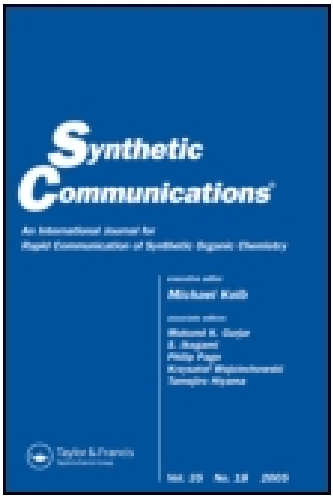

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Facile Method for the Synthesis of Vicinal Azidoiodides by the Reaction of the NaN_3-I_2 System with Unsaturated Compounds

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Facile Method for the Synthesis of Vicinal Azidoiodides by the Reaction of the NaN_3–I_2 System with Unsaturated Compounds

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Abstract: A facile and efficient method was developed for the synthesis of vicinal azidoiodides in 62–77% yields by the reaction of sodium azide and iodine with unsaturated compounds in methanol, aqueous methanol, or the water–methanol–tetrahydrofuran solvent system. The reaction in Et_2O or $CHCl_3$ produced only vicinal diiodides.

Keywords: Alkenes, azides, azidoiodination, iodine, sodium azide

INTRODUCTION

The azidoiodination of unsaturated compounds has long attracted attention as an efficient tool for C-N bond formation. Organic azides have found use in the synthesis of vinyl azides,[1] amines,[2] aziridines,[3] and lactams.[4] In recent years, interest in these compounds has quickened because of the development of a facile method for the synthesis of 1,2,3-triazoles by the reaction of azides with terminal acetylenes catalyzed by copper salts.[5] Compounds containing the 1,2,3-triazole ring are readily available, which has stimulated extensive research into their practical application. These compounds were found to have a wide spectrum of

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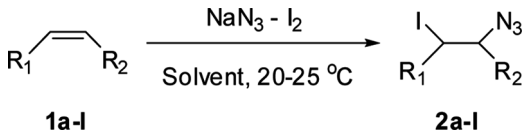
biological activities,[6] for example, antituberculosis,[7] antibiotic,[8] anticancer,[9] immunostimulating,[10] and anti-HIV[11] activities. New types of monomers have been synthesized starting from these compounds.[12] Triazoles can be used for improvement of the proton transport in fuel cells,[13] and so on. Because of their high reliability and efficiency of the assembly of the triazole ring by reactions in the presence of copper salts, these heterocycles serve as convenient linkers for joining fragments with different useful properties in a single molecule.[6a,6b,14]

The first attempt to synthesize azidoiodoalkanes by the reaction of alkenes with IN_3, which was prepared by the reaction of AgN_3 with I_2, was made as early as in 1900 by Hantsch.[15] Since that time, several procedures and techniques have been developed for the synthesis of various representatives of this class of compounds. The practical interest in azidoiodoalkanes has stimulated a search for new methods for their synthesis. Azidoiodoalkanes were prepared by the reaction of alkenes with IN_3, which was synthesized in situ from ICl and NaN_3,[16] and by the reaction of alkenes with I_2 and NaN_3 immobilized on aluminum oxide.[17] The binary tetramethylene sulfone–chloroform (exemplified by the synthesis of azidoiodocyclohexane)[18] and $CHCl_3$–H_2O mixtures in the presence of the phase-transfer catalysts Adogen 464 and 18-Crown-6 were used as solvents.[19] Azidoiodoalkenes were synthesized with the use of iodosofluorosulfate instead of iodine combined with NaN_3.[20] In the past decade, extensive research into the azidoiodination reaction was continued. Methods were developed for the synthesis of azidoiodoalkanes based on the reactions of alkenes with the following azidoiodine-containing systems more complex than I_2–NaN_3: NaN_3–NaI–cerium ammonium nitrate,[21] NaN_3–KI–oxone–wet Al_2O_3[22], bis(pyridine)iodonium(I) tetrafluoroborate–$TMSN_3$–BF_3-Et_2O,[23] and (diacetoxyiodo)benzene–$TMSN_3$–tetraethylammonium iodide.[24rsqb; Polymer-bound iodine azide can serve as the azidoiodination reagent.[25]

