethoxymethylene- triphenylphosphoranes (**2a**, **2b**) to give the new phospho-ranylidenecyclopentaylidene products (**4a**, **4b**, and **5**), respectively. The treatment of (**1**) with phosphorus ylide **2c** afforded the new phosphonium ylide **6**. Moreover, the application of reagent (**2d**) on (**1**) renders compound **7**. On the other hand, when N-phenyliminotriphenylphosphorane (**3**) reacts with (**1**), the corresponding adduct (**8**) was obtained together with triphenylphosphine. Mechanisms accounting for the formation of new products are discussed, and probable structures of products are presented based on analytical and spectroscopic data.*

Keywords Cyclopentaylidene-naphthalen-1-ylidene-acetamide; naphthylidene-malononitrile; phosphonium ylides

In recent years, considerable interest has been focused on the reaction of phosphorus ylides with α,β-unsaturated nitriles.[1–6] However, no information is available about the reaction of these reagents with a dicyanomethylene derivative of 1-tetralone. The present study deals with the reaction of 1,2,3,4-tetrahydro-1-naphthylidene-malononitrile **(1)** with resonance stabilized phosphonium ylides **2a–e** and iminophosphorane (**3**) (Scheme 1).

RESULTS AND DISCUSSION

We have found that 1,2,3,4-tetrahydro-1-naphthylidene-malononitrile (**1**) reacts with two mole equivalents of carbethoxymethylenetriphenylphosphorane (**2a**) in refluxing toluene for 25 h to give two adducts

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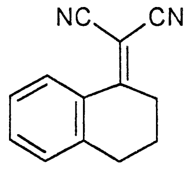


1

$Ph_3P{=}CRR^1$

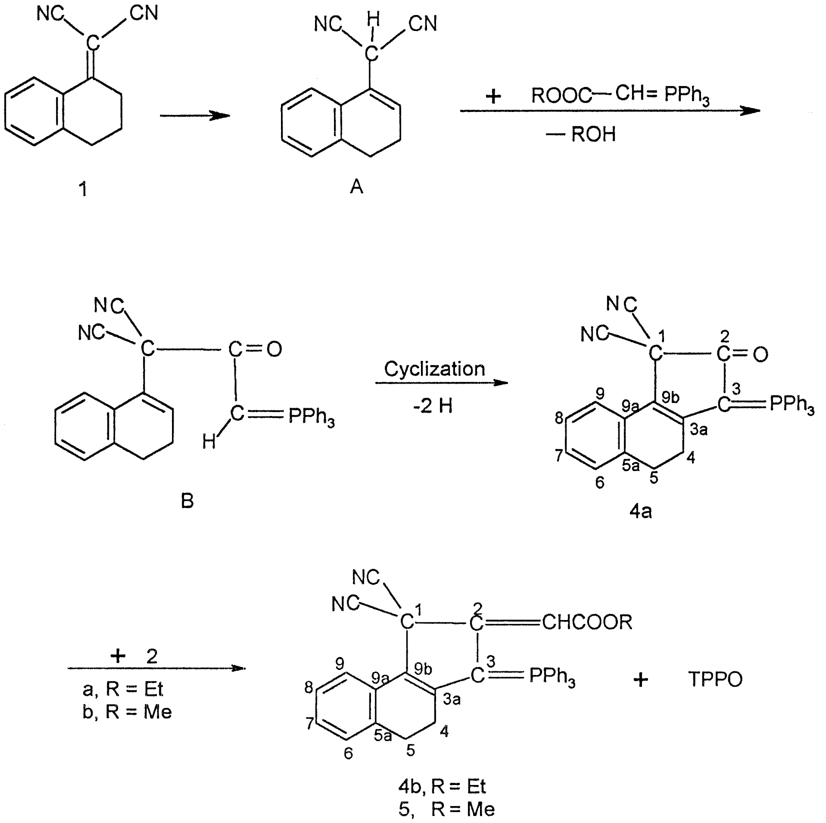
2a, R = H; $R^1 = COOC_2H_5$
b, R = H; $R^1 = COOCH_3$
c, R = H; $R^1 = CHO$
d, $R = CH_3$; $R^1 = COOC_2H_5$

$Ph_3P{=}N{-}Ph$

3

SCHEME 1

formulated as **4a** and **4b**, respectively. Triphenylphosphine oxide was also isolated from the reaction medium (Scheme 2).



