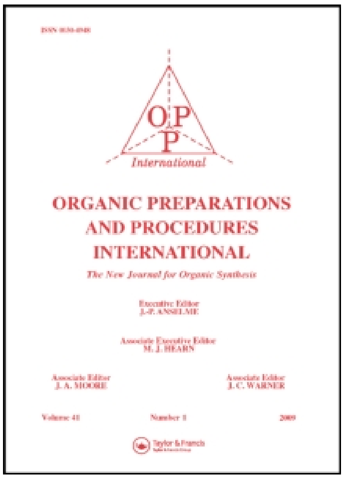

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SYNTHESIS AND REACTIONS OF PHOSPHINIMINES USING HYDRAZONOYL HALIDES

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SYNTHESIS AND REACTIONS OF PHOSPHINIMINES USING HYDRAZONOYL HALIDES

Submitted by
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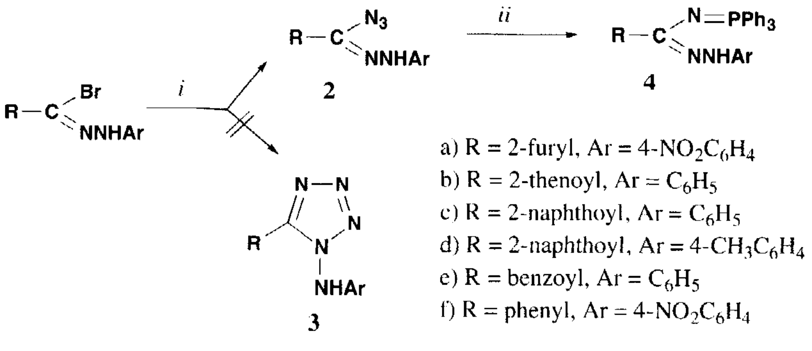
As part of our interest in the utilization of hydrazonoyl halides in heterocyclic synthesis,[1] we have investigated the preparation of azidohydrazones **2**. The azidohydrazones **2** were obtained in high yield by treatment of hydrazonoyl halides (**1**) with sodium azide under phase-transfer conditions (Eq. 1); the reaction when carried out in 80% aqueous dioxane at room temperature as previously described[2] afforded lower yields. The strong absorption band at 2120-2130 cm^{-1} in the IR spectra of the product excludes the isomeric tetrazole structure **3**. Attempts to cyclize the azidohydrazones **2** to the isomeric tetrazoles **3** by warming in inert solvents were not successful, the azidohydrazones **2** being recovered.[3] The structures of 2 were further confirmed by their conversion into the corresponding phosphonimines **4** in better than 90% yield. The IR spectra of **4** were devoid of the azide absorption band at 2120-2130 cm^{-1} region and exhibited a P=N stretching band at 1200-1300

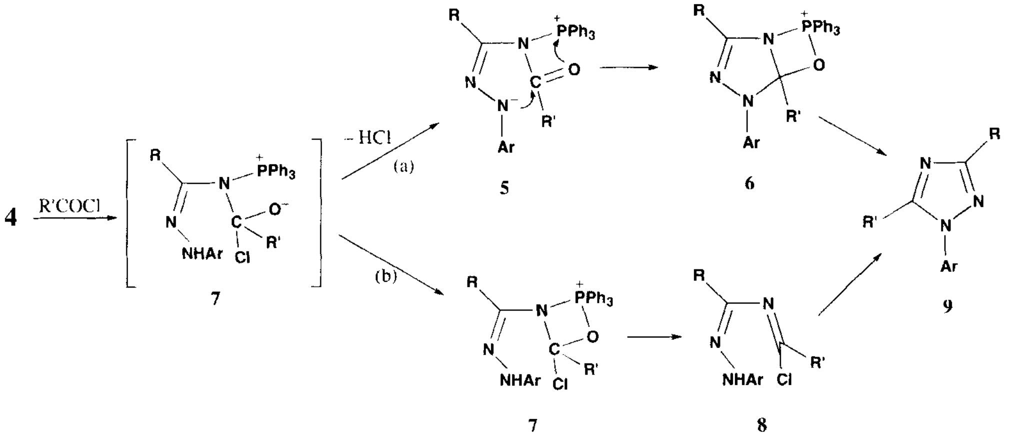


(1)