RESULTS AND DISCUSSION

When searching for facile and efficient methods for the synthesis of vicinal azidoiodides (**2a–l**), we found that these compounds can be prepared at room temperature during a rather short period of time (**2–4 h**) in good yields in the absence of catalysts, expensive solvents, and considerable excess of the reagents by the reactions of alkenes (**1a–l**) with sodium azide and iodine in methanol, aqueous methanol, or the water–methanol–tetrahydrofuran (THF) system (Scheme 1, Tables 1 and 2).

Under particular conditions, the reactions afford azidoiodides **2** along with the corresponding vicinal diiodides.

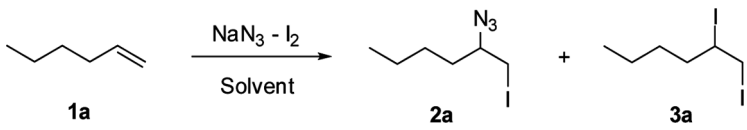


Scheme 1. Synthesis of azidoiodides **2a–l** from alkenes **1a–l**.

The nature of the solvent has a decisive influence on the composition and the yields of the reaction products as exemplified by the azidoiodination of hex-1-ene **1a** (Table 1).

Depending on the nature of the solvent, azidoiodide **2a** or diiodide **3a** can be synthesized as the only reaction product. Polar protic solvents (MeOH, MeOH–H_2O, or MeOH–H_2O–THF), in which the diiodide is virtually not formed and the target azidoiodide is produced in 71–73% yield, are most favorable for the azidoiodination. The reactions in MeOH require vigorous stirring to obtain reproducible results. The yield of azidoiodide **2a** in MeOH–H_2O is reproduced better than in MeOH. The addition of water to methanol results in the dissolution of the major portion of sodium azide, which makes the reaction weakly sensitive to the intensity of stirring. The reaction mixture can be easily homogenized with the use of the three-component MeOH–H_2O–THF solvent system, because it dissolves both organic and inorganic components of the mixture, but the presence of the third cosolvent somewhat complicates

Table 1. Yields of the azidoiodination products of hex-1-ene **1a**[a]

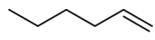
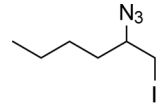
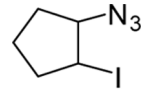
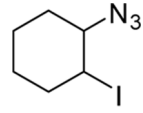
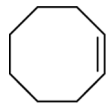
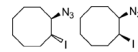
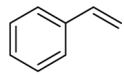
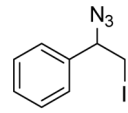


Product	Et_2O	$CHCl_3$	CH_3CN	THF	MeOH/THF (1/1)[b]	MeOH	H_2O/MeOH (1/5)[b]	H_2O/MeOH/THF (2/3/5)[b]
2a	Traces	0%	42%	31%	36%	71%	73%	72%
3a	62%	55%	Traces	26%	7%	Traces	0%	0%

[a]Reaction conditions: sodium azide (0.618 g, 9.5 mmol, 2 mol/1 mol **1a**) was added to a solution of **1a** (0.4 g, 4.75 mmol) in the solvent (10 ml), and then I_2 (1.81 g, 7.13 mmol, 1.5 mol/1 mol **1a**) was added with stirring at 20–25°C. The reaction mixture was stirred for 1.5 h.

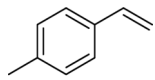
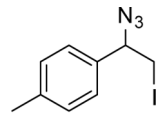
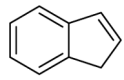
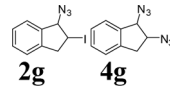
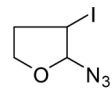
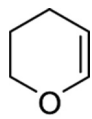
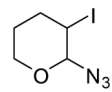
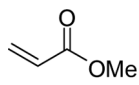
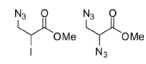
[b]The v/v ratio.