SCHEME 2

Compounds **4a** and **4b** are chromatographically pure and possess sharp melting points; elemental and mass spectral analyses for compound **4a** corresponded to an empirical formula of $C_{33}H_{23}N_2OP$. The structure assigned for compound **4a** was based on the ^{31}P-NMR shifts (+22.8 ppm, vs. 85% H_3PO_4), which correspond to a ylide-phosphorane structure.[7]

The IR spectrum of **4a**, in KBr, reveals the presence of a strong absorbtion band at 1731 cm^{-1} (C=O), 2195(CN), 1680, 1510 cm^{-1} (C=P), and 1430.990 cm^{-1} (P—C, Phenyl).[8]

The ^{1}H-NMR spectrum of compound **4a** in $CDCl_3$ indicated the presence of signals at $\delta = 2.31$(d, 2H, $^4J_{HP} = 5$ Hz, H-4), 2.61(d, 2H, H-5), and 7.05–8.25 (m, 19H) corresponding to the aromatic protons. The ^{13}C-NMR spectrum (270 MHz) provided strong evidence in support of the ylide linkage incorporated in structure **4a**. The ^{13}C-NMR spectrum of **4a** in $CDCl_3$ shows doublets at $\delta = 134.05$(P=C, J = 115 Hz).[9,10]

Moreover, the ^{13}C-NMR spectrum of **4a** exhibited signals (ppm) at 57.8 [C(CN)$_2$], 115.2(CN), 194.35(C=O), 138.1(C-9b), 118.67(C-3a), 135.3(C-9a), 138.4(C-5a), 37.4(C-4), 29.7(C-5), 126.7, 127, and 128 (Ar-carbons). The mass spectrum of compound **4a** contains a prominent peak for M$^+$ at m/e 494 (100%), which supports the phosphoranylidenecyclopentaylidene structure **4a**.

The structure elucidation of product **4b** is based on the following evidence: Elemental analyses and molecular weight determination (MS) of **4b** support the molecular formula of $C_{37}H_{29}N_2O_2P$(564.61) accordingly; MS: m/z = 564 (M+, 100% base peak).

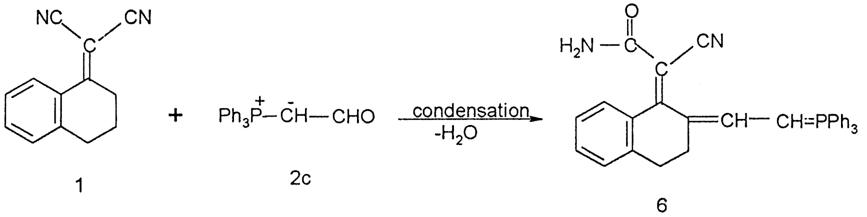
Its IR spectrum, in KBr, exhibits strong absorption bands at 1720 cm^{-1} (C=O, ester), 2198(CN), 1680, 1510 cm^{-1} (C=P), and 1430, 990 cm^{-1} (P—C, Phenyl). The ^{1}H-NMR spectrum of **4b** in $CDCl_3$ indicated the presence of signals at δ 1.05 (t, 3H, $J_{HH} = 6$ Hz, CH_3), 4.15 (q, 2H, $J_{HH} = 6$Hz, CH_2), and 6.1 (d, 1H, $^4J_{HP} = 5$ Hz, =CH); the chemical shift recorded for the methine proton suggested the Z form rather than the E one, which would requir a downfield chemical shift.[11] 6.95–7.95 (m, 19H, Ar). The ^{31}P-NMR spectrum of **4b** gave one signal at $\delta = 19.05$ that supports the phosphoranylidene structure.[7] Moreover, the ^{13}C-NMR spectrum of **4b** shows doublets at $\delta = 141.53$ (P=C, J = 123 Hz).[9,10] and signals at 77 [$\underline{C}$(CN)$_2$], 116.27 (CN), 141.2 (d, $\underline{C}$=CH, $^2J_{CP} = 30.5$ Hz), 167 ppm (C=O, ester), 13.89(CH_3), 60.5(CH_2).

