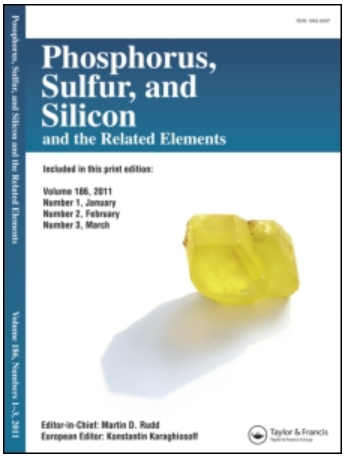


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE TRANSAMINATION REACTION OF TRIS(N,N-DIALKYLAMINO)PHOSPHINES WITH N-(O)-ALKYL-O-ALLYL-THIOPHOSPHORYL)-N'-BENZOYLUREAS

Zhaojie Liu[a]; Xianfeng Li[a]; Jinglin Zhang[a]
[a] Institute of Organic Synthesis, Central China Normal University, Wuhan, People's Republic of China

To cite this Article Liu, Zhaojie , Li, Xianfeng and Zhang, Jinglin(1988) 'THE TRANSAMINATION REACTION OF TRIS(N,N-DIALKYLAMINO)PHOSPHINES WITH N-(O)-ALKYL-O-ALLYL-THIOPHOSPHORYL)-N'-BENZOYLUREAS', Phosphorus, Sulfur, and Silicon and the Related Elements, 40: 3, 215 — 218
To link to this Article: DOI: 10.1080/03086648808072916
URL: http://dx.doi.org/10.1080/03086648808072916

Phosphorus and Sulfur, 1988, Vol. 40, pp. 215–218
Reprints available directly from the publisher
Photocopying permitted by license only

THE TRANSAMINATION REACTION OF TRIS(N,N-DIALKYLAMINO)PHOSPHINES WITH N-(O)-ALKYL-O-ALLYL-THIOPHOSPHORYL)-N′-BENZOYLUREAS

ZHAOJIE LIU,* XIANFENG LI and JINGLIN ZHANG

Institute of Organic Synthesis, Central China Normal University, Wuhan, People's Republic of China

(Received June 18, 1988; in final form June 21, 1988)

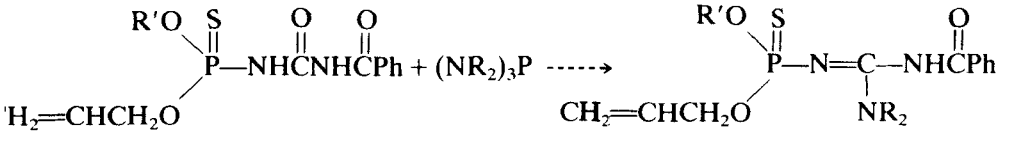
Tris(N,N-dialkylamino)phosphines undergo a transamination reaction with N-(O-alkyl-O-allyl-thiophosphoryl)-N′-benzoylureas. Eight new compounds were synthesized by this method and characterized by IR, ^{1}H NMR and ^{31}P NMR.

Key words: Transamination; N-(O-alkyl-O-allyl-thiophosphoryl)-N′-benzoyl urea; tris(N,N-dialkylamino)phosphine; amide formation; restricted rotation; synthesis.

INTRODUCTION

Burgada reported a one-step method for the conversion of carboxylic acid to their N,N-dialkylamides.[1] Later Quin *et al.* successfully converted cylic dicarboxylic acids to their bis-(N,N-dimethyl) amides with this method.[2,3] Also, they[4] have found this reaction can have utility with phosphorus-based acids. Phosphinic acids in the 3-phospholene series were transformed into phosphinamides. They performed some exploratory studies on the transamination with other types of acids but with less promising results. Up to the present, the transamination reaction of tris(N,N-dialkylamino)phosphines with other types of phosphorus compounds has not been reported.