Table 2. Synthesis of azidoiodoalkanes **2a–l**

Run	Alkene	Azidoiodoalkane	Reaction time (h)	Yield (%)[a]
1	 **1a**	 **2a**	3	74
2	 **1b**	 **2b**	3	74[b]
3	 **1c**	 **2c**	3	72[b]
4	 **1d**	 **2d' 2d"**	3	**2d′** + **2d″**, 77
5	 **1e**	 **2e**	2	75[b]

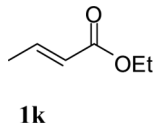
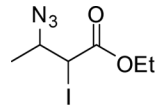
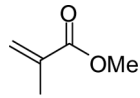
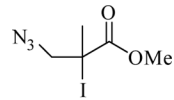
(*Continued*)

Table 2. Continued

Run	Alkene	Azidoiodoalkane	Reaction time (h)	Yield (%)[a]
6	 **1f**	 **2f**	2	76[b]
7	 **1g**	 **2g** **4g**	2 48	**2 g**, 72 **2 g**, 55; **4 g**, 15
8	 **1h**	 **2h**	0.5	71
9	 **1i**	 **2i**	0.5	73
10	 **1j**	 **2j** **4j**	5 24	63 **2j**, 35; **4j**, 29

(*Continued*)

Table 2. Continued

Run	Alkene	Azidoiodoalkane	Reaction time (h)	Yield (%)[a]
11	 **1k**	 **2k**	5	65
12	 **1l**	 **2l**	5	62

[a]The yield based on the isolated product.
[b]Experiments on the synthesis of **2b, c, e**, and **f** were scaled with an increase in the amounts of the reagents by a factor of 10.

the experimental technique. In aprotic solvents ($CHCl_3$ or Et_2O), the azidoiodination is almost completely absent; in THF, **2a** and **3a** are produced in approximately equal yields (30%).

Taking into account the results of optimization of the synthesis of 2-azido-1-iodohexane (Table 1), we performed the azidoiodination of a series of unsaturated hydrocarbons, ethers, and esters with the NaN_3–I_2 system in MeOH–H_2O with the aim of preparing the corresponding azidoiodine-containing compounds required for further investigations (Table 2).

Vicinal azidoiodides are produced in higher yields (71–77%) from alkenes, styrenes, and enol ethers (runs 1–9) and in somewhat lower yields (62–69%) from esters (runs 10–13). A mixture of *cis* and *trans* isomers **2d′** and **2d″** is formed in a total yield of 77% from cyclooctene **1d** (run 4). In runs 7 and 10, the azidoiodination of indene and methylacrylate over a longer period of time (48 and 24 h) affords vicinal diazides **4g** and **4j**, apparently as a result of the nucleophilic displacement of the iodine atom with the azido group in azidoiodine adducts **2g** and **2j**. Among the unsaturated compounds listed in Table 2, cyclic enol ethers exhibit the highest reactivity in the reaction with NaN_3–I_2 (0.5 h, runs 8 and 9). The reactions with unsaturated compounds conjugated with electron-withdrawing groups proceed more slowly (5 h, runs 10–12).

CONCLUSIONS

A facile and efficient procedure was developed for the synthesis of vicinal azidoiodides in yields up to 77% from linear and cyclic alkenes, styrene, its analogs, cyclic enol ethers, and unsaturated compounds containing an electron-withdrawing group. This method is based on the reaction of sodium azide with iodine (used in a small excess) with an unsaturated compound in methanol, aqueous methanol, or the water–methanol–THF solvent system.

EXPERIMENTAL

NMR spectra were recorded on Bruker AC-200 (200.13 MHz for ^1H and 50.32 MHz for ^{13}C) and Bruker Avance 300 (300.13 MHz for ^1H and 75.48 MHz for ^{13}C) spectrometers in $CDCl_3$. Analytical thin-layer chromatography(TLC): Silufol UV-254, Silpearl as the sorbent, starch as the binder. Flash chromatography was performed on silica gel (63–200 mesh, Merk). Alkenes, NaN_3, and $Na_2S_2O_5$ were purchased from Acros. Methanol, ethanol, THF, hexane, $CHCl_3$, CH_3CN, Et_2O, and iodine (all of reagent grade) were used without additional purification.