Similarly, carbmethoxymethylenetriphenylphosphorane **2b** reacts with 1,2,3,4-tetrahydro-1-naphthylidene-malononitrile **(1)** (2b:1; 2:1) to give adducts **4a** and **5** respectively. Triphenyl-phosphine oxide was also isolated from the reaction mixture. Struture **5** was deduced from correct microanalysis and IR, ^{1}HNMR, ^{13}CNMR, and mass spectral data (cf. Experimental Section).

It is worth mentioning that adducts **4a**, **4b**, and **5** were obtained in good yields when two mol equivalents of the Wittig reagents **2a**,**b** were used with respect to one equivalent of α-tetralon-malononitrile

1. A possible explanation of the course of the reaction of phosphonium ylides **2a** and/or **2b** with nitrile **1** is shown in Scheme 2. The reaction was assumed to take place via the formation of the intermediate A, which is formed due to strong withdrawing properties of nitrile groups. Condensation between compound A and phosphonium ylide **2a** and/or **2b** followed by elimination of one molecule alcohol afforded compound B. The latter via cyclization and subsequent dehydrogenation gave finally compound **4a** (Scheme 2). Addition of another molecule of ylide **2a** and or **2b** resulting in the formation of **4b** and **5**, respectively, along with triphenylphosphine oxide.[12]

The reaction of **1** with formylmethylenetriphenylphosphorane (**2c**) has also been investigated. The treatment of **1** with mol equivalents of **2c** in refluxing toluene leads to the formation of the new phosphonium ylide **6** as the sole reaction product. Triphenylphosphine and triphenyl-phosphine oxide are neither isolated nor identified in the reaction medium (Scheme 3).

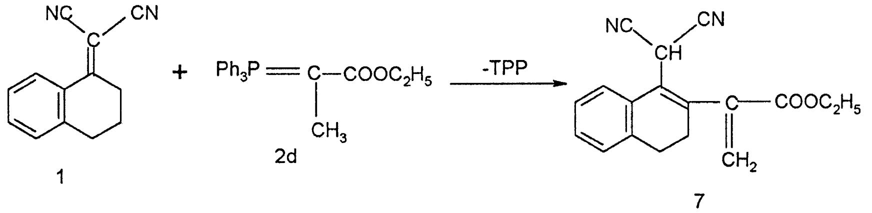


SCHEME 3

Compound **6** possesses an ylide-phosphorane structure since it exhibits a positive shift in its ^{31}P NMR ($\delta = +17.51$) spectrum in the region characteristic for this class of compounds.[7] On the basis of IR, ^{1}HNMR, ^{13}CNMR, and MS and elemental analyses, the structure of compound **6** was deduced (cf. Experimental Section).

The formation of 2-cyano-2-{2-[2-(triphenyl-λ^5-phosphoranylidene)-ethylidene]-3,4-dihydro-2H-naphthalen-1-ylidene}-acetamide (**6**) involves the condensation between the aldehydic group of **2c** and the active methylene group in **1** followed by the hydrolysis of one of the nitrile groups.

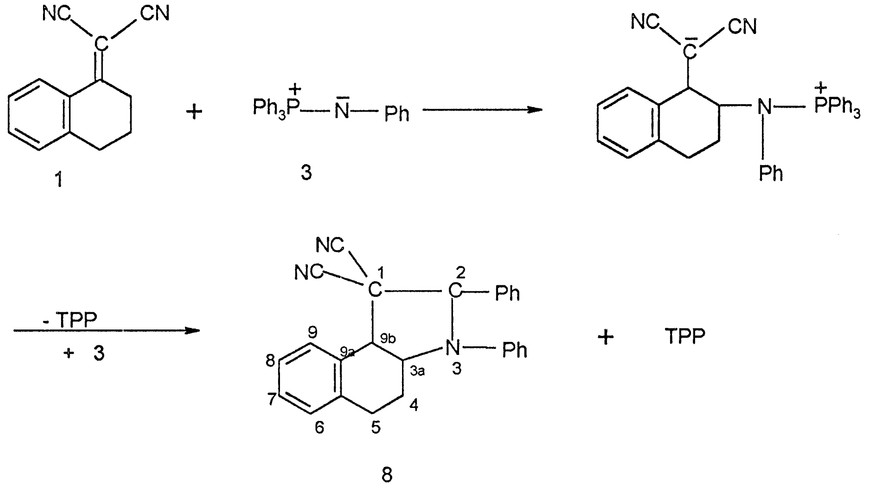
When ethyl 2-(triphenylphosphoranylidene)propionate (**2d**) reacts with **1** in refluxing toluene, compound **7** and triphenylphosphine were isolated in good yields (Scheme 4). Structural assignments for 2-(1-dicyanomethyl-1,2,3,4-tetrahydro-naphthalen-2-yl)-acrylic acid ethyl ester (**7**) are based upon elemental and mass spectral analysis (IR, ^{1}HNMR, ^{13}C NMR, and MS; cf. Experimental