In this investigation, we report a new transamination reaction of tris(N,N-dialkylamino)phosphines that we discovered in the course of an exploratory study of the properties of N-(O-alkyl-O-allyl-thiophosphoryl)-N′-benzoyl ureas. The latter were reported in our previous work.[5]



1 **2** **3a-h**

RESULTS AND DISCUSSIONS

It has been reported that tris(N,N-dialkylamino)phosphines reacted with amides to give N-phosphorylated products[6] and with 2-phenylhydrazona-2,3-dihydro-1,3-

TABLE I

Physical data of compounds 3a–h

Compound	R	R′	Molecular formula	Elementary analysis %[a] C	H	P	Yield %[b]
3a	Me	Me	$C_{14}H_{20}N_3O_3PS$	49.6 (49.4)	6.1 (5.9)	9.3 (9.1)	51
3b	Me	Et	$C_{15}H_{22}N_3O_3PS$	50.7 (50.9)	6.5 (6.3)	8.7 (8.7)	55
3c	Et	Me	$C_{16}H_{24}N_3O_3PS$	52.1 (52.2)	6.6 (6.6)	8.3 (8.4)	50
3d	Et	Et	$C_{17}H_{26}N_3O_3PS$	53.6 (53.4)	6.8 (6.9)	8.0 (8.1)	55
3e	Et	*n*-Pr	$C_{18}H_{28}N_3O_3PS$	54.3 (54.6)	7.3 (7.1)	8.0 (7.8)	47
3f	Et	*i*-Pr	$C_{18}H_{28}N_3O_3PS$	54.5 (54.6)	7.0 (7.1)	7.8 (7.8)	49
3g	Et	*n*-Bu	$C_{19}H_{30}N_3O_3PS$	55.6 (55.6)	7.1 (7.4)	7.7 (7.6)	49
3h	Et	*i*-Bu	$C_{19}H_{30}N_3O_3PS$	55.9 (55.6)	7.7 (7.4)	7.6 (7.6)	51

[a] Calculated values in parenthesis.
[b] Yield of isolated pure product.

benzothiazole to afford fused tricyclic triazaphespholes by an intermolecular cyclocondensation reaction.[7] When tris(N,N-dialkylamino)phosphines reacted with N-(O-alkyl-thiophosphoryl)-N′-benzoyl ureas, compounds 3a-h were isolated in 47–55% yields (Table I). This reaction did not provide good yields but the products were unexpected. For compounds 3a–h, the IR spectra showed one broad absorption at υ_{N-H} 3150 cm^{-1} and one strong absorption at $\upsilon_{C=O}$ 1690 cm^{-1}. Also, we have observed one absorption at 1610 cm^{-1}, a frequency assigned to C=N bond most probably. The constitution of 3a–h were assigned mainly on the basis of their ^1H NMR and ^{31}P NMR. In the ^{31}P NMR spectra the signal appears as a singlet in the region 61.05–63.00 ppm. There exists little difference in the spectra when compared with that of their corresponding precursors 1a–f. It is apparent that compounds 3a–h only contain one four-coordinate phosphorus atom and no amine exchange reaction takes place. The alkyl groups at nitrogen in compounds 3a–h are chemically non-equivalent and this is clearly reflected in their ^1H NMR spectra. The two singlets can be observed for the methyl groups (3H:3H, $\Delta\delta = 0.095$ ppm), the methylenes of the ethyl groups appear as two quadruplets (2H:2H, $\Delta\delta = 0.198$ ppm). This is due to restricted rotation about the C—NR_2 bond resulting from the partial double bond character of the C—NR_2 bond. Apparently, this effect is larger with ethyl groups than with methyl groups because of the higher steric hindrance of the ethyl group. Also, the ^1H NMR spectra is significant in the determination of the presence of the C=N bond. Only one signal for the protons of the amido groups appears. It is singlet at 10.44–10.64 ppm and no couplings of N—H can be detected. For this observation, we can determine the position of the C=N bond in compounds 3a–h.

As a representative example, the mass spectrum of 3d was examined (Table II). The mass spectrum showed a parent ion $(M+H)^+$ at $m/e = 384$. The base

TABLE II

Mass spectrum of compound 3d

m/e	Rel. Int (%)	Fragment
384	2.0	M + 1
326	21.7	$(C_2H_5O)(C_3H_5O)P(S)—N=C—NH—C—Ph^{1+}$ NH——O
310	12.4	$(C_2H_5O)(C_3H_5O)P(S)—N=C=N—COPh^{1+}$
228	21.0	$(HO)(HS)P(S)—N=CH—NHCOPh^{1+}$
212	11.6	$228—O^{1+}$
151	3.3	$(HO)(HS)P—N=CH—NH—C\equiv O^{1+}$
105	100.0	$C_6H_5—C\equiv O^{1+}$
77	66.4	$C_6H_5^{1+}$
72	35.2	$C_2H_5NHCHCH_3^{1+}$
58	8.9	$C_2H_5NHCH_2^{1+}$
51	17.5	$C_4H_3^{1+}$

peak (at $m/e = 105$) was assigned to the fragment $C_6H_5—C\equiv O^+$ produced by the cleavage of the C—N bond, followed by loss of a carbonyl group to give another main fragment $C_6H_5^+$ (at $m/e = 77$). The peak at $m/e = 130$ arose from the loss of the amino group and hydrogen. This behavior perhaps is a prominent feature of mass spectra of these compounds. Other fragments examined are listed and explained satisfactorily.