Azidoiodination of Hex-1-ene (1a), Table 1

Hex-1-ene **1a** (0.4 g, 4.75 mmol) was dissolved in 10 ml of the solvent (Et_2O, $CHCl_3$, CH_3CN, THF, MeOH, MeOH–THF (5 ml + 5 ml), H_2O–MeOH (2 ml + 8 ml), or H_2O–MeOH–THF (2 ml + 3 ml + 5 ml). Sodium azide (0.618 g, 9.5 mmol, 2 mol/1 mol **1a**) was added at 20–25°C, and then I_2 (1.81 g, 7.13 mmol, 1.5 mol/1 mol **1a**) was added with stirring. The reaction mixture was stirred for 90 min, CH_2Cl_2 (50 ml) and H_2O (30 ml) were added, and the CH_2Cl_2 layer was separated, washed with 5% $Na_2S_2O_5$ until it became colorless (with caution, extensive elimination of N_2) and again with H_2O (2 × 20 ml), and dried over $MgSO_4$. The product was isolated by column chromatography.

Azidoiodination of Alkenes (1a–g, j–l) (General Procedure), Table 2

Alkene **1a–g, j–l** (0.4 g) was dissolved in a mixture of MeOH (or EtOH in run 11; 15 ml) and H_2O (2 ml; if required, THF was added for homogenization). At 20–25°C, NaN_3 (4 mol/1 mol **1a–g, j–l**) was added. Then I_2 (2 mol/1 mol **1a–g, j–l**) was added with stirring. The reaction mixture was stirred during a period from 2 to 48 h and worked as described for **1a**.

Azidoiodination of Dihydrofuran (1 h) and Dihydropyran (1i), Table 2

Sodium azide (3 mol/mol **1h, i**; 1.1 or 0.93 g; 17.1 or 14.3 mmol) and dihydrofuran **1 h** or dihydropyran **1i** (0.4 g; 5.71 or 4.76 mmol) were successively dissolved in methanol (10 ml) and water (4 ml). Then iodine (1 mol/mol **1h, i**; 1.45 or 1.21 g; 5.71 or 4.76 mmol) was added with stirring. The reaction mixture was stirred at 20–25°C for 0.5 h and worked up as described for **1a**.

Data

2-Azido-1-iodohexane (**2a**)[16a]

Pale yellow oil. ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 0.90$ (t, 3H, CH_3, $J = 6.9$ Hz), 1.26–1.82 (m, 6H, CH_2), 3.18–3.30 (m, 2H, CH_2I), 3.32–3.44 (m, 1H, CH). ^{13}C NMR (75.48 MHz, CDCl): $\delta = 8.6$ (CH_2I), 13.8 ($\boldsymbol{C}H_3CH_2$), 22.2, 27.9 (CH_2), 34.1 (CH_2), 62.6 (CN_3).

1-Azido-2-iodocyclopentane (**2b**)[26]

Pale yellow oil. ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 1.61$–2.42 (m, 6H, CH_2), 4.03–4.27 (m, 2H, CHI, CHN_3). ^{13}C NMR (75.48 MHz, CDCl): $\delta = 22.3$, 28.5, 29.1 (CH_2), 36.5 (CHI), 71.5 (CHN_3). Anal. Calcd. for $C_5H_8IN_3$: C, 25.33; H, 3.40; I, 53.54; N, 17.73. Found: C, 25.15; H, 3.41; I, 53.22; N, 18.01.

1-Azido-2-iodocyclohexane (**2c**)[18]

Pale yellow oil. ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 1.19$–1.63 (m, 4H, CH_2), 1.75–2.50 (m, 4H, CH_2), 3.42–3.59 (m, 1H, CHN_3), 3.87–4.01 (m, 1H, CHI). ^{13}C NMR (75.48 MHz, CDCl): $\delta = 23.7$, 26.9, 31.8, 33.2 (CH_2), 38.3 (CHI), 67.1 (CHN_3). Anal. calcd. for $C_6H_{10}IN_3$: C, 28.70; H, 4.01; I, 50.55; N, 16.74. Found: C, 29.11; H, 4.06; I, 50.26; N, 17.05.