SCHEME 4

Section).[13] The mechanism of this reaction remain obscure at this time.

Further, this study has been extended to include the reaction of 1,2,3,4-tetrahydro-naphthylidene-malononitrile (**1**) with N-phenyliminotriphenylphosphorane (**3**) to establish whether it would behave in a similar manner. When compound **1** was allowed to react with N-phenyliminotriphenylphosphorane (**3**) in a 1:2 molar ratio in boiling toluene for 25 h, triphenyl-phosphine as well as compound **8** were isolated (Scheme 5). Product **8** was obtained in a 78% yield and formulated as 2,3-diphenyl-2,3,3a,4,5,9b-hexahydrobenzo[e]indazole-1,1-dicarbo-nitrile, its IR spectrum (in KBr) revealed the presence of a strong absorbtion band at 2198 cm^{-1} (CN).



SCHEME 5

The ^1H NMR spectrum of compound **8** exhibited signals at $\delta =$ 1.99(m, 2H, H-4), 2.53(m, 1H, H-3a), 2.87(m, 2H, H-5), 3.35(m, 1H, H-9b), and 6.91–7.19(m, 14H, Ar). The ^{13}C NMR spectrum of compound **8** in $CDCl_3$ showed signals at $\delta = 118.34$(CN), 64.5(C-1), 69.4(C-3a), 35.6(C-4), 28.5(C-5), 140.3(C-5a), 45.3(C-9b), 140.3(C-9a), 112.0, 119.4, 126.4, 128.5, 130.4, and 143.5(Ar-C). The mass spectrum of compound **8** yielded a prominent ion peak for M^+, 100%, at m/e 376. A possible explanation for the course of the reaction of **1** with iminophosphorane **3** is shown in Scheme 5.

It is worth mentioning that when compound **1** was allowed to react with a mole equivalent of iminophosphorane **3**, triphenylphosphine and product **8** were obtained in a low yield.

CONCLUSIONS

In view of all facts previously cited, it can be concluded that the reaction of 1,2,3,4-tetrahydro-1-naphthylidene-malononitrile (**1**) with phosphonium ylides **2a–d** and phosphinimine (**3**) leads to different products, depending on the nature of phosphorus reagents used as well as the stability of the addition products.[14] The significance of these findings is not only the discovery of a new pattern of phosphorus ylide but also the establishment of a novel method for the synthesis of both the phosphoranylidenecyclopentaylidene (**4a**) and the benzo-[e]indazole **8** derivatives.

EXPERIMENTAL

All melting points are uncorrected and were taken on an electrothermal 9100 apparatus. 1,2,3,4-tetrahydro-1-naphthylidene-malononitrile **1** and phosphorane compounds **2a–d** and **3** were prepared according to established procedures.[15,16] IR spectra were measured in KBr pellets with Perkin-Elmer Infrared Spectrophotometer Model 157 (Gerating). The ^1H, ^{13}C, and ^{31}P-NMR spectra were obtained on Jeol GLMEX 270 MHz instrument (super conducting magnet) in $CDCl_3$ or DMSO-d_6 using tetramethylsilane as an internal standard. Mass spectra were obtained with a Finnigan MAT-SSQ 7000 spectrophotometer (70 eV). Microanalyses were performed by the Central Services Laboratory at National Research Centre.

