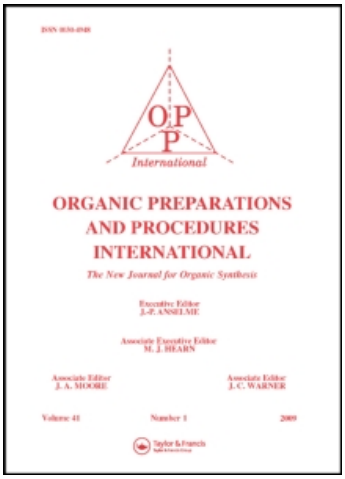

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

SYNTHESIS OF *N*-PHOSPHORYLUREAS BY REACTION OF PHOSPHORYLAMIDES WITH *N*-SUBSTITUTED TRICHLOROACETAMIDES

Jan Petrov[a]; I. Atanassova[a]; V. Ognyanova[a]
[a] Institute of Organic Chemistry, BAS Laboratory of Biologically Active Substances, Plovdiv, BULGARIA

To cite this Article Petrov, Jan , Atanassova, I. and Ognyanova, V.(1994) 'SYNTHESIS OF *N*-PHOSPHORYLUREAS BY REACTION OF PHOSPHORYLAMIDES WITH *N*-SUBSTITUTED TRICHLOROACETAMIDES', Organic Preparations and Procedures International, 26: 3, 357 — 360
To link to this Article: DOI: 10.1080/00304949409458437
URL: http://dx.doi.org/10.1080/00304949409458437

7. P. W. Collins, S.W. Kramer and G. W. Gullikson, *J. Med. Chem.*, **30**, 1952 (1987).

8. D. C. Kriesel and O. Giswold, *J. Pharm. Sci.*, **60**, 1250 (1971).

9. J. C. Stowell, D. R. Keith and B. T. King. *Org. Syn. Coll. Vol.*, **VII**, 59.

****

SYNTHESIS OF *N*-PHOSPHORYLUREAS BY REACTION OF PHOSPHORYLAMIDES WITH *N*-SUBSTITUTED TRICHLOROACETAMIDES

Submitted by Jan Petrov*, I. Atanassova and V. Ognyanova
(09/28/93)

Institute of Organic Chemistry, BAS
Laboratory of Biologically Active Substances
P. O. Box 27, 4002 Plovdiv, BULGARIA

N-Phosphorylureas have been synthesized by reaction of phosphorylisocyanates with amines or by isocyanates with phosphorylamides.[1,2] However only a limited number of them have been checked for pesticide activity.[2] Recently we reported the application of *N*-substituted trichloroacetamides for the synthesis of substituted ureas as well as acyl- or sulfonylureas, by reaction with amines, carboxamides or sulfonamides in alkaline medium.[3,4] This paper describes a convenient procedure for the synthesis of phosphorylureas **3** by reaction of *N*-aryl- or *N*-benzyltrichloroacetamides **1** with phosphorylamides **2** in a molar ratio 1:2 in the presence of sodium hydroxide.

The reaction proceeds in dipolar aprotic solvents such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF) or acetonitrile. The best results were obtained in DMSO. Partial hydrolysis of the ester of **3** occurred under the reaction conditions which accounts for the relatively low yields. The low yields of **3c** probably is due to competiting formation of the symmetrical urea.[4]

$$\underset{\mathbf{1}}{RNHCOCCl_3} + \underset{\mathbf{2}}{H_2NPO(OR^1)_2} \xrightarrow[DMSO]{NaOH} \underset{\mathbf{3}}{RNHCONHPO(OR^1)_2}$$

a) R = 2,6-$(C_2H_5)_2C_6H_3$, R^1= Et; b) R = 2,6-$(CH_3)_2C_6H_3$, R^1= Et; c) R = 3-$CH_3OC_6H_4$, R^1= *i*-Pr;
d) R = $C_6H_5CH_2$, R^1= Et; e) R = $C_6H_5CH_2$, R^1= *i*-Pr; f) 4-$CH_3OC_6H_4CH_2$, R^1= Et;
g) R = 3,4-$(CH_2O_2)C_6H_3CH_2$, R^1= Et;