a) R = 2-furyl, Ar = 4-$NO_2C_6H_4$
b) R = 2-thenoyl, Ar = C_6H_5
c) R = 2-naphthoyl, Ar = C_6H_5
d) R = 2-naphthoyl, Ar = 4-$CH_3C_6H_4$
e) R = benzoyl, Ar = C_6H_5
f) R = phenyl, Ar = 4-$NO_2C_6H_4$

cm^{-1}. The structures of 4 were further confirmed by their elemental analysis, spectral data (Table 1) and their transformation to the corresponding triazole derivatives **5**.

Treatment of **4** with an excess acyl chloride in boiling benzene led to the formation of triazole derivatives **9** along with triphenylphosphine oxide (Scheme 1). Loss of hydrogen chloride from the initial adduct lead to **5** (path a), followed by conjugate attack to yield **6**. Elimination of triphenylphosphine oxide would then give the triazole **9**. A plausible alternative would pass through the imidoyl chloride **8** (path b) followed by cyclization to **9** (Scheme 1); the formation of imidoyl chloride from the reaction of phosphonimines with acid chloride has been reported.[5]



R	R'	Ar	R	R'	Ar
a) 2-furyl	C_6H_5	$4\text{-}NO_2C_6H_4$	m) 2-naphthoyl	C_6H_5	$4\text{-}CH_3C_6H_4$
b) 2-furyl	$4\text{-}BrC_6H_4$	$4\text{-}NO_2C_6H_4$	n) 2-naphthoyl	$4\text{-}BrC_6H_4$	$4\text{-}CH_3C_6H_4$
c) 2-furyl	$4\text{-}CH_3OC_6H_4$	$4\text{-}NO_2C_6H_4$	o) 2-naphthoyl	$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3C_6H_4$
d) 2-furyl	$C_6H_5CH=CH$	$4\text{-}NO_2C_6H_4$	p) 2-naphthoyl	$C_6H_5CH=CH$	$4\text{-}CH_3C_6H_4$
e) 2-thenoyl	C_6H_5	C_6H_5	q) C_6H_5	C_6H_5	$4\text{-}NO_2C_6H_4$
f) 2-thenoyl	$4\text{-}BrC_6H_4$	C_6H_5	r) C_6H_5	$4\text{-}BrC_6H_4$	$4\text{-}NO_2C_6H_4$
g) 2-thenoyl	$4\text{-}CH_3OC_6H_4$	C_6H_5	s) C_6H_5	$4\text{-}CH_3OC_6H_4$	$4\text{-}NO_2C_6H_4$
h) 2-thenoyl	$C_6H_5CH=CH$	C_6H_5	t) C_6H_5	$C_6H_5CH=CH$	$4\text{-}NO_2C_6H_4$
i) 2-naphthoyl	C_6H_5	C_6H_5	u) C_6H_5CO	C_6H_5	C_6H_5
j) 2-naphthoyl	$4\text{-}BrC_6H_4$	C_6H_5	v) C_6H_5CO	$4\text{-}BrC_6H_4$	C_6H_5
k) 2-naphthoyl	$4\text{-}CH_3OC_6H_4$	C_6H_5	w) C_6H_5CO	$4\text{-}CH_3OC_6H_4$	C_6H_5
l) 2-naphthoyl	$C_6H_5CH=CH$	C_6H_5	x) C_6H_5CO	$C_6H_5CH=CH$	C_6H_5

Scheme 1

EXPERIMENTAL SECTION

Melting points were determined on Electrothermal melting point apparatus and are uncorrected. Infrared spectra were recorded on a Pye Unicam SP-3000 infrared spectrophotometer. ^1H NMR spectra were measured in $CDCl_3$ and DMSO-d_6 with a Varian Gemini 200 instrument, chemical shifts are in ppm (δ) from internal TMS. Microanalyses were performed at the microanalytical unit on the University of Cairo, Giza, Egypt. Hydrazonoyl bromides **1a-f** were prepared as previously described.[6a-e]