The Reaction of 1,2,3,4-Tetrahydro-1-naphthylidene-malononitrile (1) With Carbethoxy-methylenetriphenylphosphorane 2a

A mixture of 1,2,3,4-tetrahydro-1-naphthylidene-malononitrile **1** (0.19 g, 0.001) and ylide **2a** (0.68 g, 0.002 mmol) in dry toluene

(30 mL) was refluxed for 25 h. The volatile material was evaporated under reduced pressure. The residue was subjected to silica gel column chroma-tography to give two products formulated as **4a** and **4b**, respectively.

2-Carbethoxymethylene-3–(triphenyl-λ^2-phosphoranylidene)-2,3,4,5-tetrahydrocyclo-penta[a]naphthalene-1,1-Dicarbonitrile (4b)

Eluent: benzene/ethylacetate (50:50,v:v). Product (4b) was separated as yellow crystals, yield (35%), m.p. 180–181°C. Anal. calcd. for $C_{37}H_{29}N_2O_2P$(564.61): C,78, 71; H, 5.18; N, 4.69; P, 5.49. Found: C, 78, 79; H, 5. 25; N,4.60; P, 5.41%. IR (KBr): 1720(C=O), 2198(CN), 1680, 1510 (C=P), 1430, 990 cm^{-1} (P-C, Phenyl). ^{1}H-NMR(CDCl$_3$): $\delta = 1.05$ (t, 3H, $J_{HH} = 6$ Hz,CH$_3$), 4.15(q, 2H, $J_{HH} = 6$ Hz, CH$_2$), 6.1(d, 1H, $^4J_{HP} = 5$ Hz, =CH), 6.95–7.95 ppm(m, 19H, Ar-H). ^{13}C-NMR (CDCl$_3$):$\delta = 141.53$ (d, P=C, J = 123 Hz), 77 [$\underline{C}$(CN)$_2$], 116.27 (CN), 141.2(d, $\underline{C}$=CH, $^2J_{CP} = 30.5$ Hz), 167($\underline{CO}$OC$_2$H$_5$), 13.89(CH$_3$), 60.5 ppm(CH$_2$).^{31}P-NMR(CDCl$_3$): $\delta = +19.05$ ppm. MS: m/z (%) 564 (100).

2-Oxo-3-(triphenyl-λ^2-phosphoranylidene)-2,3,4,5-Tetrahydrocyclopenta[a]naphthalene-1,1-dicarbonitrile (4a)

Eluent: ethylacetate/methanol (40:60, v:v). Product (4a) was separated as brown crystals, yield (45%), m.p. 190–191°C. Anal. calcd. for $C_{33}H_{23}N_2OP$ (494.52): C, 80, 15; H, 4.69; N, 5.66; P, 6.62. Found: C, 80.21; H, 4.76; N, 5.54; P, 6.67%. IR (KBr): 1731(C=O), 2195(CN), 1680, 1510 cm^{-1} (C=P).^{1}H-NMR(CDCl$_3$): $\delta = 2.31$(d, 2H, $^4J_{HP} = 5$ Hz, H-4), 2.61(d, 2H, H-5), and 7.05–8.25 (m, 19H, Ar-H).^{31}C-NMR(CDCl$_3$): $\delta =$ 134.05 (d, J = 115 Hz P=C), 115.22 (CN), 57.8[$\underline{C}$(CN)$_2$], 194.35(C=O), 138.1(C-9b), 118.67(C-3a), 135.3(C-9a), 138.4(C-5a), 37.4(C-4), 29.7(C-5), 126.7, 127, 128 ppm (Ar-C).^{31}P-NMR(CDCl$_3$): $\delta = +22.8$ ppm. MS: m/z(%) 494 (100) [M$^+$]. Triphenylphosphine oxide was also isolated and identified mixed m.p. and comparative IR spectra).

Similarly, carbmethoxymethylenetriphenylphosphorane **2b** reacts with **1** in refluxed toluene to give two products formulated as **4a** and **5**, respectively.