EXPERIMENTAL SECTION

Melting points were obtained on a "Boetius PHMK 05"apparatus and are uncorrected. Infrared spectra were recorded on a Carl Zeiss SPECORD 75 IR spectrophotometer as nujol mulls. ^{1}H NMR spectra were recorded on a Bruker WM 250 spectrometer at 250 MHz and on a Tesla BS-487-C spectrometer at 80 MHz in $CDCl_3$ with TMS as an internal reference. Mass spectra were recorded on a Jeol-JMS-D300 spectrometer at 70 eV ionization potential. The starting *N*-aryl- or *N*-benzyltrichloroacetamides were synthesized according to the literature procedures.[3,5]

TABLE 1. Yields, Melting Points and Elemental Analyses of **3**

Cmpd No.	Yields (%)	mp.(°C) (solvent)	Elemental Analyses (Found) C	H	N	P[a]
3a	47	133-134 (EtOH)	54.87 (55.14)	7.67 (7.49)	8.53 (8.61)	9.43 (9.42)
3b	55	121-123 (EtOH)	52.00 (52.26)	7.05 (7.24)	9.33 (9.44)	10.31 (10.88)
3c	4	135-137 (PhH-hexane)	50.91 (50.69)	7.02 (7.03)	8.48 (8.30)	9.38 (8.95)
3d	40	125-127 (EtOH)	50.35 (50.10)	6.69 (6.53)	9.79 (9.86)	10.82 (10.25)
3e	52	122-123 (EtOH)	53.50 (53.64)	7.38 (7.45)	8.91 (8.88)	9.85 (9.91)
3f	40	84-85 (Et_2O)	49.37 (49.51)	6.69 (6.62)	8.86 (8.80)	9.79 (10.05)
3g	45	132-134 (EtOH)	47.28 (47.54)	5.80 (5.92)	8.48 (8.50)	9.38 (8.97)

a) The accuracy of the method is ± 1.00 per cent

***N*-Phosphorylureas (3a-g). General Procedure**.- *N*-Aryl- or *N*-benzyltrichloroacetamide **1** (5 mmol) was added to a stirred suspension of phosphorylamide **2** (10 mmol) and powdered NaOH (0.5 g, 12.5 mmol) in 5 mL DMSO. The mixture was stirred at 80° for 30 min, and, after cooling was poured into water (50 mL). The resultant mixture was made alkaline to pH~12 with 40% sodium hydroxide, and the solution was extracted with methylene chloride (2x20 mL). The water layer was separated, filtered and acidified to pH~2 with concentrated sulfuric acid. The precipitated phosphorylurea **3** was isolated by filtration or extraction with methylene chloride. The crude product was recrystallised (Table 1).

TABLE 2. Spectral Data of Compounds **3**

Cmpd	IR (cm^{-1})	MS m/e(M^+)	^1H NMR($CDCl_3$/TMS) (ppm), J (Hz)
3a	3250 1690 1220	328	1.19 (6 H, t, J = 7.6, $PhCH_2C\underline{H}_3$); 1.38 (6 H, t, J = 7.0, $POCH_2C\underline{H}_3$); 2.62 (4 H, q, J = 7.6, $PhC\underline{H}_2CH_3$); 4.15-4.28 (4 H, m, $POC\underline{H}_2CH_3$); 6.87-6.97 (1 H, br d, J = 5.4, P(O)N<u>H</u>); 7.08-7.26 (3 H, m, ArH); 8.36 (1 H, s, PhN<u>H</u>).
3b	3230 1680 1210	300	1.38 (6 H, t, J = 7.1, $POCH_2C\underline{H}_3$); 2.25 (6 H, s, $PhC\underline{H}_3$); 4.14-4.28 (4 H, m, $POC\underline{H}_2CH_3$); 7.05-7.23 (4 H, m, 3 ArH and 1 H, P(O)N<u>H</u>); 8.32 (1 H, s, PhN<u>H</u>).
3c	3280 1710 1220	330	1.38 (12 H, dd, J = 6.1, J' = 4.4, $POCH(C\underline{H}_3)_2$); 3.79 (3 H, s, $PhOC\underline{H}_3$; 4.68-4.81 (2 H, m, $POC\underline{H}(CH_3)_2$); 6.62 (1 H, dd, J = 8.3, J = 2.4, ArH); 6.99-7.25 (4 H, m, 3 ArH and 1 H, P(O)N<u>H</u>); 9.21 (1 H, s, PhN<u>H</u>).
3d	3320 1690 1230	286	[a]1.30 (6 H, t, J = 7, $POCH_2C\underline{H}_3$); 4.10 (4 H, q, J = 7, $POC\underline{H}_2CH_3$); 4,38 (2 H, d, J = 6, $PhC\underline{H}_2$); 7.25 (6 H, s, 5 ArH and 1 H, $CH_2N\underline{H}$, overlap); 7.95-8.25 (1 H, br d, J = 6, P(O)NH).
3e	3320 1680 1220	314	[a]1.25 (12 H, d, J = 6, $POCH(C\underline{H}_3)_2$); 4.34 (2H, d, J = 6, $PhC\underline{H}_2$); 4.40-4.75 (2 H, m, $POC\underline{H}(CH_3)_2$); 7.22 (6 H, s, 5 ArH and 1 H, $CH_2N\underline{H}$, overlap); 7.50-7.75 (1 H, br d, J = 6, P(O)N<u>H</u>).
3f	3300 1680 1220	316	1.33 (6 H, t, J = 7.1, $POCH_2C\underline{H}_3$); 3.79 (3 H, s, $PhOC\underline{H}_3$); 4.07-4.19 (4 H, m, $POC\underline{H}_2CH_3$); 4.33 (2 H, d, J = 5.7, $PhC\underline{H}_2$); 6.84 (2 H, d, J = 8.6, ArH); 6.99 (1 H, br d, J = 5.8, P(O)N<u>H</u>); 7.20 (3 H, d, J = 8.6, 2 ArH and 1 H, $CH_2N\underline{H}$, overlap).
3g	3310 1690	330	1.33 (6 H, t, J = 7.1, $POCH_2C\underline{H}_3$); 4.06-4.19 (4 H, m, $POC\underline{H}_2CH_3$); 4.29 (2 H, d, 1220 J = 5.8, $PhC\underline{H}_2$); 5.92 (2 H, s, $OC\underline{H}_2O$); 6.58-6.81 (3 ArH); 7.10 (1 H, br d, J = 6.0 , P(O)N<u>H</u>); 7.23 (1 H, br s, $CH_2N\underline{H}$).