EXPERIMENTAL

Instrumentation and Analysis. ^1H NMR spectra were taken on a Varian XL-200 spectrometer and chemical shifts are expressed in ppm relative to an internal $SiMe_4$ standard in $CDCl_3$. ^{31}P NMR spectra were taken on a Varian XL-200 spectrometer and chemical shifts are expressed in ppm relative to an external H_3PO_4(85%) standard. Positive values are for downfield shifts. IR spectra were measured on a Perkin–Elmer-983 spectrometer. Mass spectra were determined on a HP-5988 GC/MS spectrometer at 70 ev. Elemental analysis were performed by the Analytical Laboratory, Institute of Organic Synthesis, Central China Normal University, Wuhan, China.

General procedure for the synthesis of compounds 3a–h. Under reduced pressure, 0.01 mol of N-(O-alkyl-O-allyl-thiophosphoryl)-N′-benzoyl urea and 0.03 mol of tris(N,N-dialkylamino)phosphine were heated at 100 C (oil bath) for 0.5–1.0 h in a dried nitrogen atmosphere. A red oil separated. Purification by chromatography on silica gel (50:50 petrolether:ether) gave a yellowish sticky oil (3a-h) in 47–55% yields.

Compound **3a**. IR($CHCL_3$): 3150(N—H), 1693(C=O), 1620(C=N), 1024(P—O—C), 753(P—N), 649(P=S) cm^{-1}. ^1H NMR: 3.06, 3.16(2s, 6H, $\underline{NCH_3}$), 3.66(d, 3H, $\underline{OCH_3}$, $J = 13.3$ Hz), 4.46(m, 2H, $\underline{OCH_2}CH=CH_2$), 5.12–6.00 (m, 3H, $\underline{CH=CH_2}$), 7.48–8.10 (m, 5H, ArH), 10.64(s, 1H, NH). ^{31}P NMR: 62.59.

Compound **3b**. IR($CHCL_3$): 3161(N—H), 1693(C=O), 1620(C=N), 1022(P—O—C), 731(P—N), 648(P=S) cm^{-1}. ^1H NMR: 1.26(t, 3H, $OCH_2\underline{CH_3}$), 3.06, 3.16(2s, 6H, $\underline{NCH_3}$), 4.04(m, 2H, $O\underline{CH_2}$), 4.48(m, 2H, $O\underline{CH_2}CH=CH_2$), 5.12–5.05(m, 3H, $\underline{CH=CH_2}$), 7.48–8.14(m, 5H, ArH), 10.64(s, 1H, NH). ^{31}P NMR: 61.5.

Compound **3c**. IR($CHCl_3$): 3148(N—H), 1693(C=O), 1609(C=N), 1023(P—O—C), 752(P—N), 652(P=S). ^1H NMR: 1.32(m, 6H, $NCH_2\underline{CH_3}$), 3.38, 3.58(2q, 4H, $N\underline{CH_2}CH_3$), 3.68(d, 3H, $\underline{OCH_3}$, $J = 10.0$ Hz), 4.50(m, 2H, $O\underline{CH_2}CH=CH_2$), 5.16–5.40 (m, 3H, $\underline{CH=CH_2}$), 7.54–8.18(m, 5H, ArH), 10.44(s, 1H, NH). ^{31}P NMR: 63.00.

Compound **3d**. IR($CHCl_3$): 3150(N—H), 1693(C=O), 1609(C=N), 1022(P—O—C), 765(P—N), 648(P=S) cm^{-1}. ^1H NMR: 1.20(t, 3H, $OCH_2\underline{CH_3}$), 1.26(m, 6H, $NCH_2\underline{CH_3}$), 3.38, 3.58(2q, 4H, $N\underline{CH_2}CH_3$), 4.03(m, 2H, $O\underline{CH_2}$), 4.47(m, 2H, $O\underline{CH_2}CH{=}CH_2$), 5.12–5.60(m, 3H, $\underline{CH{=}CH_2}$), 7.45–8.06 (m, 5H, ArH), 10.42(s, 1H, NH). ^{31}P NMR: 61.37.