Adduct **5** was separated using the eluent benzene/ethyl acetate (60:40, v:v) as yellow crystals, yield (65%), m.p. 160–161°C. Anal. calcd. for $C_{36}H_{27}N_2O_2P$(550.59): C, 78, 53; H, 4.94; N, 5.09; P, 5.63. Found: C, 78, 60; H, 5.05; N, 5.15; P, 5.69%. IR (KBr): 1710(C=O), 2196 (CN), 1680, 1510(C—P), 1430, 990 cm^{-1} (P—C, Phenyl).^{1} H-NMR(CDCl$_3$):

$\delta = 3.95$(s, 3H, $COOCH_3$), 6.18 (d, 1H, =CH, $^4J_{HP} = 5$ Hz), 6.90–7.85 ppm(m, 19H, Ar-H). ^{31}C-NMR($CDCl_3$): $\delta = 141.49$ (d, J = 123 Hz, P=C), 77 [$C(CN)_2$],116.19 (CN), 141.18 (d, $^2J_{CP} = 30.5$ Hz, $\underline{C}$=CH), 168($\underline{CO}OCH_3$), 54.0 ppm (CH_3). MS: m/z(%) 550 (100)[M^+].

2-Cyano-2-{2-[2–(triphenyl-λ^5-phosphoranylidene)-ethylidene]-3,4-dihydro-2H-naphthalen-1-ylidene}-acetamide (6)

A mixture of ylide **2c** (0.30 g, 0.001 mmol) and **1** (0.19 g, 0.001 mmol) in dry toluene (40 mL) was refluxed for 30 h. The volatile materials were evaporated under reduced pressure. The residue was subjected to silica gel column chromatography using the eluent ethylacetate/methanol (65:35, v:v) to give product **6** as brown crystals; yield (75%), m.p. 140–142°C. Anal.calcd. for $C_{33}H_{27}N_2OP$(498.55): C, 79.50; H, 5.46; N, 5.62; P, 6.21. Found: C, 79.59; H, 5.49; N, 5.68; P, 6.29%. IR (KBr): 1717(C=O, amide), 3345(NH_2), 2181(CN), 1682, 1520 cm-1 (C=P). ^{1}H-NMR ($CDCl_3$): $\delta = 2.05$ (m, 2H, CH_2, $J_{HH} = 15$ Hz), 2.78 (m, 2H, CH_2, $J_{HH} = 15$ Hz), 4.82(dd, 1H,CH-$\underline{CH}$=, $J_{HH} = 15$ Hz ,$^2J_{HP} = 4.2$ Hz), 6.68(dd, 1H, $\underline{CH}$-CH=, $J_{HH} = 15$ Hz, ^{3} $J_{HP} = 3.3$ Hz),7.79(s, 2H, NH_2, exchangeable with D_2O), 6.85–7.54 ppm (m, 19H, Ar-H).^{31} P-NMR($CDCl_3$): $\delta = +17.51$ ppm. ($\underline{C}$=CH_2). MS: m/z(%) 498 (100)[M^+].

Ethyl-2-(4-dicyanomethyl-1,2-dihydro-naphthalen-3-yl)-acrylate (7)

Similarly, the reaction of ethyl 2-(triphenylphosphoranylidene)propionate (2d) with 1 was performed with an equimolar ratio in boiling toluene for 30 h to give product 7 as brown crystals; m.p. 139–140, yield (80%). Anal. calcd. for $C_{18}H_{16}N_2O_2$ (292.33): C, 73.95; H, 5.52; N, 9.58. Found: C, 73.87; H, 5.53; N, 9.63%. IR (KBr): 1730(C=O, ester), 2200 cm^{-1}(CN). ^{1}H-NMR ($CDCl_3$): $\delta = 2.05$ (m, 2H, CH_2, $J_{HH} = 15$ Hz), 2.78 (m, 2H, CH_2, $J_{HH} = 15$ Hz),4.20 [s, 1H, $CH(CN)_2$], 5.70(s, 2H, CH_2), 1.30 (t, 3H, $COOCH_2\underline{CH_3}$), 4.18(q, 2H, $COO\underline{CH_2}CH_3$), 7.05-7.25 (m,4H, Ar-H). ^{31}C-NMR($CDCl_3$): $\delta = 115.22$ (CN), 23.21[$\underline{CH}(CN)_2$], 142.9 ($\underline{C}$=CH_2), 128.24(C=$\underline{CH_2}$), 168.90 ppm (C=O, ester). MS: m/z(%) 292 (100)[M^+].