1-Azido-2-iodocyclooctane (the Mixture of Isomers, Ratio 1/2) (**2d′** + **2d″**):

Pale yellow oil. ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 1.28$–2.44 (m, 12H, CH_2), the first isomer 3.38–3.49 (m, 1H, CHN_3), 4.53–4.65 (m, 1H, CHI), the second isomer 3.83–3.95 (m, 1H, CHN_3), 4.18–4.30 (m, 1H, CHI). ^{13}C NMR (75.48 MHz, CDCl): $\delta = 24.0$–27.2 (8 CH_2), 31.5, 31.7, 34.2, 36.9 (CH_2), 38.9, 39.4 (CHI), 64.1, 71.1 (CHN_3). Anal. calcd. for $C_8H_{14}IN_3$:

C, 34.42; H, 5.06; I, 45.47; N, 15.05. Found: C, 34.37; H, 5.08; I, 45.43; N, 15.21.

2-Iodo-1-phenylethyl Azide (**2e**)[17]

Pale yellow oil. ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 3.39$ (d, 2H, CH_2, $J = 7.3$ Hz), 4.72 (t, 1H, CH, $J = 7.3$ Hz), 7.28–7.47 (m, 5H, Ph). ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta = 8.1$ (CI), 67.1 (CN_3), 126.6, 129.0 (CH, Ar), 137.8 (C, Ar).

1-(1-Azido-2-iodoethyl)-4-methylbenzene (**2f**)

Pale yellow oil. ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 2.39$ (s, 3H, CH_3), 3.40 (d, 2H, CH_2, $J = 7.3$ Hz), 4.71 (t, 1H, CH, $J = 7.3$ Hz), 7.20–7.27 (m, 4H, Ph). ^{13}C NMR (75.48 MHz, CDCl): $\delta = 8.1$ (CI), 21.2 (CH_3), 66.9 (CN_3), 126.5, 129.7 (CH, Ar), 134.8, 139.0 (C, Ar). Anal. calcd. for $C_9H_{10}IN_3$: C, 37.65; H, 3.51; I, 44.20; N, 14.64. Found: C, 37.42; H, 3.39; I, 44.47; N, 14.61.

1-Azido-2-iodo-2,3-dihydro-1H-indene (**2g**)[24]

Mp 55–57°C. Mp *cis*-isomer 53°C[24]. ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 3.31$–3.42 (m, 1H, CH_2), 3.59–3.71 (m, 1H, CH_2), 4.34–4.43 (m, 1H, CHN_3), 5.09–5.18 (m, 3H, CHI), 7.27–7.48 (m, 4H, Ph). ^{13}C NMR (75.48 MHz, CDCl): $\delta = 25.2$, 43.6 (CI, CH_2), 75.0 (CN_3), 124.5, 124.8, 127.7, 129.5 (CH, Ar), 138.6, 141.3 (C, Ar).

2-Azido-3-iodotetrahydrofuran (**2h**)

Pale yellow oil. ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 2.18$–2.28 (m, 1H, CH_2), 2.47–2.60 (m, 1H, CH_2), 4.08–4.26 (m, 3H, CH_2O, CHI), 5.68–5.71 (m, 1H, CHO). ^{13}C NMR (75.48 MHz, CDCl): $\delta = 23.6$, 35.4 (CH_2, CI), 68.5 (CH_2O), 98.8 (CHO). Anal. calcd for $C_4H_6IN_3O$: C, 20.10; H, 2.53; I, 53.09; N, 17.58. Found: C, 20.01; H, 2.28; I, 53.45; N, 17.51.