a) Recorded on a Tesla BS-487-C spectrometer at 80 MHz

REFERENCES

1. B. Gallencamp, W. Hofer, B. W. Kruger, F. Mauer and T. Pfister, in "*Methoden der Organischen Chemie*," Vol. E2, p. 550, M. Regitz, Georg Thieme Verlag Stuttgart, 1982; G. I. Derkatsch, *Angew. Chem.*, **81**, 407 (1969).

2. N. N. Mel'nikov, S. E. Lyubarskaya, I. L. Vladimirova, E. I. Andreeva, M. A. Sanin, M. G. Dvukhsherstov and D. M. Kabakidze, USSR Patent 525 398 (1988); *C. A.*, **109**, 224707t (1988).

3. I. Atanassova, J. Petrov and N. Mollov, *Synthesis*, 734 (**1987**).

4. I. Atanassova, J. Petrov, A. Balabanova and N. Mollov, *Synth. Commun.*, **19**, 2947 (1989); J. Petrov, I. Atanassova, A. Balabanova and N. Mollov, *Commun. Dept. Chem., Bulg. Acad. Sci.*, **23**, 53 (1990); *C.A.*, **114**, 206706r (1991).

5. I. Atanassova, J. Petrov and N. Mollov, *Synth. Commun.*, **19**, 147 (1989).

****

SYNTHESIS OF

3-ACETOACETYL-7-METHYL-2H,5H-PYRANO[4,3-b]PYRAN-2,5-DIONE

Submitted by (07/13/93)

B. Boutemeur-Kheddis, A. Bendaas

Laboratoire des Composés Hétérocycliques
Institut de Chimie Université des Sciences et de la Technologie
B. P. 32 El-Alia, Bab Ezzouar, Alger, ALGERIA

M. Hamdi*, R. Sakellariou and V. Spéziale*

Laboratoire des Interactions Moléculaires
et Réactivité Chimique et Photochimique
CNRS URA 470, Université Paul Sabatier
118 route de Narbonne, 31062 Toulouse Cedex, FRANCE

In the course of a study of pyrone derivatives, we were interested in the synthesis of 6-methyl-3-(4-hydroxy-6-methyl-2-one-2H-pyran-3-yl) methylene-2,4 (3H)-pyran-2,4-dione (**1**). Selective catalytic hydrogenation of this compound would lead to the derivative prepared by another method, and would also serve as reference for the identification of a secondary product formed in various other reactions under the investigation.[1] The only reported method is that of Hirsh and Hoefgen[2] who obtained **1** by heating 4-hydroxy-6-methyl-2-pyrone with ethyl orthoformate in either