Triphenylphosphine was also isolated and identified (mixed m.p. and comparative IR spetra).

2,3-Diphenyl-2,3,3a,4,5,9b-hexahydrobenzo[e]indazol-1,1-dicarbonitrile 8

A mixture of 1 (0.19 g, 0.001 mmol) and iminophosphorane 3 (0.70 g, 0.002 mmol) in dry toluene (30 mL) was refluxed for 25 h. The volatile materials were evaporated under reduced pressure. The residue was washed with petroleum ether and then recrystalized from benzene to give product **8** as white crystals; yield (78%), m.p. 120–121°C. Anal. calcd. for $C_{25}H_{20}N_4$ (376.45): C, 79.76; H, 5.46; N, 5.35. Found: C, 79.64; H, 5.49; N, 5.38%. IR(KBr): a strong absorbtion band at 2198 cm^{-1} (CN). ^{1}H-NMR ($CDCl_3$): $\delta = 1.99$(m, 2H, H-4), 2.53 (m, 2H, H-5), 3.35(m, 2H, H-9b), 6.91–7.19 ppm (m, 14H, Ar-H). ^{31}C-NMR($CDCl_3$): $\delta = 118.34$ (CN), 64.5 (C-1), 69.4(C-3a), 35.6(C-4), 28.5(C-5), 140.3(C-5a), 45.3(C-9b), 140.3(C-9a), 112.0, 119.4, 126.4, 128.5, 130.4, 143.5 (Ar-C). MS: m/z (%) 379(100)[M^+].

Triphenylphosphine was also isolated and identified (mixed m.p. and comparative IR spetra).

REFERENCES

[1] F. M. Soliman and M. M. Said, *Phosphorus, Sulfur, and Silion*, **61,** 335 (1991).

[2] M. R. Mahran, W. M. Abdou, N. M. Abd-El-Rahman, and M. D. Khadre, *Heteroatom Chemistry*, **3,** 93 (1992).

[3] W. M. Abdou and N. A. F. Ganoub, *Heteroatom Chemistry*, **3,** 133 (1992).

[4] N. A. F. Ganoub, *Phosphorus, Sulfur, and Silion*, **81,** 125 (1993).

[5] L. S. Boulos and E.-S. M. A. Yakout, *Heteroatom Chemistry*, 253 (1997).

[6] L. S. Boulos and H. A. Abd-El-Malek, *Heteroatom Chemistry*, **10,** 263 (1999).

[7] M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, ^{31}*P-Nuclear Magnetic Resonance* (Wiley Interscience, New York, 1967).

[8] M. Hesse, H. Meier, and B. Zech, *Spektroskopische Methoden in der Orgenischen Chemie* (G. Thieme Verlag, Stuttgart, 1979).

[9] G. C. Levy, R. L. Lichter, and G. I. Nelson, Eds. In *Carbon 13 Nuclear Magnetic Resonance Spectroscopy*, p. 135 (Wiley, New York, 1980).

[10] H. O. Kalinowski, S. Berger, and S. Braun, ^{13}*C NMR Spectroskopie* (G. Thieme Verlag, Stuttgart, 1984).

[11] H. J. Bestmann and H. J. Lang, *Tetrahedron Lett.* **25,** 2102 (1969).

[12] D. N. Nicolaides, S. G. Adamopoulos, and D. A. Lefkaditis, *J. Chem. Soc. Perkin Trans 1*, 283 (1992).

[13] K. Faber, H. Stueckler, and T. Kappe, *J. Heterocyclic Chem.*, **21,** 1177 (1984).

[14] L. S. Boulos and I. T. Hennawy, *Phosphorus, Sulfur, and Silion*, **84,** 173 (1993).

[15] D. T. Mowry, *J. Am. Chem. Soc.*, **67,** 1050 (1945).

[16] H. J. Bestmann and O. K. Kratzer, *Chem. Ber.*, **95,** 1894 (1962).