TABLE 1. Compounds **2**, **4** and **9**

Cmpd.	mp. (°C)	Yield	IR (KBr) (cm^{-1})	NMR (δ)	Analysis Calcd (Found)		
					C	H	H
2a	122	85	3265 (NH), 2115 (N_3)	6.5-8.2 (m, Ar-H)[a]	48.53 (48.70)	2.96 (3.01)	30.88 (30.59)
2b	112	87	3260 (NH), 2110 (N_3) 1645 (C=O)	6.9-7.9 (m, Ar-H)[a]	53.12 (53.41)	3.34 (3.51)	25.82 (26.10)
2c	124	90	3280 (NH), 2110 (N_3) 1650 (C=O)	7.0-8.2 (m, 12H)[a] 9.0 (s, 1H)	68.25 (68.52)	4.14 (4.30)	22.21 (22.31)
2d	115	88	3325 (NH), 2114 (N_3) 1647 (C=O)	2.4(s, 3H), 7.0-8.1 (m, 11H), 8.9 (s, 1H)[a]	69.28 (69.21)	4.59 (4.64)	21.27 (21.41)
2e	85	86	3280 (NH), 2120 (N_3) 1650 (C=O)	7.0-7.8 (m, Ar-H)[a]	63.38 (63.09)	4.18 (4.31)	26.40 (26.50)
2f	134	90	3320 (NH), 2110 (N_3)	7.0-8.2 (m, Ar-H)[a]	55.31 (55.13)	3.57 (3.61)	29.77 (29.70)
4a	190	86	1283 (P=O)	6.6-8.1 (m, Ar-H)[b]	68.76 (68.52)	4.57 (4.70)	11.06 (11.30)
4b	118	87	1275 (P=O), 1650 (C=O)	6.9-8.2 (m, Ar-H)[a]	71.28 (71.10)	4.79 (4.92)	8.31 (8.10)
4c	190	85	1290 (P=O), 1647 (C=O)	7.0-8.3 (m, 27H)[b] 8.8 (s, 1H)	78.67 (78.99)	5.13 (5.20)	7.65 (7.65)
4d	168	86	1300 (P=O), 1640 (C=O)	2.3 (s, 3H), 7.0-8.2 m, 26H), 8.9 (s, 1H)[b]	78.84 (79.01)	5.73 (5.60)	7.46 (7.52)
4e	160	85	1310 (P=O), 1655 (C=O)	6.9-8.0 (m, Ar-H)[b]	76.94 (77.21)	5.25 (5.20)	8.41 (8.36)
4f	110	85	1290 (P=O)	6.9-8.2 (m, Ar-H)[a]	(72.10) (72.01)	4.88 (4.56)	10.85 (11.01)
9a	192	66	1620(C=N)	6.6-8.3 (m, Ar-H)[b]	65.07 (65.30)	3.64 (3.86)	16.86 (17.02)
9b	226	70	1625 (C=N)	6.8-8.1 (m, Ar-H)[b]	52.57 (52.39)	2.70 (2.86)	13.62 (13.71)
9c	171	69	1618(C=N)	3.9 (s, 3H), 6.6-7.8 (m, 11H)[b]	62.97 (63.12)	3.89 (3.96)	15.46 (15.19)
9d	174	70	1630(C=N)	6.7-7.8 (m, Ar-H)[a]	67.03 (67.21)	3.94 (4.11)	15.64 (15.91)
9e	215	75	1650 (C=O) 1620 (C=N)	6.9-7.9 (m, Ar-H)[b]	68.86 (68.60)	3.95 (3.72)	12.68 (12.82)
9f	167	80	1640 (C=O) 1600(C=N)	6.8-7.9 (m, Ar-H)[a]	55.62 (55.37)	2.95 (3.10)	10.24 (10.51)
9g	182	70	1640 (C=O) 1610(C=N)	3.9 (s, 3H) 6.9-7.8 (m, 11H)[b]	66.46 (66.16)	4.18 (4.10)	11.62 (11.70)

TABLE 1. Compounds **2**, **4** and **9** (Continued)