2-Azido-3-iodotetrahydro-2H-pyran (**2i**)

Pale yellow oil. ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 1.59$–1.72 (m, 2H, CH_2), 1.90–2.11 (m, 1H, CH_2), 2.25–2.45 (m, 1H, CH_2), 3.57–3.70 (m, 1H), 3.85–3.96 (m, 1H), 4.01–4.14 (m, 1H), 4.85–4.94 (m, 1H, CHO). ^{13}C NMR (75.48 MHz, CDCl): $\delta = 26.2$, 27.3, 33.8 (CH_2, CI),

66.0 (CH_2O), 92.2 (CHO). Anal. calcd. for $C_5H_8IN_3O$: C, 23.73; H, 3.19; I, 50.15; N, 16.61. Found: C, 23.54; H, 3.02; I, 50.46; N, 16.57.

Methyl 3-Azido-2-iodopropanoate (**2j**)[16c]

Pale yellow oil. Rf = 0.43 (TLC, hexane/EA = 5/1). ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 3.62$ (dd, 1H, CH_2, J = 12.5; 5.1 Hz), 3.79 (s, 3H, CH_3), 3.89 (dd, 1H, CH_2, $J = 12.5$; 9.5 Hz), 4.37 (dd, 1H, CH, $J = 9.5$; 5.1 Hz). ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta = 14.6$ (CI), 53.2, 54.7 (CH_2, CH_3), 170.2 (CO). Anal. calcd. for $C_4H_6IN_3O_2$: C, 18.84; H, 2.37; I, 49.76; N, 16.48. Found: C, 18.80; H, 2.37; I, 49.38; N, 16.91.

Ethyl 3-Azido-2-iodobutanoate (**2k**)

Pale yellow oil. ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 1.28$ (t, 3H, CH_3, $J = 7.2$ Hz), 1.50 (d, 3H, CH_3, $J = 6.6$ Hz), 3.87 (m, 1H, CH), 4.15–4.27 (m, 3H, CH, CH_2). ^{13}C NMR (75.48 MHz, CDCl): $\delta = 13.7$, 19.2 (CH_3), 24.6 (CI), 59.3, 62.2 (CH, CH_2), 169.6 (CO). Anal. Calcd. for $C_6H_{10}IN_3O_2$: C, 25.46; H, 3.56; I, 44.83; N, 14.84. Found: C, 25.31; H, 3.42; I, 45.11; N, 14.74.

Methyl 3-Azido-2-iodo-2-methylpropanoate (**2l**)[16c]

Pale yellow oil. ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 2.07$ (s, 3H, CCH_3), 3.65 (d, 1H, CH_2, $J = 12.5$ Hz), 3.79 (s, 3H, OCH_3), 4.10 (d, 1H, CH_2, $J = 12.5$ Hz). ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta = 28.0$ (CH_3), 34.6 (CI), 53.3 (OCH_3), 61.7 (CH_2), 171.8 (CO).

1,2-Diazido-2,3-dihydro-1H-indene (**4g**)[27]

Pale yellow oil. ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 3.38$–3.44 (m, 3H, CH, CH_2), 4.71–4.81 (m, 1H, CH), 7.31–7.50 (m, 4H, Ph). ^{13}C NMR (75.48 MHz, CDCl): $\delta = 36.1$ (CH_2), 67.6, 70.2 (CN_3), 124.5, 125.1, 127.7, 129.4 (CH, Ar), 137.7, 139.0 (C, Ar).

Methyl 2,3-Diazidopropanoate (**4j**)

Pale yellow oil. Rf = 0.29 (TLC, hexane/EA = 5/1). ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta = 3.61$ (d, 2H, CH_2, $J = 5.3$ Hz), 3.82 (s, 3H, CH_3), 4.09 (t, 1H, CH, $J = 5.3$ Hz). ^{13}C NMR (50.32 MHz, $CDCl_3$): $\delta = 51.8$ (CH_2), 53.1 (CH), 61.4 (CH_3), 168.2 (CO). Anal. calcd. for

$C_4H_6N_6O_2$: C, 28.24; H, 3.55; N, 49.40. Found: C, 28.63; H, 3.55; N, 49.40.

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