Compound **3e**. IR($CHCl_3$): 3155(N—H), 1690(C=O), 1610(C=N), 1025(P—O—C), 755 (P—N), 648(P=S) cm^{-1}. ^1H NMR: 0.80(T, 3H, $OCH_2CH_2\underline{CH_3}$), 1.18 (m, 6H, $NCH_2\underline{CH_3}$), 1.50(m, 2H, $OCH_2\underline{CH_2}$), 3.40, 4.00(2q, 4H, $N\underline{CH_2}CH_3$), 4.16(m, 2H, $O\underline{CH_2}$), 4.38 (m, 2H, $O\underline{CH_2}CH{=}CH_2$), 5.12–5.90(m, 3H, $\underline{CH{=}CH_2}$), 7.38–8.00(m, 5H, ArH), 10.40 (s, 1H, NH). ^{31}PNMR: 61.41.

Compound **3f**. IR($CHCl_3$): 3173(N—H), 1689(C=O), 1614(C=N), 1013(P—O—C), 757(P—N), 665(P=S) cm^{-1}. ^1H NMR: 1.22(d, 6H, $OCH\underline{Me_2}$), 1.32(m, 6H, $NCH_2\underline{CH_3}$), 3.38, 3.58(2q, 4H, $N\underline{CH_2}CH_3$), 4.46(m, 2H, $O\underline{CH_2}CH{=}CH_2$), 4.68(m, 1H, $O\underline{CH}Me_2$), 5.10–6.00(m, 3H, $\underline{CH{=}CH_2}$), 7.46–8.06(m, 5H, ArH), 10.44(s, 1H, NH). ^{31}P NMR: 60.04.

Compound **3g**. IR($CHCl_3$): 3154(N—H), 1689(C=O), 1610(C=N), 1026(P—O—C), 765(P—N), 667(P=S) cm^{-1}. ^1H NMR: 0.87(t, 3H, $OCH_2CH_2CH_2\underline{CH_3}$), 1.27(m, 6H, $NCH_2\underline{CH_3}$), 1.58(m, 2H, $OCH_2CH_2\underline{CH_2}$), 2.06(m, 2H, $OCH_2\underline{CH_2}$), 3.38, 3.58(2q, 4H, $N\underline{CH_2}CH_3$), 3.98(m, 2H, $O\underline{CH_2}$), 4.48(m, 2H, $O\underline{CH_2}CH{=}CH_2$), 5.12–5.96(m, 3H, $\underline{CH{=}CH_2}$), 7.44–8.10(m, 5H, ArH), 10.42(s, 1H, NH). ^{31}P NMR: 61.49.

Compound **3h**. IR($CHCl_3$): 3158(N—H), 1690(C=O), 1614(C=N), 1012(P—O—C), 753(P—N), 665(P=S) cm^{-1}. ^1H NMR: 0.90(d, 6H, $OCH_2CH\underline{Me_2}$), 1.24(m, 6H, $NCH_2\underline{CH_3}$), 1.86(m, 1H, $OCH_2\underline{CH}$), 3.37, 3.57(2q, 4H, $N\underline{CH_2}CH_3$), 3.66(m, 2H, $O\underline{CH_2}$), 4.45(m, 2H, $O\underline{CH_2}CH{=}CH_2$), 5.08–5.96(m, 3H, $\underline{CH{=}CH_2}$), 7.43–8.02 (m, 5H, ArH), 10.42(s, 1H, NH). ^{31}P NMR: 61.43.

REFERENCES

1. R. Burgada, *Ann. Chim.* (Paris), **8,** 347 (1963).
2. L. D. Quin, J. Leimert, E. D. Middlemas, R. W. Miller and A. T. McPhail, *J. Org. Chem.*, **44,** 3496 (1979).
3. E. D. Middlemas and L. D. Quin, *J. Org. Chem.*, **44,** 2587 (1979).
4. J. Szewczyk, J. R. Lloyd and L. D. Quin, *Phosphorus and Sulfur,* **21,** 155 (1984).
5. Z. J. Liu, X. F. Li and J. L. Zhang, *Synthesis,* Submitted.
6. A. I. Razumov, P. A. Gurevich, S. A. Muslimov, *Zh. Obshch. Khim.*, **46,** 2749 (1976).
7. J. L. Zhang and Z. S. Cao, *Synthesis,* **11,** 1067 (1985).