Cmpd.	mp. (°C)	Yield	IR (KBr) (cm^{-1})	NMR (δ)	Analysis Calcd (Found)		
					C	H	H
9h	233	70	1645 (C=O) 1600 (C=N)	6.7-7.9 (m, Ar-H)^b	70.57 (70.80)	4.23 (4.50)	11.76 (11.51)
9i	188	70	1660 (C=O) 1627 (C=N)	6.9-8.3 (m, 16H), 9.0 (s, 1H)^b	79.98 (80.21)	4.57 (4.71)	11.19 (11.31)
9j	180	65	1665 (C=O) 1625 (C=N)	6.9-8.4 (m, 15H), 8.9 (s, 1H)^b	66.08 (66.18)	3.55 (3.41)	9.24 (9.52)
9k	162	75	1665 (C=O) 1615 (C=N)	3.8 (s, 3H), 6.9-8.4 (m, 15H), 9.0 (s, 1H)^a	77.02 (77.00)	4.72 (4.61)	10.36 10.18)
9l	173	70	1660 (C=O) 1632 (C=N)	6.6-8.4 (m, 18H), 9.1 (s, 1H)^a	80.78 (80.81)	4.77 (4.61)	10.47 (10.51)
9m	153	75	1660 (C=O) 1625 (C=N)	2.5 (s, 3H), 7.1-8.5 (m, 15H), 9.8 (s, 1H)^a	80.18 (80.01)	4.92 (4.76)	10.79 (10.91)
9n	101	74	1660 (C=O) 1625 (C=N)	2.4 (s, 3H), 7.3-8.4 (m, 15H), 8.9 (s, 1H)^a	66.68 (66.88)	3.87 (4.01)	8.97 (9.21)
9o	105	70	1660 (C=O) 1610 (C=N)	2.5 (s, 3H), 3.8 (s, 3H), 7.3-8.4 (m, 9.1 (s, 1H)^a	77.31 (77.26)	5.05 (5.22)	10.02 (10.21)
9p	180	67	1660 (C=O) 1624 (C=N)	2.5 (s, 3H), 6.9-8.4 (m, 17H) 9.0 (s, 1H)^b	80.94 (81.16)	5.10 (5.01)	10.11 (10.41)
9q	168	80	1615 (C=N)	7.0-8.2 (m, Ar-H)^a	70.16 (70.22)	4.12 (4.32)	16.37 (16.50)
9r	213	70	1610 (C=N)	6.9-8.3 (m, Ar-H)^b	57.13 (57.30)	3.12 (3.41)	13.33 (13.10)
9s	210	70	1618 (C=N)	3.9 (s, 3H) 6.9-8.4 (m, 13H)b	67.70 (67.65)	4.33 (4.21)	15.05 (15.20)
9t	212	72	1630 (C=N)	6.7-8.2 (m, Ar-H)^b	71.72 (71.74)	4.38 (4.36)	15.21 (14.99)
9u	157	70	1660 (C=O) 1605 (C=N)	7.0-7.9 (m, Ar-H)^a	77.52 (77.31)	4.65 (4.81)	12.92 (12.71)
9v	143	75	1658 (C=O) 1610 (C=N)	6.9-7.9 (m, Ar-H)^a	62.39 (62.20)	3.49 (3.33)	10.39 (10.12)
9w	157	71	1655 (C=O) 1610 (C=N)	3.8 (s, 3H), 6.9-8.5 (m, 14H)^a	74.35 (74.50)	4.82 (4.96)	11.82 (11.70)
9x	160	74	1660 (C=O) 1620 (C=N)	6.6-7.9 (m, Ar-H)^a	78.61 (78.90)	4.88 (4.66)	11.96 (12.01)

a) In $CDCl_3$ b) In DMSO-d_6

Azidohydrazones (2a-f). *Method A*.- To a solution of the appropriate hydrazonoyl bromides **1** (4 mmoles) in tetrahydrofuran (60 mL) was added a solution of sodium azide (0.33 g, 5 mmoles) in water (60 mL). To the resulting mixture tetrabutylammonium iodide (5 mg) was added. The mixture was vigorously stirred for 1 hr at room temperature. The Solvent was evaporated under reduced pressure and the oily residue solidified upon trituration with ethanol (10 mL). The crude product was collected and crystallized from ethanol to give the corresponding azidohydrazones **2** (Table 1).

Method B.- To a solution of the appropriate hydrazonoyl bromide **1** (3 mmoles) in dioxane-water mixture (80:20 v/v, 70 mL) was added a solution of sodium azide (0.26 g, 4 mmoles) in the same solvent mixture (10 mL). The reaction mixture was stirred at room temperature for 3 hrs then diluted with water (100 mL). The solid was collected and crystallized from ethanol to give the corresponding azidohydrazones **2** (Table 1). The compounds prepared by this method were identical in all respects (mp., mixed mp., IR) with those obtained by method A.

Phosphinimines (4a-f).- A solution of azidohydrazones **2** (20 mmoles) and triphenylphosphine (5.2 g, 20 mmoles) in dry ether (100 mL) was refluxed for 1 hr. The precipitated solid was collected and washed with ether. The crude products were crystallized from ethanol-benzene to give the phosphonimines **4** (Table 1).

Triazoles (9a-x).- A solution of the appropriate phosphonimines **4** (5 mmoles) and acyl chloride (10 mmoles) in dry benzene (50 mL) was refluxed for 3 hrs. The reaction mixture was treated with petroleum ether (40/60) and the solid that formed was crystallized from ethanol-benzene mixture to give the corresponding triazoles **9** (Table 1).

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OXIDATION OF 3β-ACETOXY-5α-LANOST-8-ENE WITH CHROMYL CHLORIDE. THE PREPARATION OF 5α,8β-LANOST-9(11)-EN-7-ONE DERIVATIVES

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8β-Lanostane derivatives, which possess a $\Delta^{9(11)}$-double bond and a carbonyl group in position 7, are the only substrates for the preparation of 9β,11β-epoxylanostane derivatives.[1] The real importance of 9β,11β-epoxides is their effective rearrangement to 19(10→9β)*abeo* tetracyclic triterpenes (cucurbitacins).[2] Several methods of preparation of lanost-9(11)-en-7-one from either the respective Δ^8-olefin or $\Delta^{7,9(11)}$-diene have been described.[3-6] Over the years, we have carried out numerous oxidations of dihydrolanosteryl or dihydroagnosteryl acetates and their side chain modified derivatives. These oxidations were found to be irreproducible[7] and resulted, for example, in low yield of the expected unconjugated enone **2a** from **1a**. Usually, the crude reaction product of the oxidation of 3β-acetoxy-5α-lanost-8-ene or 3β-acetoxy-5α-lanosta-7,9(11)-diene with chromium trioxide was a mixture of 8-en-7,11-dione, 9(11)-en-7-one and a large proportion of overoxidized products. The isolation of **2a** required tedious chromatographic separation irrespective of the substrate used in the oxidation. In the best procedure,[7] two additional synthetic steps, the preparation of the respective $\Delta^{7,9(11)}$-diene *via* the 8,9-epoxide, were also necessary. We explored other reagents and reaction conditions in order to find a better oxidation system for direct transformation of Δ^8-olefin to $\Delta^{9(11)}$-7-oxo compounds.

Thus, chromyl chloride appears to be the reagent of choice for the oxidation of 3β-acetoxy-5α-lanost-8-ene (**1a**) to 3β-acetoxy-5α,8β-lanost-9(11)-en-7-one (**2a**). When the reaction was carried out in methylene chloride at low temperature (-23°) a pure product **2a** was isolated upon chromatography and crystallization in 62% yield. The best yield was obtained when the oxidant was added in one portion and the reaction was carried out for 1 hour. The yield of the enone **2a** was similar on 1 g and 5 g scale. The ^{1}H NMR spectrum of **2a** showed all the features characteristic of the unconjugated enone system and also indicated no admixture of the 8α- or Δ^8 isomers, while the position of the characteristic 8β-proton signal at δ 2.87 confirmed the configuration of C-8.[5]